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SHEM-WP

Innovative Natural Solutions of Shungite & EM –technology for Water Purification

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SHEMWP PROJECT REPORT 2019-2021

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Summary

SHEM-WP (*Innovative Natural Solutions of Shungite & EM –technology for Water Purification*) funded by South-East Finland – Russia CBC was carried out in 2019-2021. The project focused on developing a new chemical free purification system for urban runoff waters. The three main steps in the concept are 1) mechanical separation, 2) sorption of urban pollutants, and 3) biological cultivation unit for biodiversity support in recipient. The system applied shungite (SH) mineral and effective micro-organisms (EM) and it is developed and verified in collaboration between Finnish and Russian partners. Shungite is Lower Proterozoic metamorphic rock from Lake Onega district of Russian Karelia with high content of elementary non-crystalline carbon. The rock is characterized by high sorption capacity for multiple urban contaminants, high mechanical strength, and low abrasion, which make it, in combination with effective micro-organisms, a perspective solution for application in filters for storm water treatment. The main role of EM is to improve the uptake of nutrients and improve the natural removal cycle in the recipient water bodies. The overall objective of the project was *to maintain and preserve freshwater reservoirs*, which was addressed by developing the methodology that can be implemented into conveyance systems existing in cities. Improvement in water quality in various water elements (constructed wetlands, parks, canals, and their recipients) improves the wellbeing of citizens and attracts tourists with a cleaner environment. The activities covered material studies to optimize shungite rock grade, and activation and maintenance procedures required. Biological cultivation unit was combined in the shungite adsorption, and EM cultivation on various growth media in addition shungite was optimized. These two technologies were combined, and several fit-to-case solutions with novel filter designs were proposed. The prototypes were verified in field test: 2 sites in Lappeenranta, and 4 sites in St. Petersburg. The project activities consisted of activity cycles: development of filter media, design of filters, field test verification. The cycle was repeated to upgrade the system and produce 2nd generation of filter medium based on the first results. This report contains the main results and conclusions. The results were disseminated also in several other publications, public events, education events for university students and pupils, TV, radio and other media (including YouTube videos). As an outcome the project presents a novel concept for innovative runoff water purification systems that is based on natural materials and aiming to be implemented as part of existing natural based solutions. The solutions have been assessed for economic, technological, social, and environmental feasibility, and concluded as a highly promising novel concept.

Table of Contents

1. Introduction and reasoning

1.1. SHEM-WP project

In urban and suburban areas, rain and storm water runoff has been identified as a significant contributor to water quality impairment. In Finland, *Constructed Wetlands* (CW) are recognized as a cost-effective and socially acceptable water treatment option within urban landscapes, satisfying a range of urban design objectives, including flood protection and treating runoff water. Rain and urban runoff are diverted to constructed wetlands, which will remove contaminants before they reach the catchment area. For example, in region of city Lappeenranta (SE Finland) about 100 wetlands and hundreds of kilometers of runoff water drainage pipelines have been constructed during the last decade. Reducing rainwater runoff and associated nonpoint source pollution is a potentially valuable component of an integrated strategy to protect public health at the least cost, even as part of regional environmental strategy.

The structure and technical specifications of constructed wetlands depend on the location, features and size of the leaching source. In urban area, the system is designed to drain excess rain and ground water from impervious surfaces such as paved streets, car parks, parking lots, footpaths, sidewalks, and roofs. In suburban or in rural areas, the system may focus on catching the leachate from peat production, farming, or swamp areas to protect the catchment waterbody.

These modern wetland and other water landscape approaches aim to rebuild the natural water cycle, i.e., to store runoff water (e.g., retention basins, or constructed wetlands) for a certain time. Purification of water in liquid form ultimately depends on natural filtration, chemical absorption and adsorption by soil particles and organic matter, living organism uptake of nutrients, and living organism decomposition processes in soil and water environments. Soils, especially in wetland and riparian areas, along with vegetation and microorganisms play very important roles in this natural water purification. Microorganisms in soils, wetlands and riparian areas either utilize or breakdown numerous chemical and biological contaminants in water. The most common natural methods of treatment include constructed treatment wetlands, soil filters, stabilization ponds, and the use of aquatic plants or floating islands. Filter developed SHEM-WP project aim to higher level purification targets. Figure 1 shows the project activity circles where urban runoff water quality defines purification target, followed by the laboratory and field tests to support R&D of the novel technology.

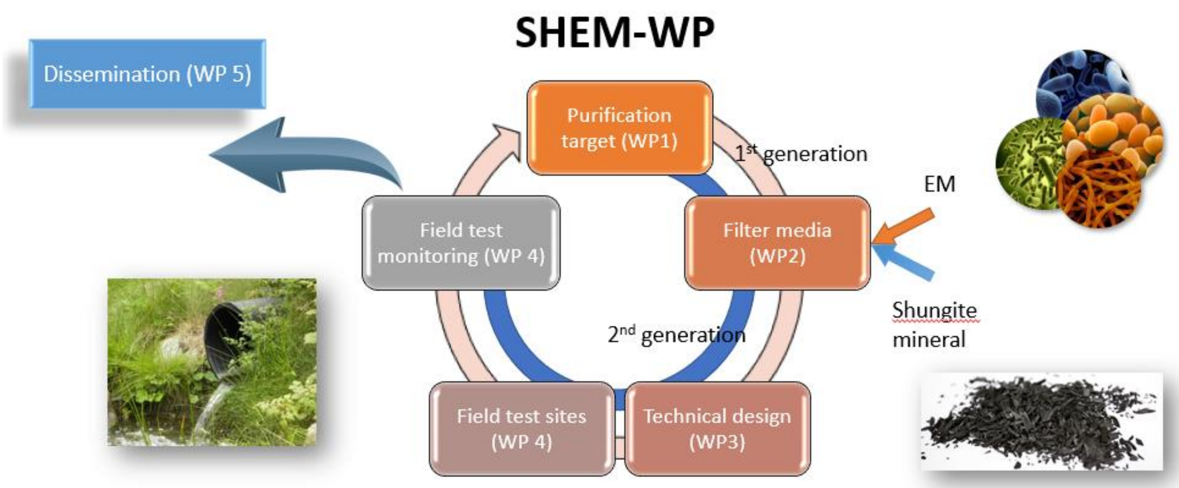


Figure 1 SHEM-WP consists of work packages (Activities): Development of the filter media, designing of the filters, field tests and monitoring of run-off water quality at the sites. Dissemination has had a significant role, and project has been presented in various media as well as in events.

The approach in SHEM-WP utilizes bio-based and chemical-free purification technology by combining: 1) shungite mineral, and 2) effective micro-organisms. These materials are applied in **novel filters** to form a chemical-free filter media. The shungite applications are identified efficient in removal of various metal and organic pollutants including odor. Adding safe micro-organisms into shungite media is aiming to improve removal of nutrients. Technical solutions are target dependent. The filters can be applied in a wide range of applications. However, flow rate, site construction, and water quality of the influent effect on the solution.

Shungite is a mineral containing 10-90 % of carbon. Shungite is mined mainly at the Zazhoginsky deposit, located in Karelia Republic, the Russian Federation. For centuries it has been applied to water purification and healing. Shungite for water purification has typically two major elements; carbon (30-60 %), and silica; and minor elements: iron, aluminum, suplhur, etc. There might also live micro-organisms most beneficial for purification purposes. In SHEM-WP project, certain 1-5 mm sized Shungite powders with thermal and chemical activation were found most suitable for purification purposes. Shungite was found effective in removal of metals (even phosphorus), odors, and many organic compounds. However, in nutrient removal Shungite is not optimal and other minerals, chemicals, or microbes were required. Shungite is commercially available for water purification purposes, as well as for healing or jewelry. Still the shungite for runoff water filters had to be optimized. That concerned 1) physical and chemical composition for optimal sorption capacities, 2) activation, re-usage and maintenance procedures and 3) development of end-of-use scenario.

Effective Microorganisms (EM) is a liquid mixed culture made up of lactic acid bacteria, photosynthesis bacteria and yeast. The special composition of EM makes the liquid exceptionally valuable and rich in extremely antioxidant, life-supporting substances (enzymes, vitamins, amino acids, bioactive substances etc.). They are added into a functional growth media consisting of natural stone material or ceramic material. Various EM products are commercially available, and it is a biological treatment technology, which efficiency in aquatic environment has been proven. However, no application applying EM as part of purification filters has been presented. In SHEM-WP project, various EM solutions and solid material as growth media were studied. It was concluded that the nutrient removal effect depends on successful growth and amounts of micro-organisms in the recipient.

The research and development were done in the laboratory environment and in field tests. The experts from LUT University (Lappeenranta, Finland) and Institute of Geology, Karelian Research Centre RAS, (Petrozavodsk, Russia) were collaborating in development of the filter material and technology. Namely the shungite material was studied and proposed by the Karelian Research Center. The most potential grades for runoff water purification were delivered to Lappeenranta for parallel and complementary studies.

The novel methodology was tested in 6 field test sites (2 sites in Lappeenranta and 4 in St. Petersburg). In these test sites prototypes of filters combining shungite and EM were tested with sampling campaigns. The urban run-off water quality and effect of filters were monitored during 2019-21. The Regional Environmental Center of Lappeenranta had the main responsibility of the field test in Lappeenranta, and SC Mineral company in St. Petersburg.

1.2. Policy relevance

Protection of the aquatic environment is one of the global challenges. In-land surface, ground and marine waters are vital elements of the Earth ecosystem being a part of various bio-chemical processes, home for billions of specious and vital resources for human being. At least two out of seventeen UN Sustainable Development Goals 2030 directly address water issues: clean water and sanitation, life below water. Achieving many other SDGs such as zero hunger, good health and wellbeing, affordable and clean energy, climate change, does not look feasible without sustainable exploitation of aquatic resources. All that illustrates the importance and urgency of actions to protect the aquatic environment at all levels.

In line with the UN SDGs, protection of aquatic environment is one of the pillars for the great number of international and national policies. These policies address various sources of human pressure on the aquatic environment. Achieving the good environmental status of marine waters is the ultimate goal of the EU Marine Strategy Framework Directive. The same targets for inland and coastal waters are set by the EU Water Framework Directive, which also considers good environmental status of marine environment as the ultimate goal. Prevention of releases of nutrients, hazardous substances, microplastic is addressed in a number of other EU policies such as Industrial Emission Directive, Urban Wastewater Treatment Directive, Nitrate Directive and many others. Recently issued the European Green Deal declares such ambitious goal as zero pollution for toxic free environment. The Green Deal also focuses on various aspects of climate change adaptation and mitigation which largely concerns the aquatic environment and storm water management including minimization of flood risks.

In relation with strong commitment to mitigate climate change and increase resilience to its consequences and in the light of the concept of sustainable “bleu economy”, nature-based solutions (NBS) to address societal challenges have been identified as an important policy instrument to achieve the aspirations of the European Green Deal and other key policy objectives such as those set out in the EU Biodiversity for 2030 Strategy and the ambitions of “building back better” from the impact of COVID-19 in the EU Recovery plan and EU Adaption to Climate Change Strategy.

Basic principles of the aquatic environment protection are established by the Federal Law of Russian Federation on Environment Protection and Federal Water Code. These basic principles are specified in a great number of Federal and regional legal acts regulating various aspects of human activities with the ultimate goal to prevent pollution of waters. Among these acts are: Federal law on water supply and water discharge, rules for Water Supply and Wastewater Disposal Systems and other documents prohibiting discharge of untreated wastewaters in the environment and establishing regulations for storm water management.

Protection of the Baltic Sea Marine environment is the ultimate goal of the Helsinki Convention. A large number of HELCOM documents, including the main regional policy agreement – the Baltic Sea Action Plan identify measures which are to be jointly undertaken by the Baltic Sea countries to prevent contamination of the marine environment. Since the Baltic Sea serves as a recipient body for land-based sources, they dominate in overall input of various contaminants to the marine environment. Nutrients causing eutrophication of the Baltic Sea marine environment remain top priorities but hazardous substances and microplastic are at the top of the regional environmental agenda. Wastewater management including stormwaters has been addressed in a large number of HELCOM Recommendations and policy messages. Regionally agreed HELCOM requirements for wastewater treatment are significantly stricter than once set for the whole European Union. And recently adopted HELCOM Recommendation reduction of discharges from urban areas by the proper management of storm water systems promotes innovative approaches on planning and design of stormwater systems based on the most up-to-date scientific knowledge.

All above-mentioned international and national policies demonstrate high priority of the studies aimed to prevent contamination of the aquatic environment utilizing economically feasible and environmentally friendly innovative technologies. Utilizing of locally available materials with a high level of reusability is prioritized in the light of the concepts of circular economy and minimization climate footprint. Shungite, is a unique material available in large amounts in the Baltic Sea region. This Precambrian rock demonstrates unique sorption features and resistance to mechanical and chemical disintegration which makes it also easily recyclable and increases economic feasibility of shungite application as natural filter. Physical and chemical properties of this material have not been well tested yet, and natural variability of its chemical and mineralogical composition also complicate selection of the most effective species. On the other hand, available scientific knowledge already proves its high relevance of this material as innovative and coast effective solution for prevention releases of large number of anthropogenic pollutants to the aquatic environment. All the above-mentioned proves the high relevance of this study to global and regional policy priorities and make technical solutions which can be developed based on the project findings of high demand.

1.3 SHEM purification concept

The proposed concept is aimed to improve efficiency of urban wetlands, or other urban water landscape bodies. It can be implemented into existing conveyance systems. It can be seen as a natural resource-based technology improving the natural processes to achieve the treatment without additional chemical inputs. It consists of a mechanical filtering, sorption and oxidation unit and natural biological removal step with a cultivation tank for microorganisms (Figure 2). The sorption unit applies shungite rocks. In the present concept the micro-organisms are fermented in laboratory and placed into a cultivation tank at-site. The order of sorption biological unit may vary. They might be implemented as independent units or a combined unit. They are aimed to be implemented into existing runoff water conveyance systems in urban environment. The fourth functional unit is aquatic eco-system where the EM is led to alter the existing micro-organism composition to favor of more beneficial types, and to improve growth of vegetation. Appendix 3 presents alternative concepts for the SHEM water purification process proposed.

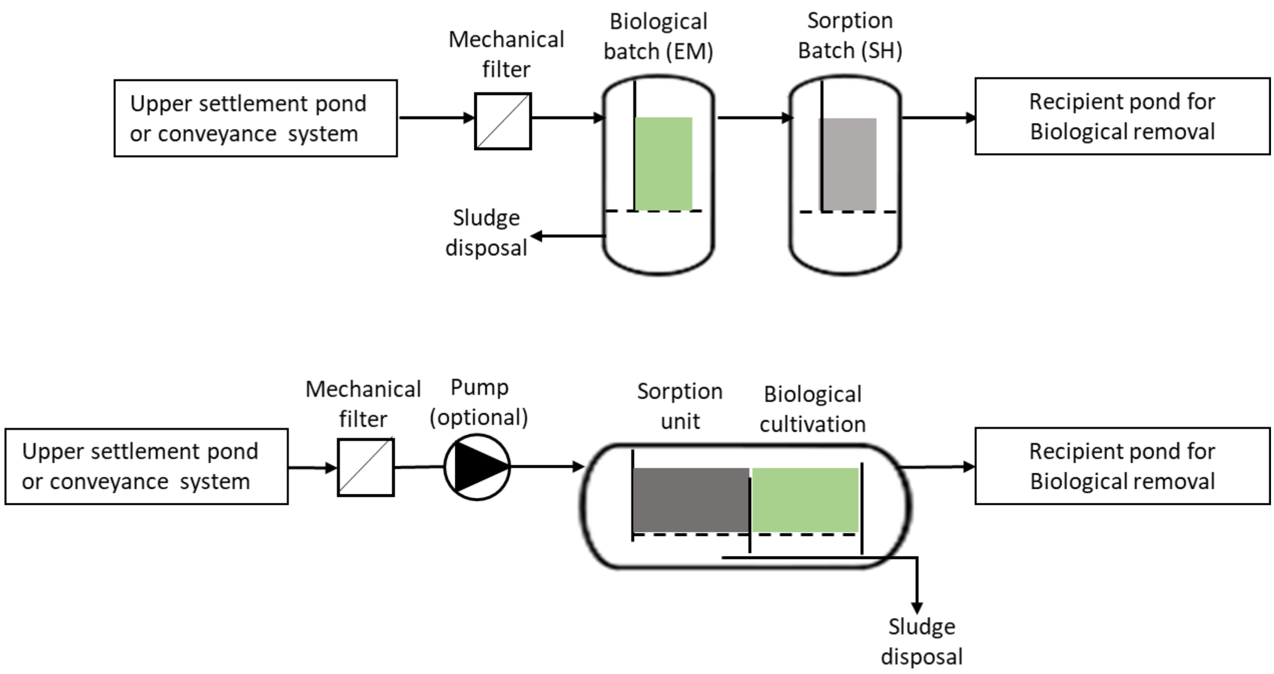


Figure 2 Main SHEM Water Purification concepts.

2. Filtering media

2.1.SHUNGITE AS FILTER MEDIA

Shungite rocks, their origin, mineralogical and chemical characteristics.

Shungite rocks are Lower Proterozoic metamorphic carbon-bearing rocks (2.0 to 2.1 Ga) of the Shunga district near Lake Onega, Karelia, Russia of Karelia (Russia). The characteristic feature of the rock is presence of elementary non-crystalline carbon with a metastable structure incapable of graphitization. Specific physical properties of these rocks are due to the structure and properties of carbon as well as the complex (silicates, aluminosilicates and carbonates) mineral composition.

The occurrences of shungite-bearing rocks represent a combination of a petrified oil field, petrified organosiliceous diapirs and oil spills. These are exemplified by three types of deposit: (i) in situ stratified, (ii) migrated diapirs and (iii) redeposited clastic. In situ stratified deposits are composed of metamorphosed oil shales (<50 wt.% C), rocks containing autochthonous kerogen residue and allochthonous organic matter (50–75 wt.% C) and migrated bitumen, originally liquid hydrocarbons (>80 wt.% C). Diapiric deposits form non-stratified, cupolas or mushroom-shaped bodies composed of shungite containing 35–75 wt.% SiO_2 and 20–55 wt.% C. These are considered to represent organosiliceous rocks, originally gels or mud. Occurrences of clastic shungite are hosted by lacustrine volcanoclastic greywackes deposited from turbiditic flows. Shungite occurs in rocks as <1 mm to 20 cm clasts of lustrous shungite that probably represent redeposited, oxidized oil derived from oil spills. Further formation and alteration of shungite rocks was under the conditions of the green shale facies of metamorphism, at a temperature of no more than 450 °C and a pressure of no more than 7 kbar. However, these parameters varied widely in given ranges during thermal and hydrothermal processes, which led to a broad variation in composition, structure and properties of shungite rocks in different deposits and outcrops. Altogether nine stratigraphic horizons of shungite rocks were conventionally identified in Onega depression as the most free-carbon-rich sections of the stratified strata.

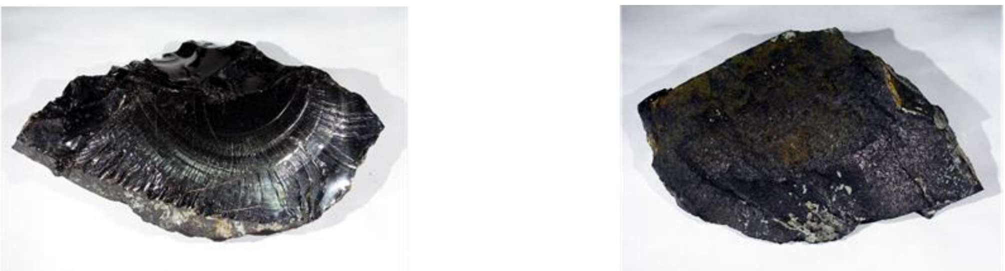


Figure 3 Samples of shungite rocks of different genesis.

In addition to carbon, mineral composition of shungite rock includes quartz, mica, chlorite, albite, calcite, dolomite and sulfides. Chemical composition of shungite rocks is a wide range of macro and microelements. Macroelements (Si, Fe, Ti, Al, Ca, Mg, Mn, K, Na) are mainly included in the above-listed rock-forming minerals, while microelements (Cu, Zn, Co, Ni, Cr, V, Mo, Pb, S, As, Se, etc.) are associated with accessory, mainly sulphide minerals. Among the latter are pyrite, violarite, chalcopyrite, sphalerite, millerite and others, as well as layered silicates, roscoelite and paragonite. Examples of chemical and mineralogical compositions of shungites are given in *Table 1* and *Table 2*.

Table 1 Examples of chemical compositions of shungite rocks.

	Examples of shungite rock			
oxides, %	#1	#2	#3	#4
SiO2	52.28	40.78	30.99	38.6
TiO2	0.21	0.28	0.42	0.34
Al2O3	3.56	5.11	6.96	7.02
Fe2O3	4.23	2.14	6.49	1.47
FeO	0.53	0.53	2.93	0.53
MnO	0.015	0.015	0.1	0.01
MgO	1.11	0.94	5.46	1.03
CaO	0.07	<0.01	2.83	0.58
Na2O	0.06	0.05	1.82	1.5
K2O	0.54	1.20	0.22	1.87
LOI*	35.4	47.03	40.95	46.27
P2O5	0.10	0.05	0.07	0.14
S	1.89	1.86	0.76	0.28
C**	34	48	35	40

**LOI, loss on ignition (includes losses of C, water, sulfides, carbonates). **C was determined by derivatography.*

Table 2 Examples of mineralogical compositions of shungite rocks

	Examples of shungite rock			
Minerals wt.%	#1	#2	#3	#4
Quartz	56	37	2	32
Muscovite	6	12		14
Pyrite	2	3		
Microcline				14
Actinolite			34	
Albite			19	
Kaolinite			2	
Chlorite			8	

Shungite rocks demonstrate several specific physical and chemical properties, which determine the prospects for their practical use in metallurgy as coke, in chemistry as a catalyst, in water purification as an effective sorbent, and as an active filler of composite materials. One of the prospective practical uses of shungite rocks is their application as a sorbent and filtering material in water purification and water treatment for industrial, household or storm waters. According to various studies, shungite as a sorbent features several positive characteristics: high mechanical strength and low abrasion; high filtering capacity (processability, due to low pressure resistance); the ability to sorb many substances, both organic (petroleum products, benzene, phenol, pesticides, etc.) and mineral (iron, manganese, phosphorus, arsenic).

Unfortunately, for many consumers, the term “shungite” and “shungite rock” refers only 99 to the rock determined by its carbon content, without consideration of the carbon structure, mineral composition, rock texture and consequently their physical and chemical properties. Therefore, expectedly, various studies of shungite rocks reveal variability of properties, which are often not confirmed by subsequent tests due to involvement of different rock shungite rock species. That is why, one of the goals of this study is to prove sorption capacity of certain shungite rock types in laboratory and field tests in Finland and in Russia.

Shungite field work

The selection of the optimal shungite rock was carried out in two stages. The study on applicability of shungite rock types for water filtering started from selection of 4 potential shungite species. The main types of shungite rocks were tested, differing in geological conditions of formation, and belonging to the sixth (shungite rocks #1 and #2 in *Table 1* and *Table 2*), second (#3) and fourth (#4) shungite-bearing horizons (Figure 5). Main studies were made in Institute of Geology, Karelian Research Centre RAS, Petrozavodsk, Russia. Samples were also delivered to LUT University, Finland, for parallel investigation in 2019. As result from environmental feasibility and sorption capacity studies carried out, it was shown that the most promising as a filter material are rocks of the second shungite-bearing horizon (Kovalevski, Reinikainen, Reinikainen, Rozhkova, & Sihvonen, 2020), available on natural outcrops that are not currently being industrially developed. During the field season in 2019, several samples of shungite rocks were extracted from natural outcrop of second shungite-bearing horizon to select the best filter material for water treatment. A technological sample (about 80 kg) was also extracted manually for the preparation of the filter material for the purpose of testing it in full-scale conditions in Finland. The extracted sample was previously cleaned by visual selection of polluting components (stuck pieces of earth, moss, quartz and mica fragments). Further, the sample of shungite rock was crushed in a jaw crusher, dispersed, and classified to obtain 40 kg of filter material of a fraction of 1-3 mm. 20 kg of shungite was dispatched to Finland for investigation of its adsorption features and application in filters in 2019-2020.

Selecting the optimal rock specie considering the commercial aspects and adsorption capacity continued, and the third portion of shungite rock (120 kg) was extracted, grinded, and a part of the obtained sample of a fraction of 1-3 mm weighing 20 kg was delivered to the Finnish partners in 2021. Figure 4 shows the stratigraphy of rocks of the Onega structure, around the northwestern part of Lake Onega according to (Deines, Kovalevski, Kochneva, Moshnikov, & Rozhkova, 2020) with marked shungite rock types for water filtering and photos from field site visit to industrially developed fields (sixth horizon) and to undeveloped natural outcrops (fourth and second horizons). And Figure 5 shows a field work at the Zazhoginsky deposit and on industrially undeveloped outcrops for manual extraction of technological samples of shungite rocks in 2019-2021.

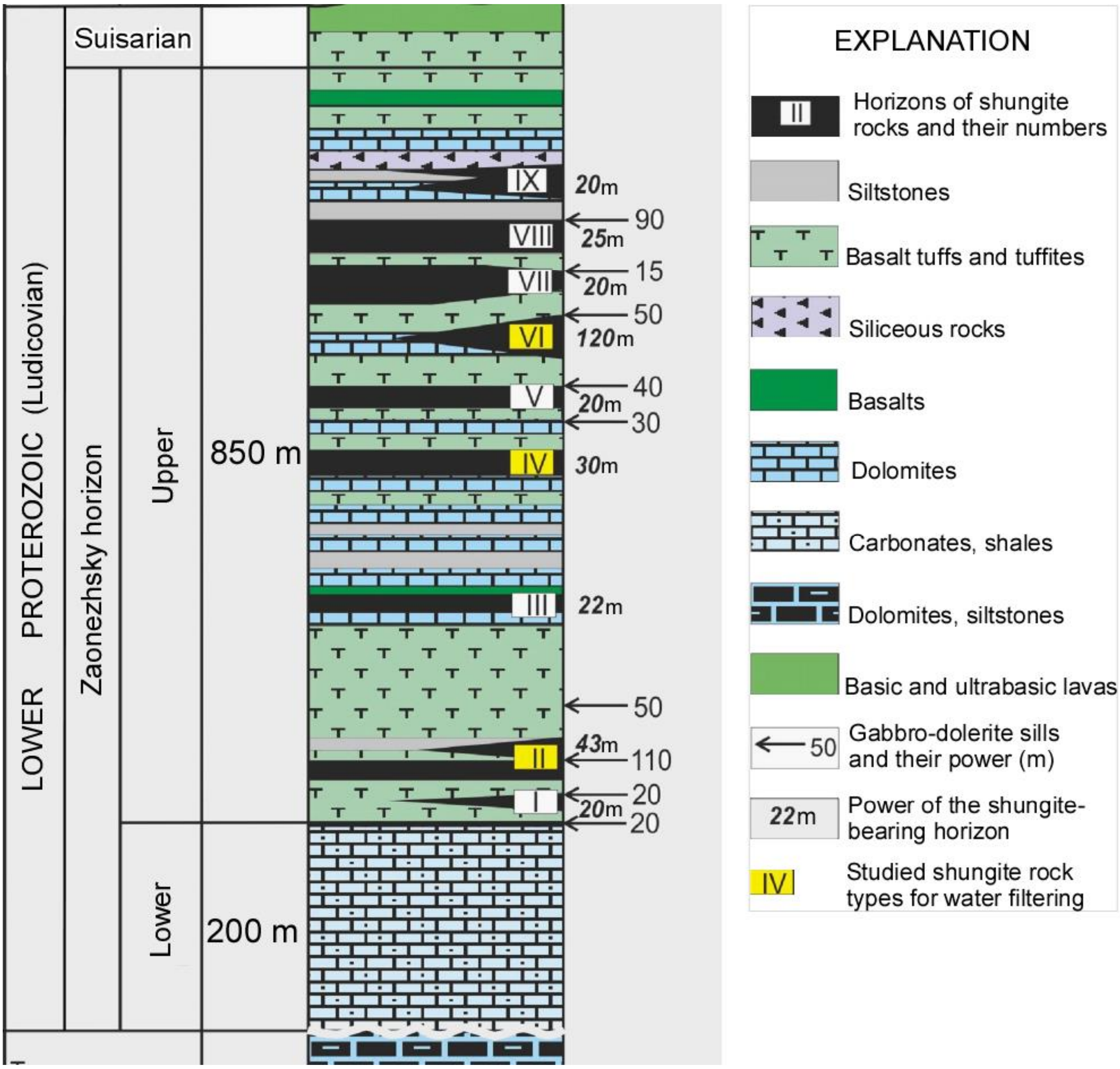


Figure 4 Stratigraphy of rocks of the Onega structure, around the northwestern part of Lake Onega according (Deines, Kovalevski, Kochneva, Moshnikov, & Rozhkova, 2020) with marked shungite rock types for water filtering and photos from field site visit to industrially developed fields (sixth horizon) and to undeveloped natural outcrops (fourth and second horizons).

Figure 5 Field work at the Zazhoginsky deposit and on industrially undeveloped outcrops for manual extraction of technological samples of shungite rocks in 2019-2021.

Preparing and selecting Shungite

To determine the effect of the preparation conditions, the shungite rock was crushed in a jaw crusher, and then finely ground to a size of < 0.1 mm in two different ways, in a vibrating grinder and in a jasper mortar. The obtained powders were subjected to additional processing, ultrasonic dispersion at a frequency of 22 kHz for 10 minutes. The assessment of the adsorption activity of shungite rock was carried out by adsorption of methylene blue (MB) and methanyl yellow (MY) from aqueous solutions on samples immediately after their creation and after 90 days of exposure to air. The amount of dye absorbed from the solution (Q, mg/g) by the sample of the test material (fraction >1 mm) under static conditions was taken as a measure of its activity. The dye concentration in the solution was determined using Raman spectroscopy according to the method proposed elsewhere (Rozhkova & Kovalevski, 2019).

Scanning electron microscopy and EDS analysis of the surface of powder particles obtained by grinding in a mortar revealed the presence on the surface of the particles a dense layer (a shell) consisting of a mixture of microfragments of minerals and carbon (Figure 7a, Table 3). The surface of the particles obtained in the vibrating grinder is cleaner and contains only a small amount of microfragments of minerals and carbon (Figure 7c). Ultrasonic treatment has significantly changed the appearance of the particle surface, all the mineral-carbon components introduced during the grinding process have been removed (Figure 7 b, d). The mineral components detected on the surface of the ultrasound-treated particles (Figure 7b, Table 3) are not introduced, but are part of the analyzed particle sites, as can be determined based on their morphology.

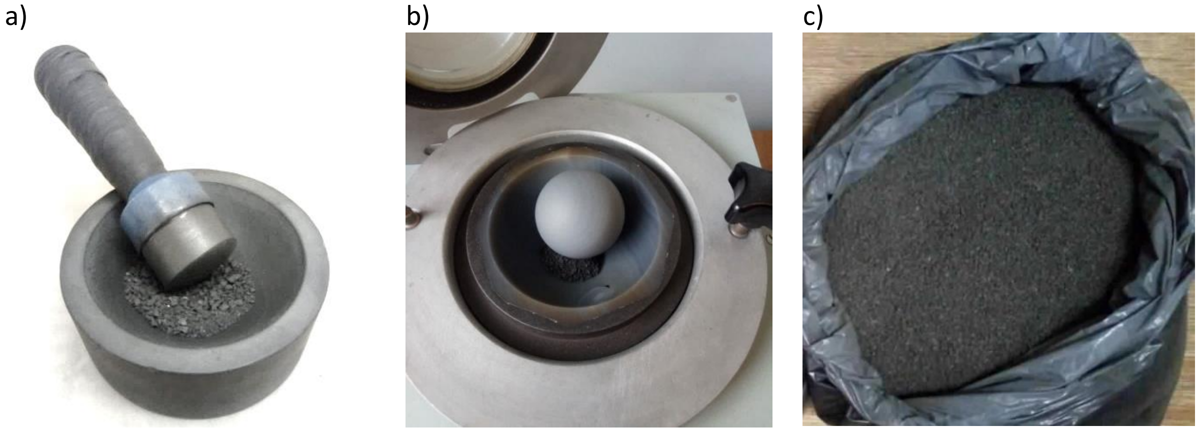


Figure 6 A) Crushing by abrasion (agate mortar), B) Crushing by splitting up (vibration impact mill), C) Shungite after crushing.

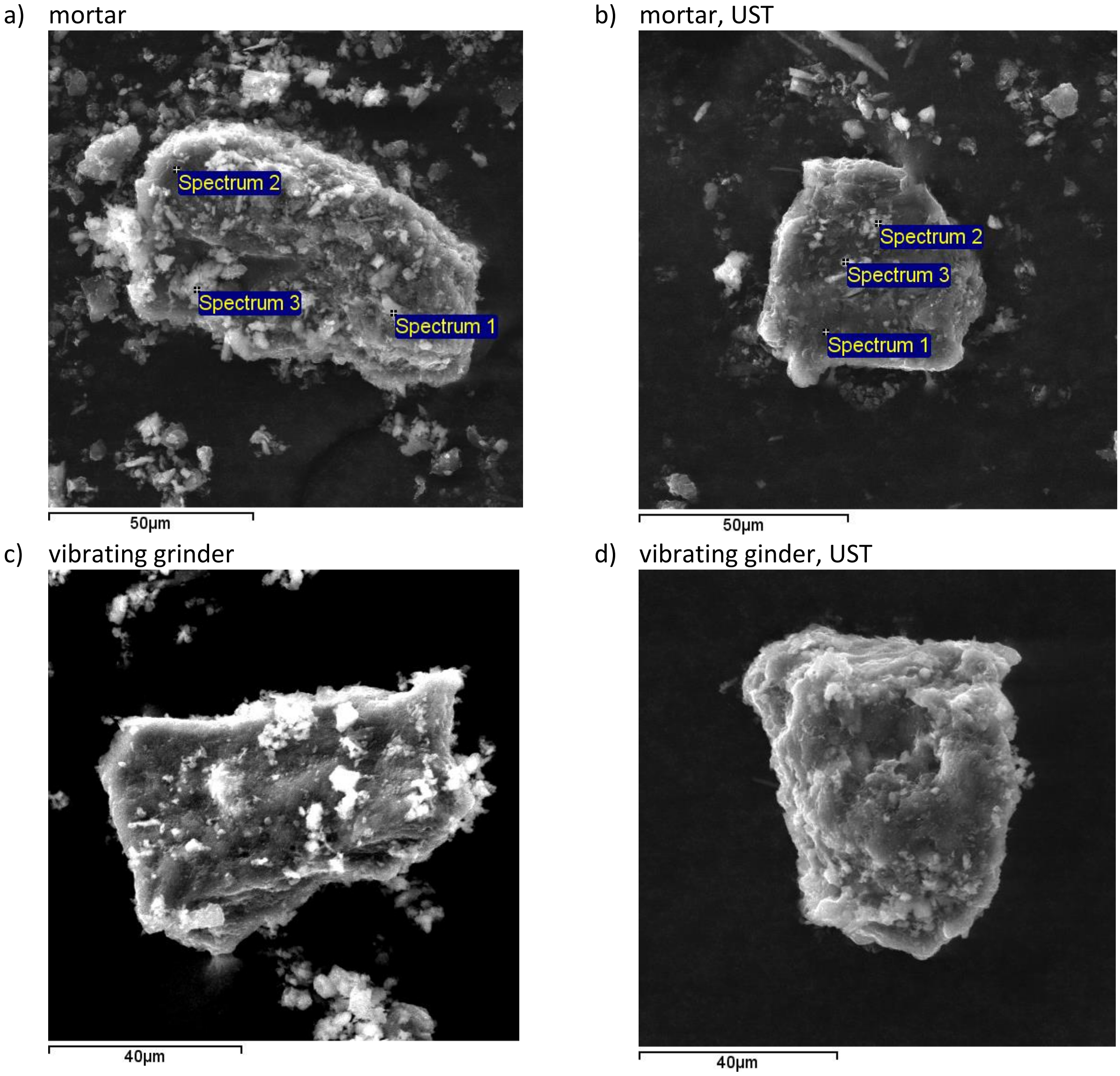


Figure 7 Carbon-mineral sites on the surface of particles crushed in a mortar (a, b) and in a vibrating grinder (c, d), before (a, c) and after ultrasonic treatment (b, d).

Table 3 Element composition of some sites on the surface of ShR particles crushed in a mortar before (a) and after (b) ultrasonic treatment (Figure 7).

Elements	before ultrasonic treatment			after ultrasonic treatment		
	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
C	37.35	95.34	36.10	91.24	72.44	28.13
O	33.4	4.66	34.95	8.10	19.62	47.75
Na	0.55	-	-	-	-	-
Mg	4.38	-	4.8	-	1.44	4.64
Al	2.16	-	4.84	-	11.36	2.11
Si	12.35	-	6.7	0.66	3.08	10.5
Ca	3.5	-	-	-	-	2.26
Fe	6.33	-	12.6	-	1.8	4.6
Total	100	100	100	100	100	100

* The analysis was carried out on unpolished particles and is actually semi-quantitative.

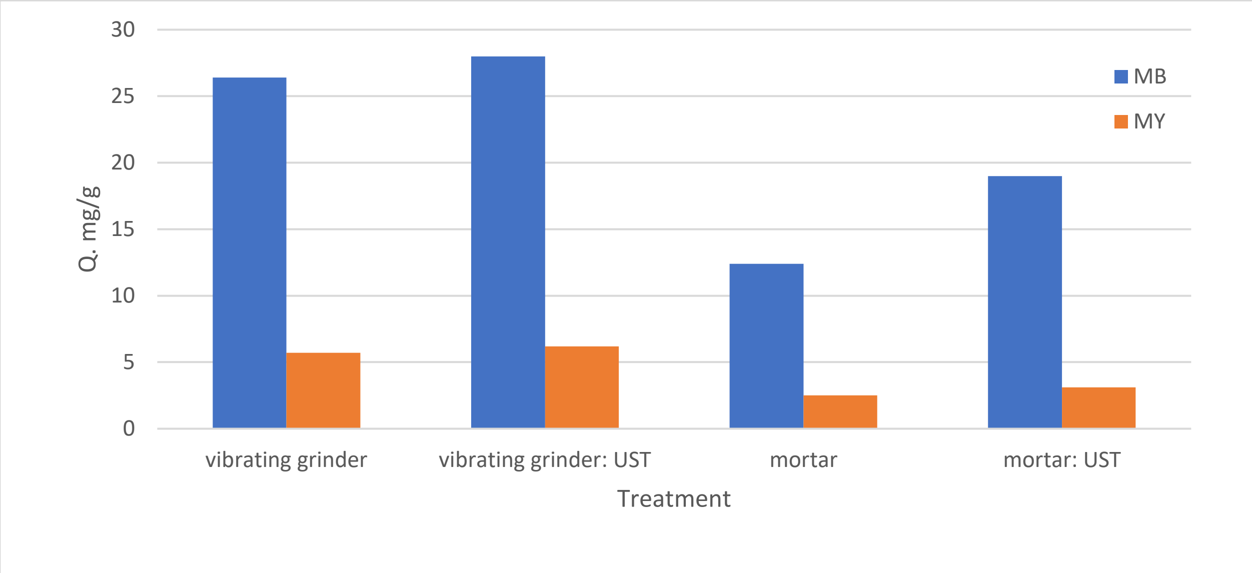


Figure 8 The adsorption capacity (for the removal of MB and MY) of SH samples crushed with mortar, and in a vibrating grinder: Before and after ultrasonic treatment (UST).

It has been found that the sorption of both basic (MB) and acidic (MY) dyes is greater for the powder obtained on a vibrating grinder (Figure 8, MB – 26.4 mg/g; MY – 5.7 mg/g) than for powder subjected to grinding in a mortar (Figure 8, 12.4 mg/g and 2.5 mg/g, respectively). Ultrasonic treatment leads to the increasing of sorption activity of the powders both for the powder crushed in a vibrating grinder (Figure 8, MB - 28 mg/g; MY - 6.2 mg/g) and ground in a mortar (Figure 8, 19 and 3.1 mg/g, respectively).

With various types of mechanical effects on shungite rock, such as rubbing and impact, various changes in surface properties occur. In particular, when grinding shungite rock, a thin carbon-mineral shell is formed on the surface of the particles, which makes sorption difficult. Over time, the carbon-mineral shell can be oxidized and enriched with active centers, which leads to an increase in the sorption activity of the shungite material. The results obtained indicate that grinding in a vibrating grinder is a more optimal way to obtain shungite material as a medium for water treatment. It should also be noted that a similar effect of increasing the sorption activity of shungite material is observed with prolonged exposure at room conditions (temperature ~ 20 ° C and relative humidity ~ 50-70%.).

Environmental Acceptability and leaching

Leaching of chemical elements from shungite rocks is controlled by several factors. As previously shown, both sorption and leaching properties of shungite are equally important for its application for water purification. Those are determined by the type of shungite rocks, content and composition of carbon and minerals, and their structure and physicochemical properties (the value of the specific surface and its chemical state, for instance). Aqueous extracts from different shungite rocks differ in ionic and micro component composition. Leaching of ions from the minerals constituting different shungite rocks is determined not only by the composition of the rock but also by pH of water. In fact, lower pH provides higher intensity of hydrolytic processes decomposing minerals, particularly sulfides. However, the content of certain elements (Na, Ca) in the solutions does not depend on the acidity of the aquatic media and their content in the rocks (Rozhkova V. S., Kovalevski, Kochneval, & Lozovik, 2012).

Hydrogen index (pH) is one of the most important indicators of the interaction between shungite rocks and water. For the selected rocks, the pH had different values ranging from 6.1 to 3.4. Measurements made in Finland on fractions about 2 mm at 24-hour exposure differ significantly. Additional experiments conducted in Russia showed changes in pH over time. pH was decreasing to various degrees for different shungite rocks after immersing samples to water with subsequent stabilization of the parameter in a few days. Samples 1 and 4 demonstrated similar pH values in test made in Russia and Finland (Kovalevski, Reinikainen, Reinikainen, Rozhkova, & Sihvonen, 2020). Variations of pH values for samples 2 and 3 measured in two countries revealed a certain difference. The difference may be result of either heterogeneity of samples 2 and 3 or other processes affecting the leaching processes. These pH changes were observed only in a closed volume and may be enhanced by the presence of water flow.

pH in the contact layer of shungite rock and water affects the leaching of chemical elements from samples, their ion exchange reactions and sorption properties. The results of experiments on the leaching of some chemical elements from shungite rocks in closed volume are shown in Figure 9. The total number of metals determined from the leachate with ICP-MS was 26, including phosphorus. Samples 1 and 2 showed high degree of leaching of chemical elements, among which Ni (0.4 mg/kg) and Zn (4 mg/kg). These concentrations exceed permissible levels which makes the application of these shungite rock species environmentally unacceptable. Shungite from sample 2 also demonstrated exceedance of inert material values for leaching of Cu, Cd and Se.

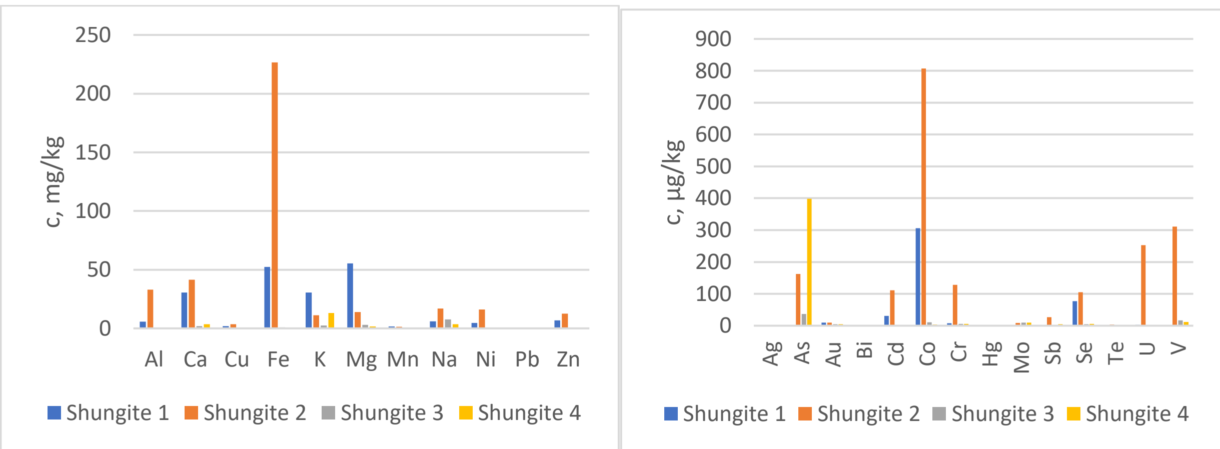


Figure 9 Results of some metals from leaching test (L/S = 10, SFS-EN 12457-2:2002). Inert waste has threshold values for example to Ni (0.4 mg/kg), and Zn (4 mg/kg). Therefore, shungite grades #1 and #2 would not be environmentally feasible in Finland: SH#1 leached 4.5 mg_{Ni}/g, and 6.9 mg_{Zn}/g and SH#2 17 mg_{Ni}/g, and 6.9 13 mg_{Zn}/g

Shungite is not available in Finland as a commercial product for water purification or land construction purposes. Therefore, the environmental acceptability needs to be determined before it is applied. The

Finnish Government Decree on Landfills (331/2013) requires the measurement of a specific set of analyzes from the waste material before its disposal to land. Similar analyses were carried out to evaluate environmental applicability/suitability of shungite. The test included similar analyses that are applied in land construction material and recycled waste:

- Dry matter (%)
- Leaching test (SFS-EN 12457-2:2002): Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)
    - Total organic carbon, TOC (%w/w)
    - PCB compounds (mg/kg)
    - Mineral oil, C10-C40 (mg/kg)
    - PAH compounds (mg/kg)
    - pH
    - Acid neutralization capacity, ANC
    - Soluble metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn) (mg/kg)
    - Chloride, Cl (mg/kg)
    - Fluoride, F (mg/kg)
    - Sulphate, SO4 (mg/kg)
    - Phenol index
    - Dissolved organic carbon, DOC (mg/kg)
    - Total dissolved solids, TDS (mg/kg)

The leaching tests were applied as criteria for selection of “environmentally acceptable shungite grades” for water purification filters. Only the metal leaching from some shungite grade exceeded inert waste threshold limits. Figure 9 illustrates results from one stage leaching test for 4 different shungite grades. The most common metals leaching in significant amount were Ni and Zn (limits for inert material were exceeded). There were also grades where the minor elements were leaching out, for example As, Cd, U, and V. In LUT laboratory concentrations of a total of 26 metals were analyzed to ensure ecotoxicological safety of applied shungite grades. For SHEM-WP filters the shungite material was tested before applying it in the filters. Leaching of some metals that are not classified as toxic in these concentrations can be seen as beneficial for water purification purposes. Iron and aluminum compounds, as an example, can improve removal of phosphor.

Bacteriological features of shungite rocks

Despite the importance of microbiological processes in many areas of practical use, the microbiota of shungite rocks remains poorly studied. One of the reasons for this condition is that the conditions of formation and occurrence of shungite rocks are very complex and differ in physical, physico-chemical, geochemical and geological features, which causes the corresponding diversity of the microbiota of shungite rocks. It should be noted that direct observation of microbiota on shungite rocks using microscopy methods does not always allow the detection of microbial cells, which indicates a low biomass of microorganisms in individual samples. Methods of DNA analysis of the bacterioflora of shungite rocks are more effective.

Strains related to the genus *Bacillus* have been isolated from the microflora of shungite into a pure culture for a number of signs; the presence of a gram-positive cell wall, the ability to form endospores and synthesize catalase. According to the complex of morphophysiological, cultural, biochemical characteristics and the results of genotyping, the isolated cultures can be attributed to the species *Bacillus subtilis*. Based on the results of determination of nucleotide sequences of 16S rRNA genes for *Bacillus subtilis* culture the complete sequence (1487 nucleotides) of the bacterial component of the amplification of the gene encoding 16SrRNA has been determined. No archaeal component has been identified for this sample. No minor components were detected on the spectrograms (Figure 10).

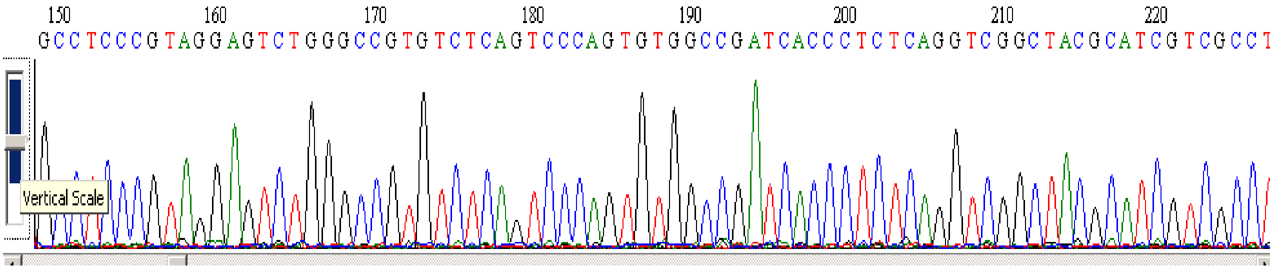


Figure 10 Pictogram section of Bacillus subtilis strain found in shungite rock

The analysis of primers for *Bacillus subtilis* obtained using BLAST analysis and their percentage reliability are presented in Table 4. According to the results obtained, the taxonomic position of the *Bacillus subtilis* culture according to the RDP Classifier at 80% and 95% confidence levels (Wang, Garrity, Tiedje, & Cole, 2007) corresponds to genus Bacillus, family *Bacillaceae*, order *Bacillales*, class Bacilli, phylum Firmicutes, domain Bacteria. Data on the nucleotide sequences of 16S rRNA genes of representatives of the genus indicate 98-99% similarity with the species *B. amyloliquefaciens*, 99% similarity with the species *B. atrophaeus* and 100% similarity with the species *B. vallismortis*, *B. subtilis* and *B. nematocida*.

*Table 4 Comparative analysis of primers for Bacillus subtilis obtained by **Blast** analysis*

№	Identified species	Max score	Total score	Query cover	E value	Ident	Accession
1	Bacillus amyloliquefaciens strain NBRC 15535 16S ribosomal RNA gene, partial sequence	2715	2715	99%	0.0	99%	NR_112685.1
2	Bacillus amyloliquefaciens strain NBRC 15535 16S ribosomal RNA gene, partial sequence	2713	2713	98%	0.0	99%	NR_041455.1
3	Bacillus vallismortis strain DSM 11031 16S ribosomal RNA gene, partial sequence	2713	2713	100%	0.0	99%	NR_024696.1
4	Bacillus subtilis subsp. subtilis strain 168 16S ribosomal RNA, complete sequence	2708	2708	100%	0.0	99%	NR_102783.2
5	Bacillus nematocida strain B-16 16S ribosomal RNA gene, partial sequence	2708	2708	100%	0.0	99%	NR_115325.1
6	Bacillus subtilis subsp. inaquosorum strain BGSC 3A28 16S ribosomal RNA gene, partial sequence	2702	2702	100%	0.0	99%	NR_104873.1
7	Bacillus amyloliquefaciens strain BCRC 11601 16S ribosomal RNA gene, partial sequence	2700	2700	98%	0.0	99%	NR_116022.1
8	Bacillus atrophaeus strain JCM 9070 16S ribosomal RNA gene, partial sequence	2700	2700	99%	0.0	99%	NR_024689.1
9	Bacillus subtilis strain DSM 10 16S ribosomal RNA gene, partial sequence	2697	2697	100%	0.0	99%	NR_027552.1
10	Bacillus subtilis strain IAM 12118 16S ribosomal RNA, complete sequence	2691	2691	100%	0.0	99%	NR_112116.2
11	Bacillus halotolerans strain DSM 8802 16S ribosomal RNA, partial sequence	2691	2691	100%	0.0	99%	NR_115063.1

It should be noted that in the composition of geological and biological systems, most microorganisms function as a combined consortium attached to the surfaces of minerals, united by common trophic connections. Such consortia consist of metabolically similar species that perform interdependent physiological processes and form specific ecological and physiological groups; they have a wide range of adaptive reactions to solar radiation, drying and rehydration, temperature fluctuations and lack of nutrients (Costerton, Lewandowski, Caldwell, Korber, & Lappin-Scott, 1995). The strains of the genus *Bacillus* are extremely diverse, many of them are not definitively classified as species and may have potentially demanded properties. Recent studies have shown that the Bacillus subtilis strain has a broad antibacterial spectrum: it can inhibit the growth and reproduction of *Staphylococcus aureus*, *Enterococcus*, *salmonella* and *chicken Escherichia coli* and other bacteria such as gram-positive bacteria (Lu, Guo, & Liu, 2018). It has been established that *Bacillus subtilis* demonstrate different growth morphologies when building reliable systems in various environmental conditions (Tasaki, Nakayama, & Shoji, 2017). Also, the *Bacillus subtilis strain IAM 12118*, found in shungite rocks, is 99% identical according to the results of 16S RNA analysis to the *Bacillus sp. BSC154 strain*, which is capable of nitrate reduction, assimilation and dissimilation of sulfates (Bailey, et al., 2014). *Bacillus subtilis strain IAM 12118* can also be used as a test object in biodegradable plastics used for adsorption of hydrophobic organic pollutants (Matsuzawa, Kimura, Nishimura, Shibayama, & Hiraishi, 2010). In general, the presence of a natural microbial component on shungite rocks can be an additional positive factor providing microbiological wastewater treatment

Shungite sorption

Sorption is a physical and chemical process by which one substance becomes attached to another. It covers absorption, adsorption, and ion exchange. Chemical absorption or reactive absorption is a chemical reaction between the absorbed and the absorbing substances. Sometimes it combines with physical absorption (water). Adsorption occurs as adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. The process differs from absorption, in which a fluid (the absorbate) is dissolved by or permeates the absorbent. Adsorption is a surface phenomenon, while absorption involves the whole volume of the material. Adsorption does often precede absorption. Ion exchange is a reversible interchange of one kind of ion present on an insoluble solid with another of like charge present in a solution surrounding the solid with the reaction. All these sorption mechanisms can occur in shungite rock applications. In alkaline solutions the cation exchange can be expected to predominate, while anion exchange is more likely in acidified solutions. Organic compounds, and some metal compounds can be oxidized. Hydroxyl, oxides and carbonyls may participate in hetero-oxidation of various compounds, and the mechanisms are complicated. In SHEM-WP the aim is focused on applicability of shungite in filters. The laboratory studies aimed at defining procedures in selection of potential shungite rock and in recommendations of maintenance of the system. Field tests were applied to verify laboratory results in practice. Therefore, theoretical phenomenon behind the sorption got less weight, and the evaluation focused on most relevant issues in development of the application.

Sorption and reusability topics addressed in SHEM-WP

- Indicator development for identification of sorption capacity
    - Anionic and cationic adsorption capacity
    - Urban origin compounds adsorption capacity of heavy metals: mainly Cu, Zn and Ni
    - Sorption of phosphor, ammonium and oil compounds studied in laboratory tests
    - In field tests the effect of purification systems studied with more details

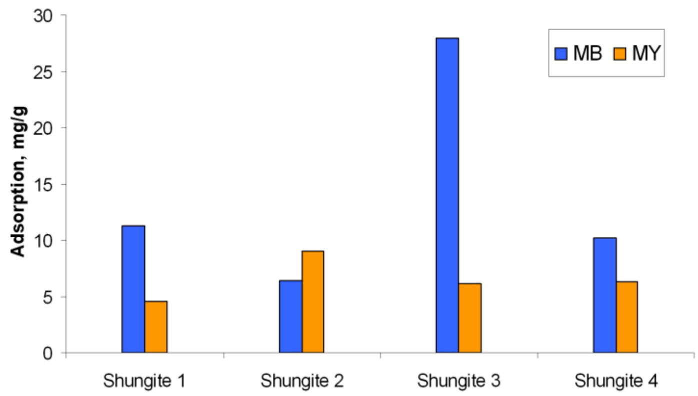


Figure 11 Sorption activity of shungite rocks to cationic and anionic complexes on the example of methylene blue (MB) and methanyl yellow (MY) for shungite 1, 2, 3 and 4. The method can be applied in selecting potential shugite grade. The methodology is novel Raman based analytics and published by SHEM-WP project partner (Rozhkova & Kovalevski, 2019)

A quick method for choosing shungite with high sorption capacity was developed and applied in selection of shungite material. The method is based on Raman spectroscopy for determining the concentration of methylene blue and metanil yellow dyes in aqueous solutions, with acetonitrile as an internal standard. The proposed method makes it possible to efficiently and quickly determine the adsorption of anionic and cationic dyes by different shungite grades. Figure 8 and Figure 11 show results determined with the novel quick test.

The adsorption tests are often made applying artificial solutions with 1-5 chemical compounds. In the adsorption test pH is adjusted and the adsorption is measured in equilibrium concentration. Figure 12 shows results from an experiment to determine the sorption activity of shungite rocks by ions of various metals and complexes. A high adsorption capacity was found in samples 3 and 4 for the sorption of C, Zn and P, while negative values for the sorption of Na, Mg and Ca indicate the leaching of these elements from the third sample during the experiments. A mixture containing Cu - 57.5 ppm, Zn - 94.9 ppm, Na - 96.3 ppm, and P - 42.4 ppm was applied in this experiment. Changes in the concentration of metals in the solution affect the sorption efficiency (Figure 13). At the same time, based on the sorption kinetics, it follows that ion-exchange processes occur very quickly and do not require a long contact time.

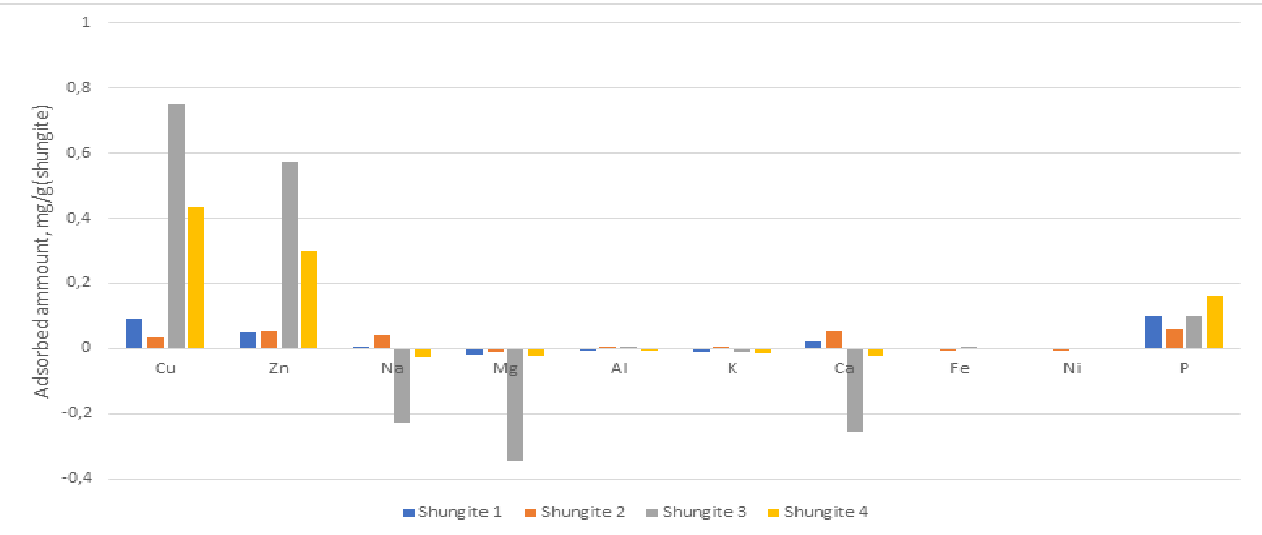


Figure 12 Results from the metals adsorption test of 4 different untreated shungite grades. Results given in mg/g(shungite). Negative bars indicate that the element in question has been released from the shungite during the adsorption experiment.

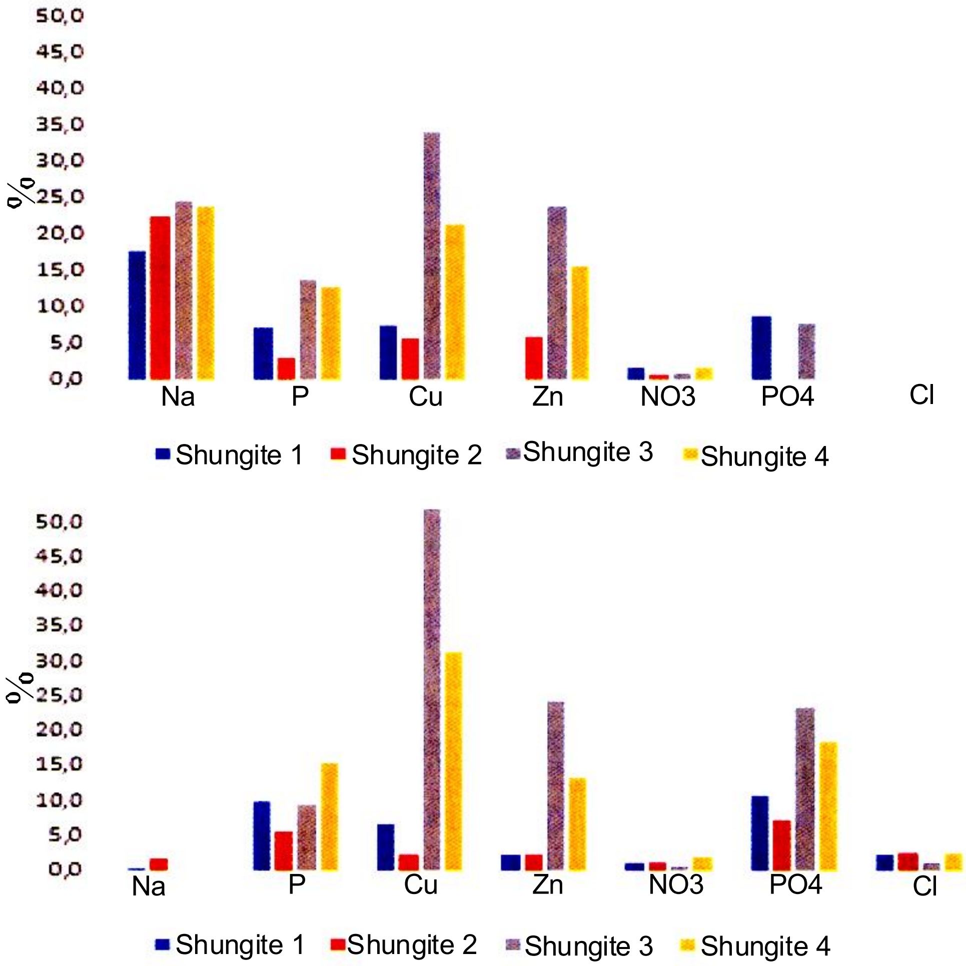
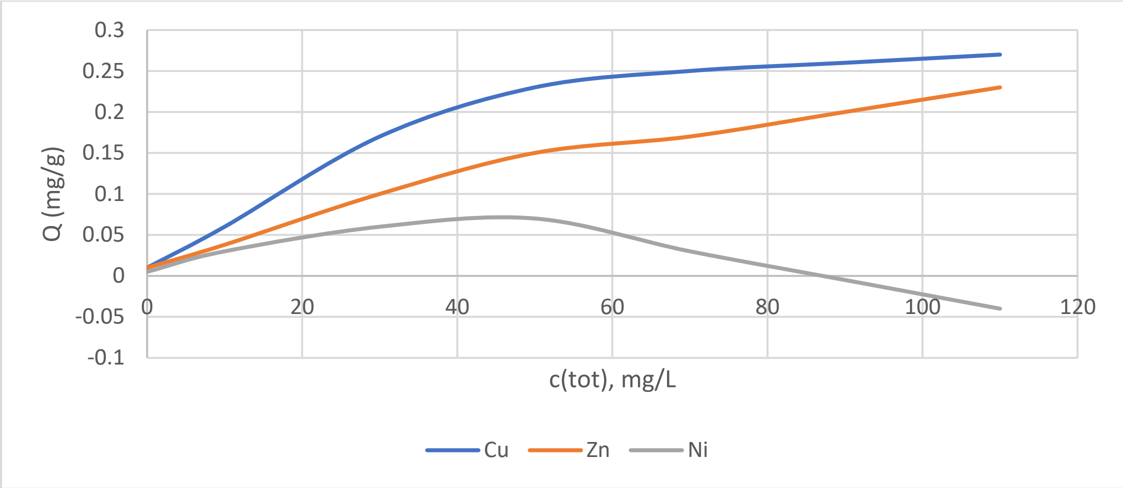
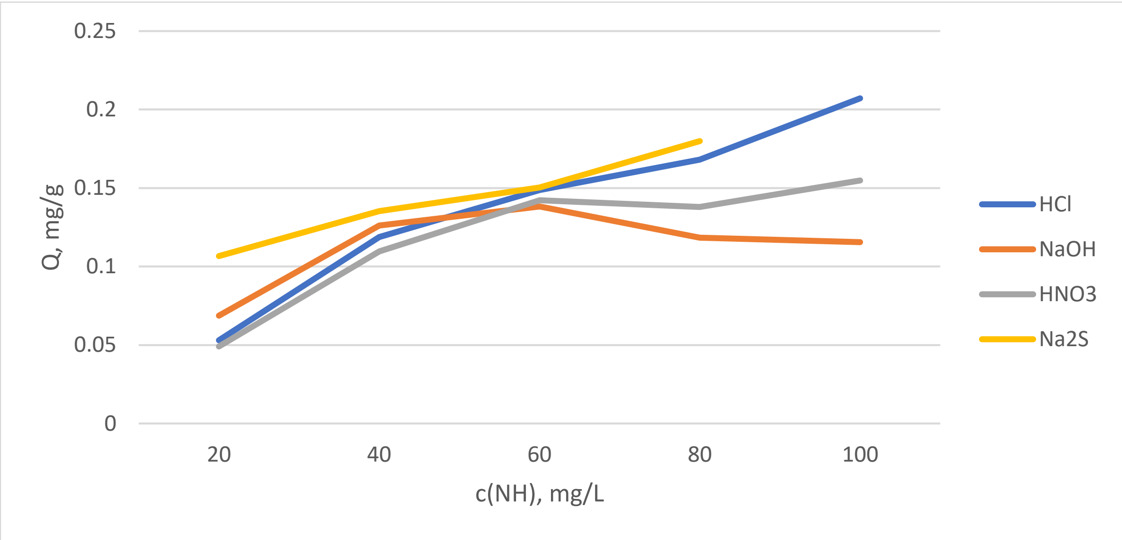


Figure 13 Results from the metals adsorption test. Results given in % in a) high concentration, and b) lower concentration of the metals. Adsorption mechanisms are affected by the ion concentration in the solution (Na). Nitrate removal is inefficient with any shungite fraction studied.

Adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. Adsorption isotherms provide information on the interactions of molecules with surfaces in equilibrium solution. The Freundlich isotherm assumes that the adsorption occurred on heterogeneous sites with non-uniform energy level, which was not restricted to the monolayer. Contrarily, the Langmuir isotherm is based on the assumption that the adsorption takes place only at homogenous sites within the adsorbent surface with uniform energy level, which would conclude that the adsorption is monolayer in nature. Equilibrium isotherms described using the Langmuir-Freundlich model gave the best fit to empirical results (Figure 15), that indicates a heterogeneous adsorption process involving multiple uptake mechanism. Langmuir isotherm estimates the maximum adsorption capacity (Q_m) for Zn absorption as 0.52 $mg_{Zn}/g_{shungite}$ for the NaOH treated shungite sample. NaOH treatment of shungite made the surface visibly more hydrophilic, and alkali treatment is known to improve adsorption capacity of metals (cations). Q_m depends on pH, temperature, ionic concentration, pressure, etc., and shungite is heterogenous material. Experimental results in real conditions and water matrices give more reliable and realistic estimates for adsorption and other sorption mechanisms of shungite. Zn, Cu, Ni and Al are in general related to emissions from urban build environment to runoff water. Thus, improving their uptake from runoff water was in focus.



A)



B)

Figure 14 Concentration of ions effect in adsorption. A) Cu and Zn are more attracted to the surface than Ni. Results suggest that in certain concentration Ni in shungite is replaced with Cu or Zn and Ni is leaching out. Experiments were carried out in laboratory environment (T = 20-21 ºC, pH adjusted to 5 at equilibrium concentration). B) Activation effects on ammonia removal depends on ammonium concentration (c(HCl) = 1.5 moll/L, c(NaOH) = 0.2 mol/L, c(HNO3) = 6 mol/L (T = 90 ºC), c(Na_2S) = 0.2 mol/L). For all tests shungite was washed with HCl solution and water and dried in 105 ºC oven before experiments. (Potila, 2020)

Metal (e.g., Al, Ca, Ce, Fe, La, Mg, Mn, Zn, Zr) hydroxides/oxides provide excellent adsorption capacities of phosphate, in addition to other advantages such as fast kinetics and good selectivity. These compounds have been incorporated into zeolites, mesoporous silica, activated carbon, biochar, and bio-derived materials, to enhance their adsorption capacities. P has many natural and anthropogenic origins, being considered a major pollutant as it can accumulate and reach dangerous concentrations in water bodies. Eutrophication can be induced due to high P concentrations, but even smaller amounts can stimulate excessive algal growth, particularly blue-green algae (i.e., Cyanobacteria). In field tests, the runoff water contained sudden high amounts of phosphorus. The main mechanisms in present systems for phosphorus are sedimentation as metal compounds and nutrient uptake of plants. EM is improving the natural uptake and accelerating the growth. However, also shungite has P adsorption capacity. According to the experiments adsorption capacity 15-20 mg-P/g can be achieved. Non-activated shungite had lower Q_m = 1-8 mg-P/g, while highest Q_m > 130 mg-P/g were reached with thermal+NaOH treatment in colon tests. Commercial P adsorbents have been reported to have been reported to have comparable adsorption capacities: granular ferric hydroxide 105 mg-P/g, ferrihydride 22 mg-P/g, Magnetite 19 mg-P/g, Geothite 16 mg-P/g, Fe-Mn oxide 18 mg-P/g, Zn-Al layered double hydroxide (LDH) 22 mg-P/g, and Calcinated Zn-Al LDH 36 mg-P/g.

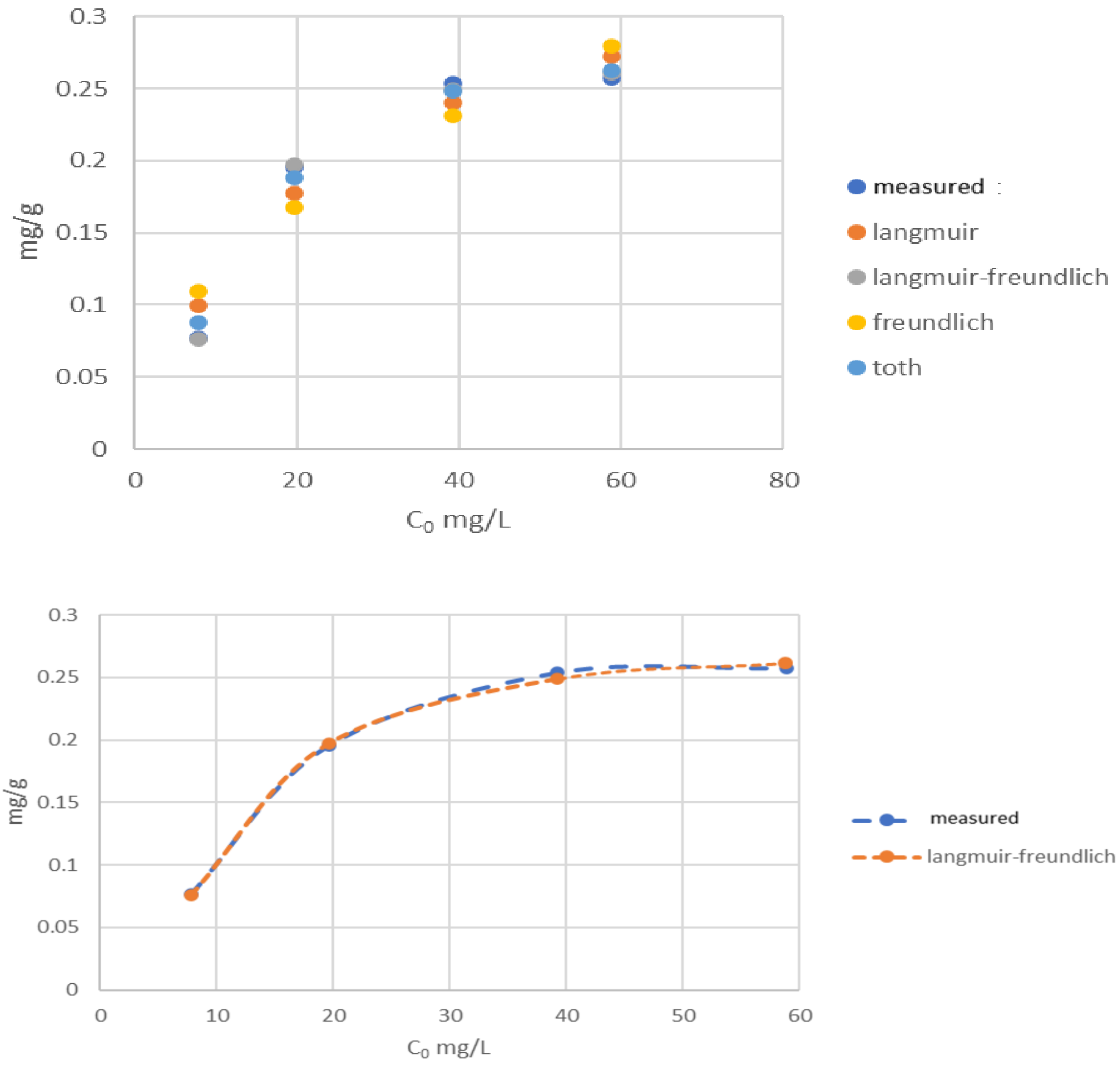


Figure 15 Adsorption isotherm models computed for Zn adsorption and comparison to measured experimental data of shungite samples. The isotherms, namely Langmuir-Freydlich isotherm reveals that the adsorption energy is normally distributed on the surface when treated with alkali (0.2 mol/L NaOH). NaOH seems to make the surface more hydrophilic, which allows metal components closer to the surface increasing the reactivity. (Potila, 2020)

The most common methods of biochar modification are the impregnation of feedstock with concentrated magnesium chloride or calcium chloride solution, followed by pyrolysis. In SHEM-WP one proposed shungite activation procedure involves $CaCl_2$ treatment before pyrolysis. Both, activated carbons and biochars, have also been reported to be functionalized with transition or post-transition metals, namely iron, aluminum, lanthanum, cerium, and zirconium, with increased affinity for phosphate. Of these, the most common is iron, which is cheaper, environmentally friendly, and easily available. Iron can be incorporated by several methods and in different forms, such as ferrous or ferric oxides by impregnation followed by pyrolysis in biochars, by oxidation followed by impregnation in activated carbon. Shungite has naturally iron (e.g., Fe S) that can be oxidized. Many activated carbons have Q_m = 2-10 mg-P/g, and wood biochars 10-15 mg-P/g, while Ca, Mg, La, Fe activated or doped biochars might have even 100-300 mg-P/g maximum adsorption capacities (Bacelo, Pintor, Santos, Boaventura, & Botelho, 2020). Shungite contains Ca, Mg, Fe and Al that can offer phosphorus removal mechanisms in certain conditions. According to the experiments of SHEM-WP, the sorption capacity of shungite can be increased with chemical treatment to 20 mg-P/g, or even to 100-200 mg-P/L.

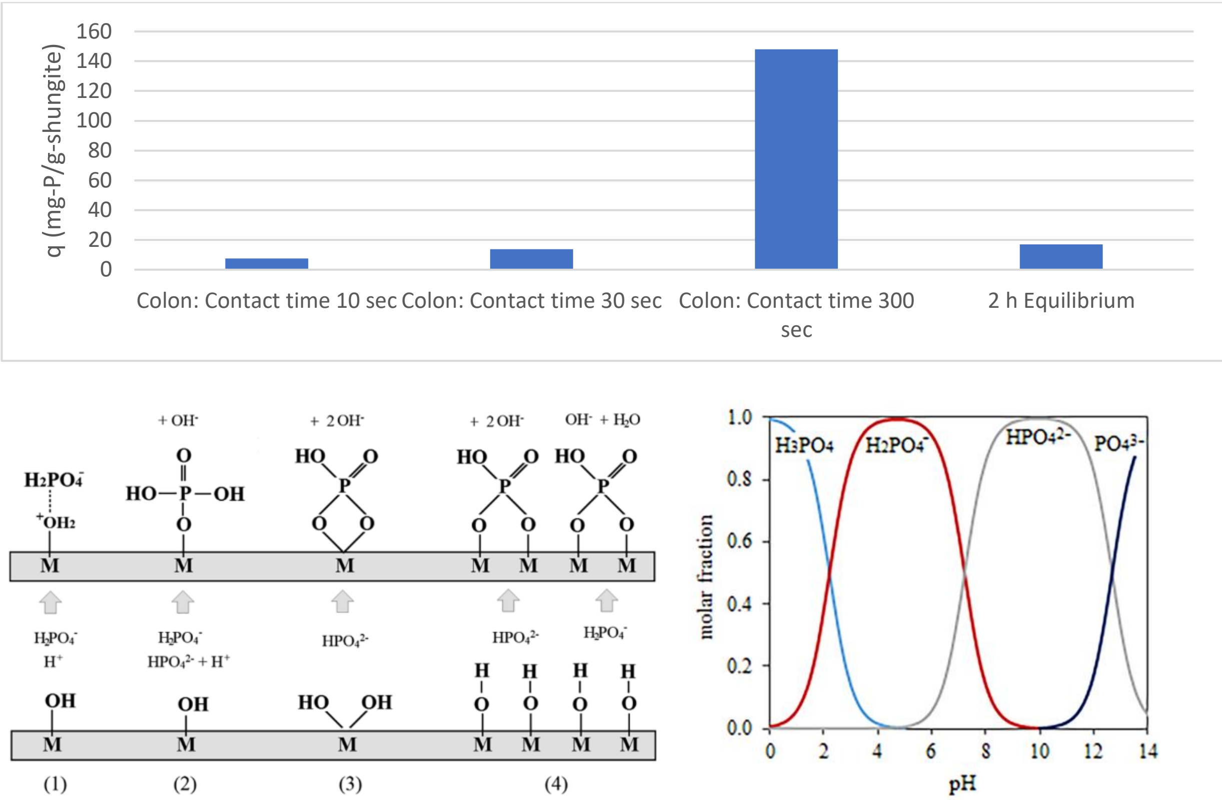


Figure 16 Phosphate sorption in NaOH activated shungite. A) Sorption in 21ºC (pH = 5) from phosphate solution (c(PO4) = 50 mg/L, V = 0.4 L). Mass of shungite = 5 g in a small colon with flow with varying contact time, and in an equilibrium experiment. Results from colon tests imitating a filter differ clearly from the equilibrium concentration experiment. sorption kinetics propose equilibrium setting fast and short contact time could be expected to give comparable results to 2 h equilibrium concentration experiments. Long contact time in filter colon indicates clearly higher phosphate sorption capacity. One explanatory factor could be pH that was not adjusted during the colon test. B) Phosphate mechanisms proposed for adsorption mechanisms: 1) electrostatic attraction, 2-4) ligand exchange forming covalent bonds between phosphate and the metal cation. In addition, for example, ion exchange is a potential sorption mechanism. C) Orthophosphate species as a function of pH (at 25°C). In Shungite filters the phosphate occurs actually as $H_2PO_4^-$ and in runoff water the second oxidation form will appear $H_2PO_4^{2-}$. (Bacelo, Pintor, Santos, Boaventura, & Botelho, 2020)

Field test water samples did not contain enough oil compounds for analysis. In the laboratory environment pilot scale experiments were carried out. Shungite filter (5 kg) were set into a basket filter and contaminated water (50-400 L) were filtered through the shungite. Shungite were activated with saturated CaCl2 and 0.5 moll/L NaOH solutions. As a conclusion, it was found that shungite filter removed 90-95 % of C10-C40 length oil compounds. The concentrations of shorter C10-C12 carbon compounds decreased under detection limit (50 mg/L) and the real reduction could not be concluded. Due to a high removal rate in 50 L test, a test with 400 L volume flow was carried out. The removal rate as percentage decreased, but capacity as $mg_{oil}/kg_{shungite}$ increased. Results are presented in Table 5. The results are from filtering experiment, and not from an adsorption test.

Table 5 Pilot scale filter: 50 L of liquid contaminated with oil was filtered through basket filter containing 5 kg of shungite. Three experiments reveal a conclusion that alkali treated shungite removes oil compounds more efficiently than $CaCl_2$ treated shungite. Shungite capacity without activation in removal of oil compounds was not studied in laboratory or pilot tests.

	Original liquid, mg/L	Filtrated through CaCl2 activated SH, mg/g (%)	Filtrated through NaOH activated SH, mg/g (%)
1. Oil index	2100 (50 L)	0,39 (95 %)	> 0,40 (> 96 %)
1.1 Mineral oils (C21-C40)	1900 (50 L)	0,37 (96 %)	> 0,40 (> 96 %)
1.2 Mineral oils (C10 - C20)	130 (50 L)	0,02 (38 %)	> 0,04 (> 40 %)
2. Oil index	1400 (50 L)	0,25 (90 %)	> 0,40 (> 96 %)
2.1 Mineral oils (C21-C40)	1300 (50 L)	0,24 (94 %)	> 0,40 (> 96 %)
2.2 Mineral oils (C10 - C20)	120 (50 L)	> 0,04 (40 %)	> 0,04 (> 40 %)
3. Oil index	1300 (400 L)	1,3 (47 %)	1,8 (70 %)
3.1 Mineral oils (C21-C40)	1200 (400 L)	1,3 (47 %)	1,6 (68 %)
3.2 Mineral oils (C10 - C20)	100 (400 L)	1,1 (55 %)	1,4 (68 %)

Testing of shungite sorption capacity in the laboratory of Vodokanal St.Petersburg.

In order to evaluate sorption capacity of natural shungite material a specific test was performed in the laboratory of the State Unitary Enterprise "Vodokanal St.Petersburg" providing water supply and waste water management services in the city of St.Petersburg (Russia). The aim of this test was the investigate the ability of shungite to absorb contaminants contained in urban runoff collected in surface water treatment plant "Murinsky Kvartal". Water samples were taken from inflow to the treatment plant before purification.

The tests were carried out in the Chemical and Bacteriological Laboratory № 2 of the Center for Laboratory Wastewater Control of the State Unitary Enterprise Vodokanal of St. Petersburg.

Shungite material (300 ml) was placed into 2 separating funnels of 1000 ml volume each. Before loading the shungite was washed with distilled water to a visually clear filtrate. Totally, about 5 liters of distilled water were used to wash 300 ml of shungite. The 1st separating funnel was adjusted to a filtration rate of 10 ml/min and 2nd one - 20 ml/min.

Unfiltered wastewater was poured into separating funnels and passed through a layer of shungite in the amount of 4 dm3, which is sufficient for chemical analysis.

Samples of filtrate from two funnels were analyzed as well as original untreated stormwater. The following parameters were measured: pH, suspended solids, BOD5, phosphate phosphorus, ammonium nitrogen, oil products, phenol, iron, aluminum, manganese. Measurements were performed in the laboratory of the Federal State Budgetary Institution "TsLATI in the North-Western Federal District". The results of the analysis are presented in Table 6.

Table 6 Concentrations of contaminants in urban runoff after filtration through shungite layer.

Parameters	Units	Original runoff water	Filtered water	
			10 ml/min	20 ml/min
pH	pH	6.7	3.5	3.9
Susp. Solids	mg/l	232	17 (93%)	16 (93%)
BOD5	mgO_2/l	93	64 (31%)	74 (20 %)
Phosphate	mg/l	0.14	0.05 (64%)	0.058 (59%)
Ammonia	mg/l	2.2	1.1 (50%)	1.5 (32%)
Oil products	mg/l	2.1	0.50 (76%)	0.70 (67%)
Phenol	mg/l	0.0020	0.0012 (40%)	0.0008 (60%)
Iron	mg/l	0.059	0.38	0.23
Aluminum	mg/l	0.074	0.42	0.44
Manganese	mg/l	0.021	0.23	0.23

Laboratory tests revealed similar results for both funnels. pH level in the runoff water filtered through shungite reduced from 6.7 to 3.5 and 3.9 in funnels 1 and 2 respectively. Removal rate for suspended solids, nutrients and organic contaminants was the following:

- for suspended solids - up to 93%
- BOD5 - up to 31%
- phosphate - up to 64%
- ammonia - up to 50%
- oil products - up to 76%
- phenol - up to 60%.

At the same time a significant increase of heavy metals' concentrations was observed: iron - 4-6 times; aluminum - 6 times; manganese - 11 times.

Activation and re-use procedures

Physical activation and chemical activation are the main methods applied on production of activated carbon. These methods could have significantly beneficial effects on carbonous material chemical/physical properties. There is a growing interest of the scientific community in production of activated carbon using biochar. The similar pyrolysis is not applicable for mineral char according to SHEM-WP studies. Typical process applied would be a pyrolysis step in an inert atmosphere (N_2 gas) at a temperature of 450°C for 30 minutes, followed by pyrolysis process in another atmosphere in higher temperature (800°C for e.g., 1-2 hours). The experiments with shungite activation were made in LUT Mikkeli unit laboratory, which is specialized in producing activated carbon from biochar. The resulting carbon is expected to have improved properties in surface area and total pore volume. For shungite increasing the temperature over 500 ºC will lead to mass-loss. In activation experiments 12 % of mass was lost already at 400 ºC. However, in regeneration experiments less than 1 % mass-loss were obtained when thermal treatment cycles were repeated.

Table 7 Shungite BET analysis, and mass-loss in inert atmosphere (N_2) in 45 min analysis.

T, ºC	Inner surface area (BET) (m2/g)	Δm, %
20	4.23	0
400	4.65	12 % ± 1 %
600	6.93	35 % ±2 %
900	7.38	73 % ± 4 %

The pyrolysis in inert or normal atmosphere did not lead to optimal improvement of sorption or the related physical factors. Surface area and sorption capacity increased significantly in 900 ºC. However, the particle size decreased and functional impurities, such as iron compound containing mineral layers cracked. The resulting shungite residual is not optimal for runoff water filters that require durable 1-5 mm particle size. Therefore, the thermal treatment temperature is recommended not to exceed 450 ºC. This temperature has an activation effect, but the main purpose is cleaning the material.

Several activation procedures were tested:

- Physical activation (thermal, mechanical) as discussed in previous chapters.
- Chemical: Acidic (HCl, H_2SO_4), alkali (NaOH), $CaCl_2$, oxidation with H_2O_2, $NaSO_4$ and other chemicals to increase sorption of specific compounds. It was concluded that activation with 0.2 mol/L NaOH solution is environmentally feasible and low-cost solution, that improved in general the sorption capacity. It might increase the surface area, make the surface more hydrophilic, and improve O:C and H:C ratios in the shungite surface.

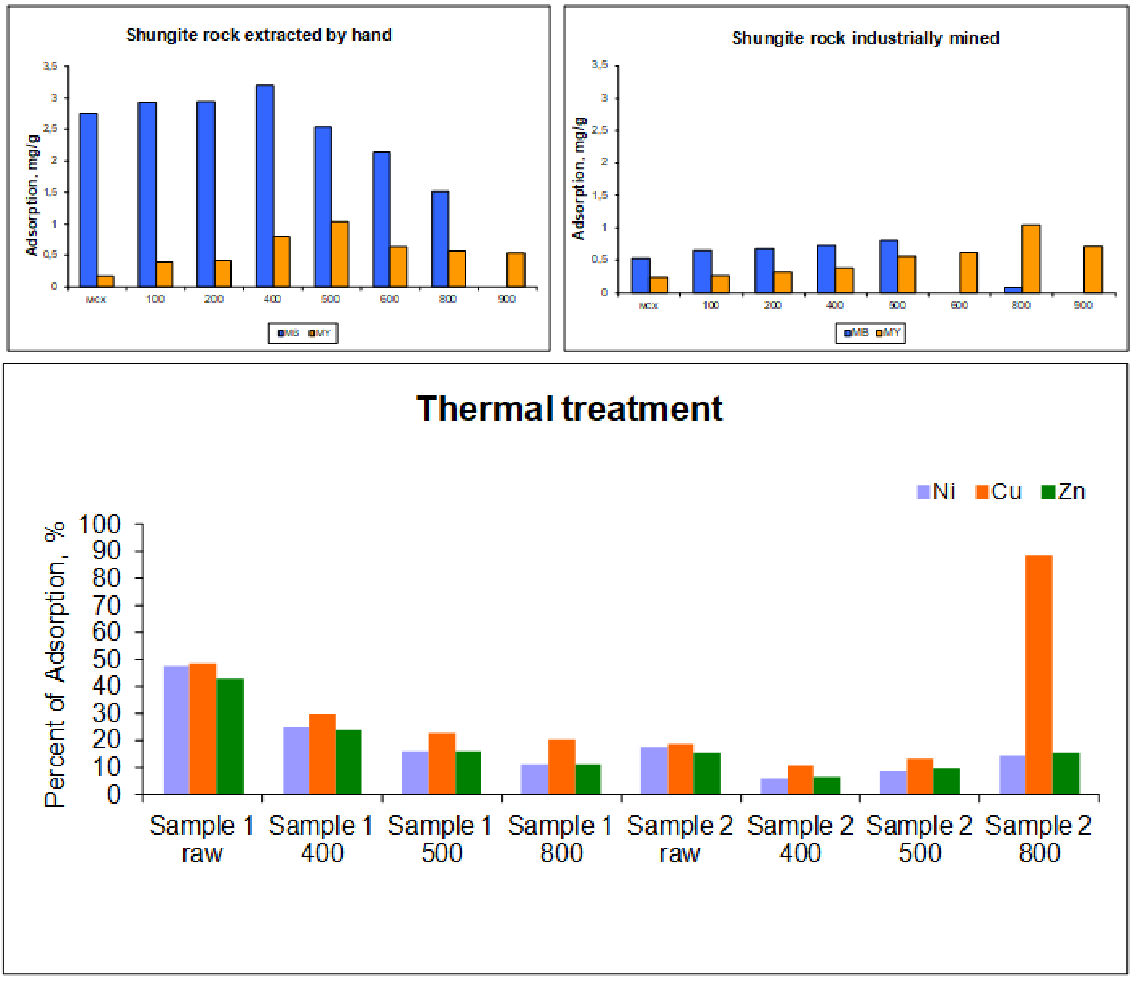


Figure 17 Effect of thermal treatment on adsorption (Kovalevski, Reinikainen, Reinikainen, Rozhkova, & Sihvonen, 2020)

To determine the effect of modification of shungite rocks on the properties of the filter material, sample 1 and sample 2 were selected (Figure 17, correspond to #3 and #2 in Table 3). The purpose of the study was to find a way to improve the properties of the selected filter material (using sample 1 as an example), and to determine the possibility of using industrially extracted, but not satisfying the conditions of the European Union, the initial (untreated) shungite rock (using sample 2 as an example). The treatment was carried out at a temperature of 100, 200, 400, 500, 600, 800 and 900 °C for 30 min in a reducing atmosphere. Sorption of acidic (MY) and basic (MB) dye was determined for the initial and heat-treated samples. For sample 1, the maximum sorption of the main dye was achieved at 400 °C, and the acidic at 500 °C. In the case of sample 2, the maximum values correspond to shungite rock treated at 500 °C for MB and at 800 °C for MY.

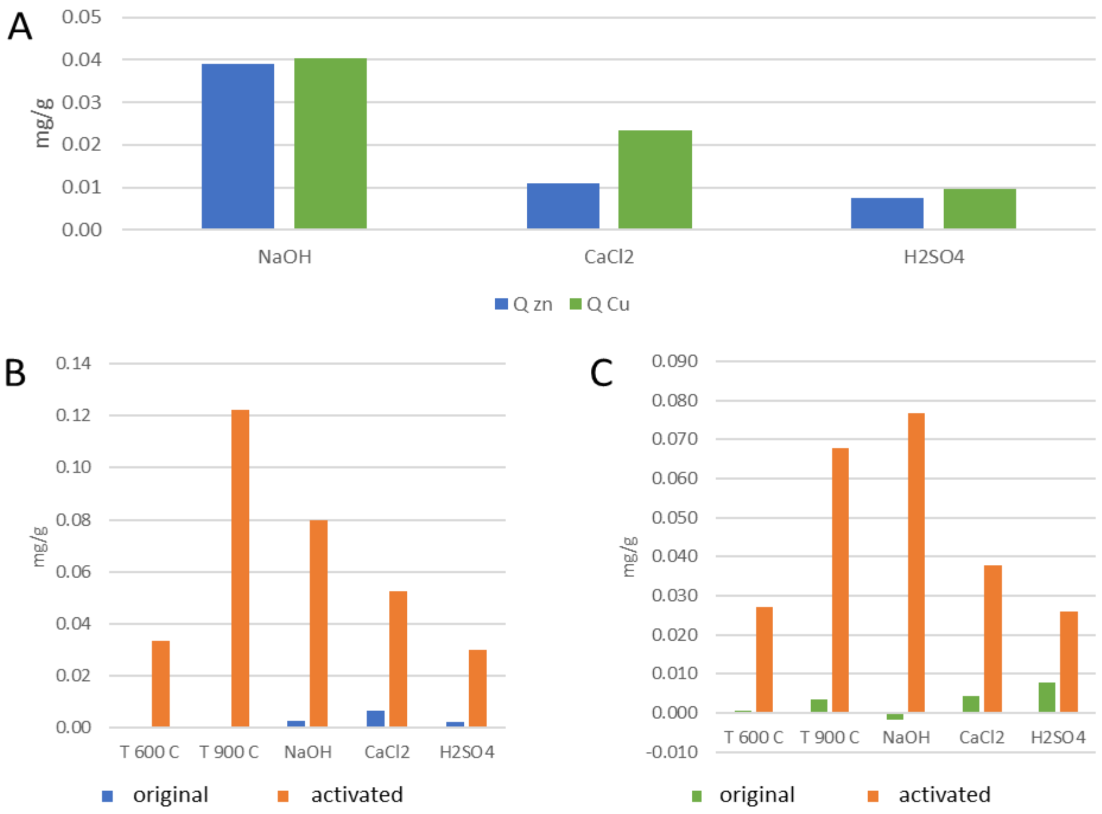


Figure 18 Chemical activation influences adsorption capacity: Even mild treatment with 0.2 M chemicals increase adsorption of metals. Shungite were cleaned with 1.5 M HCl and purified water before activation treatment. The chemicals (NaOH, $CaCl_2$ and H_2SO_4) were 0.2 mol/L. Zn and Cu concentrations were 4 +4 mol/L. With alkali treatment > 99 % of Cu and Zn were sorpted in 2 h: A) Comparison of Zn and Cu adsorption after chemical treatment. B) Cu sorption, and C) Zn sorption after thermal and chemical treatment. The treatment at 900 ºC would equal the end-use temperature of shungite. Mass lost in it were 70-80 %. Even 600 ºC is too high temperature for annual treatment since even 30 % of shungite mass can be lost. Adsorption depends on concentrations of metals in the solution applied.

The sorption activity of heat-treated shungite rocks was studied using model solutions prepared by dissolving the following salts in water: CuSO4×5H2O, ZnSO4×7H2O и Ni(NO3)2×6H2O. According to ICP MS data, the concentration of Cu, Zn and Ni ions was 50, 130 and 50 mg/l, respectively. A sample of shungite rock weighing 3 g was poured with a model salt solution of 30 ml, kept, stirring periodically, for 96 hours. The concentration of Cu, Zn and Ni of the obtained solutions was determined using ICP MS. It was found that for sample 1, temperature treatment leads to a decrease in the sorption of metals. For sample 2, treatment at 400 and 500 oC also reduces the sorption values of the selected metals, whereas in the case of 800 oC, the sorption of Cu increases sharply (almost to complete sorption from solution) with the sorption of Ni and Zn practically unchanged compared to the initial rock. The result of Cu sorption by heat-treated rock turned out to be unexpected and was rechecked several times, which only confirmed the identified effect. The results obtained allow us to suggest the use of heat-treated at 800 °C rock 2 as an effective sorbent for water purification from Cu. The results also raise the question of the mechanisms of sorption of various metals on shungite rock and the use of modification to create more effective multilayer shungite sorbents.

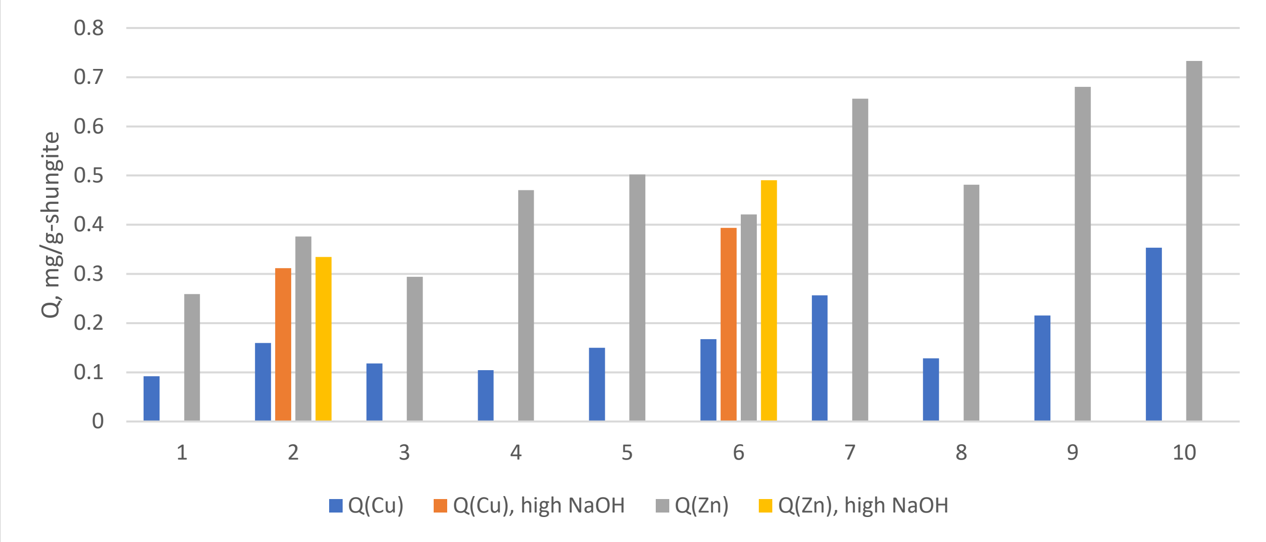


Figure 19 Re-usability: shungite samples from filters were treated chemically with HCl (0,2 mol/L), physically (thermal 45 min, 400 ºC) and finally with NaOH (either with 0.2 mol/L or 5 mol/L). After 10 treatment cycles the adsorption capacity was still high or increasing. Mass loss was approximately 1 % in each treatment (total 9 % of shungite was lost in 10 cleaning and activation cycle). The shungite is a durable and stable material.

Maintenance and end-of-use

1. Before utilizing in filter: crushed, grinded shungite has to be washed with water to remove the fine particles.
2. Cleaning step continues with acidic (HCl) or alkali treatment (NaOH). Activation of shungite with alternative chemicals can be applied.
3. Thermal treatment in 400-450 ºC (flowed by washing with water)
4. Second cleaning with NaOH is highly recommended
5. Storage in dry place. Oxidation of shungite was visibly detected. Shungite might adsorb compounds from air.
6. After utilization in filter (4-6 months) repeat the cleaning and activation (steps 1-5). Max 10 cycles is recommended.
7. End-use: pyrolysis at 900 ºC is recommended. The mass-loss will be up to 80 % and yield highly reactive residue that can be applied as a special adsorbent.

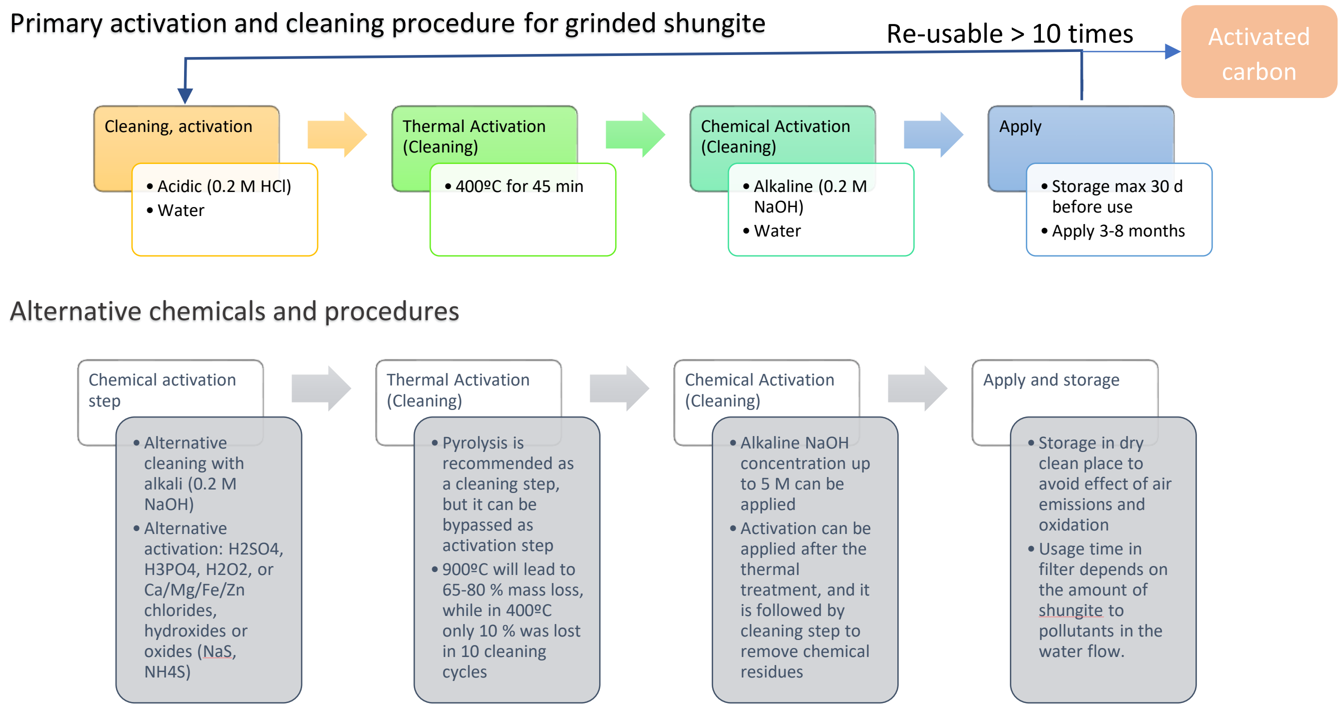


Figure 20 Recommended activation and cleaning procedures for shungite

Conclusions on Shungite in Filters

Short conclusions on shungite utilization is listed into Table 8.

Table 8 Conclusions of recommendations on shungite for runoff water filtering.

Description	Recommendation
Shungite type	Second shungite-bearing horizon to select the best filter material for water treatment. In selection commercial aspects and environmental feasibility are to be considered. See chapter “Preparing and Selecting Shungite”
Mechanical preparation	Grinding in a vibrating grinder to proper particle size (< 0.5 mm). See chapter “Preparing and Selecting Shungite”
Environmental leaching test	Recommended to fulfill the Finnish Government Decree on Landfills (331/2013) and as minimum leaching tests for heavy metals should be carried out.
Sorption capacity test	Cationic and anionic sorption capacity should be checked with Raman spectroscopic method (Rozhkova & Kovalevski, 2019)
Thermal activation	Thermal activation under 450 ºC increase sorption capacity without altering the strength.
Chemical activation	Alkaline activation is recommended as general procedure. Substance sensitive activation can be optimized for various pollutants.
Cleaning for re-use	Interval depends on influent quality. As minimum 6 months interval is recommended. General cleaning and activation procedure is presented in Figure 20. Cleaning and activation cycle can be repeated 5-10 times.
End-use and disposal	Thermal treatment in > 900 ºC will produce highly active ash that can be applied in special products.

2.2 EM FOR FILTERS

Effective micro-organism products

Effective microorganism (EM) technology uses naturally occurring microorganisms, which are able to purify and revive nature. The concept of "friendly microorganisms" was developed by Professor Teruo Higa, from the University of the Ryukyus in Okinawa, Japan in 1980s (Higa, 1998). Present EM technology has wide application areas, and it has been introduced as an independent and as a hybrid treatment method, e.g., in-lake restoration, algae growth alteration, manipulation of sludge in wastewater treatment plants, increase growth of vegetation, in odor control, etc. (Dondajewska, Kozak, Rosińska, & Gołdyn, 2019)

Effective microorganisms (EM) are various blends of common predominantly anaerobic microorganisms, that exist freely in nature and are not manipulated in any way. EM consists of 80 different kinds of effective, disease-suppressing micro-organisms. Each of these effective micro-organisms has a specific task. EM consists of the following five families of micro-organisms: (Higa, 1998)

1. Lactic acid bacteria: for their sterilizing properties. They suppress harmful micro-organisms or fungus and encourage quick breakdown of organic substances.
2. Yeasts: provide anti-microbial and useful substances for plant growth.
3. Actinomycetes: to suppress harmful fungi and bacteria but can live together with photosynthetic bacteria.
4. Photosynthetic bacteria: the leading role in the activity of EM. They synthesize useful substances from organic matter and/or harmful gases (e.g., hydrogen sulphide) The metabolites developed by these micro-organisms are directly absorbed into plants. In addition, these bacteria increase the number of other bacteria and act as nitrogen binders.
5. Fungi: to break down the organic substances quickly. They suppress smell and prevent damage by harmful insects.

Various commercially available EM solutions were applied in studies. Examples of EM products commercially available in Finland are shown in Figure 21. In course of research these solutions were applied and no significant difference in purification results between different solutions were found.

Figure 21 Commercial EM products applied in studies: A) Emma EM-Active concentrate (Multicraft), B) Tohtorin EMa (Viidakkotohtori), C) example of storage solution, D) EM liquid in tube

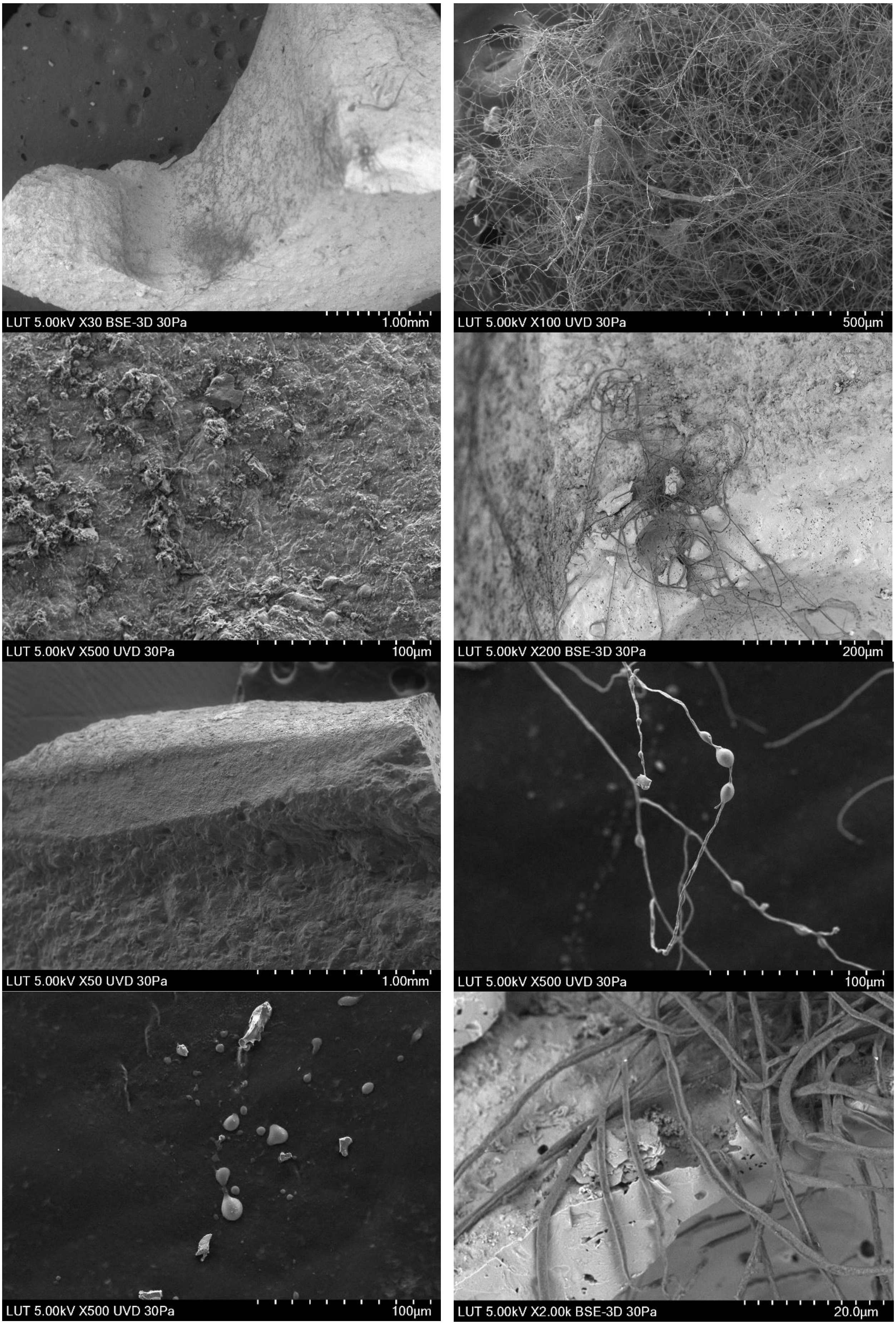


Figure 22 Scanning electron microscope was applied to study the growth of EM. Example SEM images of 10 days cultivated EM on shungite.

Nutrient removal efficiency in pre-tests

EM storage liquids were activated with sugar compounds and fermented with ceramic Intalox saddles or other growth media. Their activation was confirmed with confirmed in laboratory environment. Figure 23 shows examples where 1:10 m-% of activated EM:[artificial nutrient solution] is mixed in 100 mL sample bottle. Bottle is partially covered with plastic film to prevent evaporation but allowing oxygen to enter. Bottle is left at approximately 20 ºC (into laboratory hood). Samples are taken after 0-4 d cultivation. This procedure is aimed to confirm that the activation has been successful, and the EM is ready to be transferred to filter. Removal rate depends on original concentration of nutrients and EM.

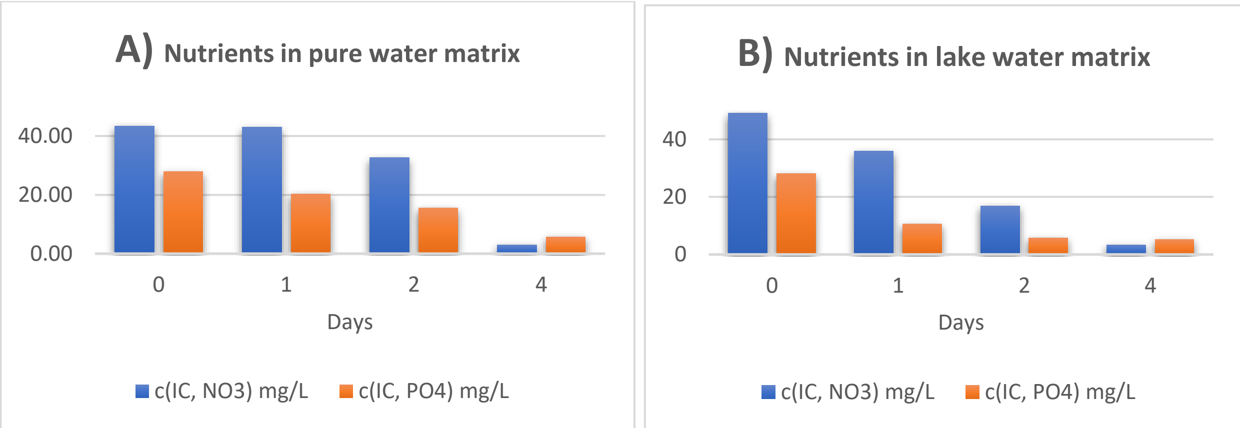


Figure 23 Examples of test results of activation and effect of EM solution in laboratory environment. EM solution is added to artificial nutrient solution prepared to distilled laboratory water or lake water. Results should be visible in 2-4 days as significant decrease in concentration. nitrate concentration tends to decrease slower than phosphate. If lake water or run-off water is applied as matrix, the decrease is faster due to the micro-organisms in the water matrix present.

Figure 24 Examples of run-off water samples applied in testing EM. Presence of EM boosted samples containing algae more than samples without visual algae growth. Bacteria on Green filamentous Algae is expected to have a significant role in nutrient removal and laboratory results supported the assumption. Results reported in this chapter are gained from water samples without visually clearly seen biomass (similar to samples 2 and 5).

Effect of EM in removal of the nutrients depend on the aquatic environment. In laboratory environment only short experiments to confirm functionality is recommended. It is typical that in 30 d the bio-population in samples starts to die in the laboratory environment. Thus, it is recommended that the activation phase in the laboratory is no longer than 2 weeks. Figure 24 visualizes laboratory experiments with natural water samples.

Figure 25 illustrates

a) In laboratory conditions phosphate or phosphorus concentrations were found to increase after 3 weeks laboratory experiment. Similar behavior was not found in nitrogen results.
b) EM effect can also be seen as change in portion of ammonium in total nitrogen content.
c) Temperature and daylight had a minor effect on efficiency in range 6-20 ºC. Recommended temperature minimum is 10 ºC according to the solution manufacturer.
d) Reference sample in similar conditions to EM activation samples is recommended during activation evaluation since the nutrient content may decrease in samples via other mechanisms.

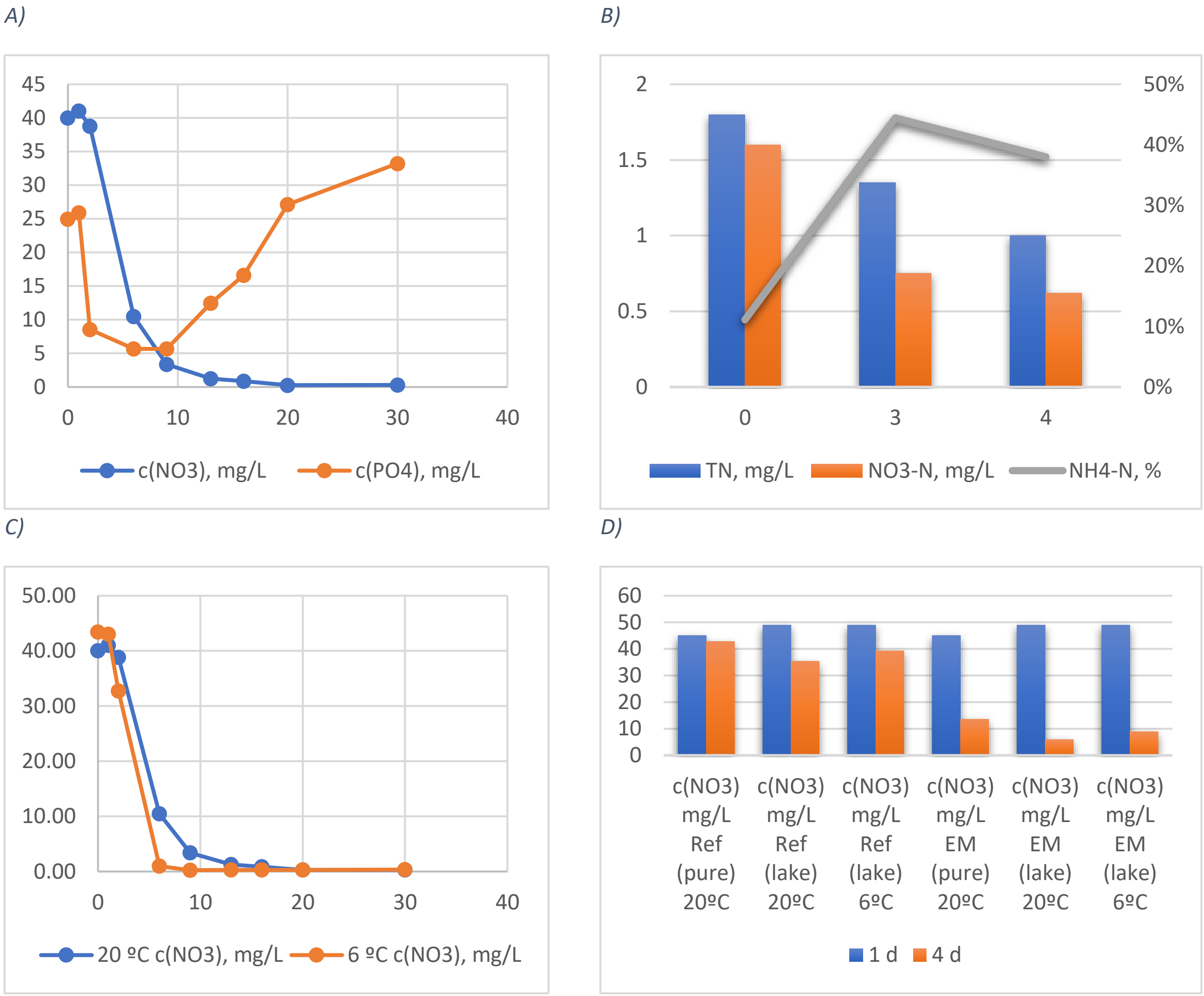


Figure 25 Examples of results from activation of EM in laboratory environment. a) After 2 weeks growth in ceramic growth media, EM solution 1:10 m-% were added to nutrient solution. The nutrients ran out in laboratory tube in 10 d and phosphate was released back to liquid. B) Ammonium-% of total nitrogen increases in run-off water sample when EM is introduced. Run-off water sample was taken from Sammonlahti CW and 1 % of activated EM solution was added in laboratory. Original 11 % ammonium content increased to 44 % in 3 d. C) Sample with EM was divided into two subsamples. One sample was left in laboratory hood at +20 ºC, and second sample was placed in fridge at +6ºC. There was no significant difference in nutrient removal efficiency. Nitrate presented as an example. D) Reference sample without EM is recommended, namely if sample is biologically active. even artificial solutions prepared from distilled laboratory water show some decrease in nutrient content. and phosphate concentrations can decrease even 30 % without any EM treatment, if lake water samples are left in laboratory hood in room temperature. With EM solution the decrease is clearly higher (> 85 %).

Growth media studies

Four different grades of shungite mineral, zeolite-basalt mixture and other crushed lava gravel (porous pond substrate), biochar (wood-based char from pyrolysis) and ceramic powder were studied in laboratory environment. Depending on the density of the solid material 5-10 g of each material was placed in 90 mm petri dishes. Activated EM solution (Multikraft) was added (10 m-%). Activation of EM solution before adding it to solid growth media was done with a solution containing molasses and other sugar compounds in purified water. For testing EM solution activity, a solution containing nutrients were prepared from pro analysis quality chemicals: c(TN) = 20 mg/L and c(TP) = 5 mg/L. For nitrate and phosphate analyses ion chromatography were applied (Thermo Scientific DIONEX ICS 5000). The activated EM solution was mixed with 1:10 ratio to nutrient solution in a glass reagent bottle (100 ml), covered with plastic film allowing air pass but limiting evaporation. EM test samples and reference nutrient samples were left in fume hood for 4-6 days and monitored for nitrate and phosphate contents to ensure micro-organisms activation.

Activated EM solutions were added to growth mediums. Samples were placed into fume hood, and they were covered with a plastic lid allowing air circulation but preventing the evaporation and direct daylight. Growth of micro-organisms were monitored for 2 weeks. Microscopes applied were scanning electron microscope (HITACHI SU3500), and optical microscopes: Malvern MOR-PHOLOGI G3 particles size analyzer, and Olympus Microscope SZX9 with HD camera.

In the laboratory environment there was clear biological activity in all growth medium samples after they were exposed to the EM solution. The reference samples without EM solution had no visible biological activity. The shungite samples were covered with various micro-organisms that seemed to be specific to each rock sample. Figure 27 illustrates surfaces of various shungite grades. Rod shape cells, that could be for example various *bacillius bacteria* were found dominating in half of the shungite samples. There was strong filamentous growth in one, while one grade had very heterogenous micro-organism distribution. When comparing shungite to biochar, the biochar had a stronger filamentous population dominating. On the ceramic material surface, the population growing had spherical, rod-shaped, and spiral populations. Less filamentous growth appeared. Growth in ceramic material and pure EM liquid were applied as reference in this pre-test. It was concluded that the activated EM solution increases the growth of existing bio-population in all materials tested. Ceramic material was chosen to the water filter application to secure growth the healthy EM organisms.

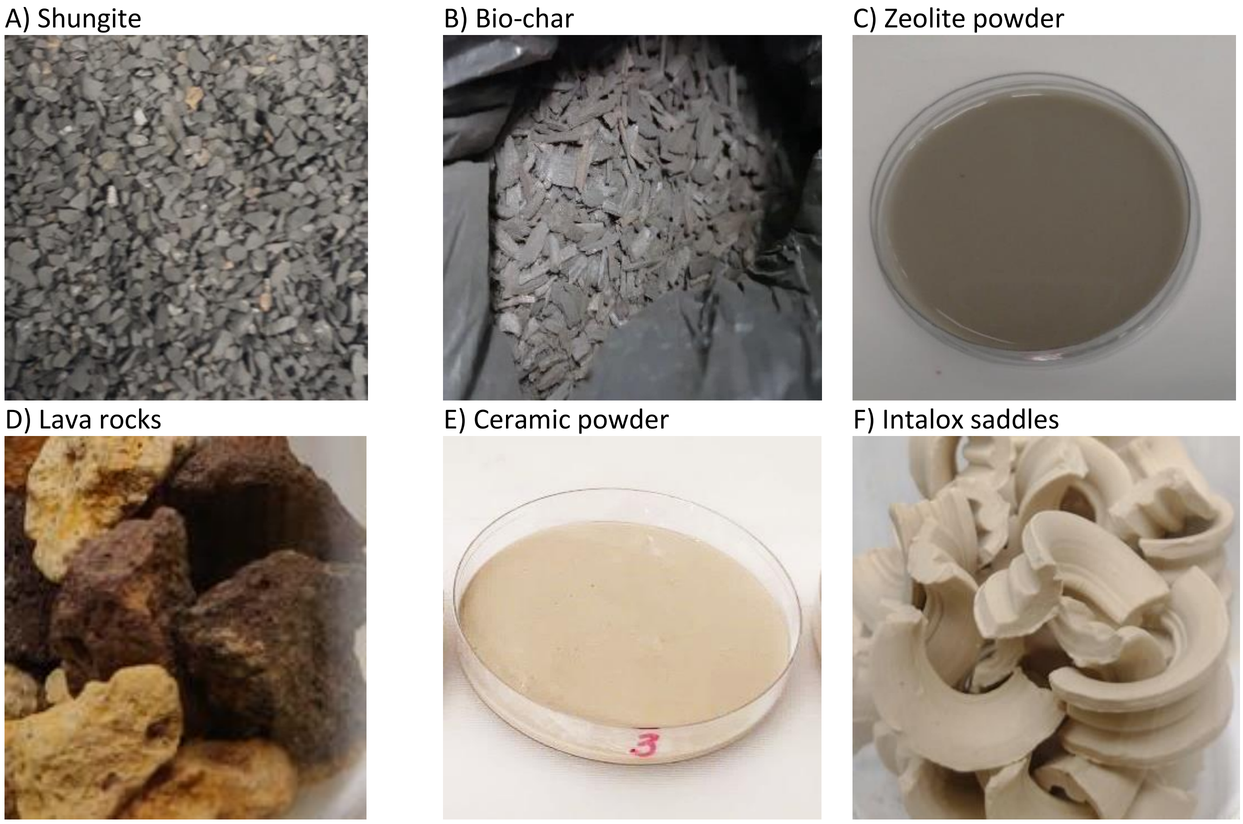


Figure 26 Examples of materials studied as growth media for EM: A) Shungite, B) Biochar from wood (mixture) combustion, C) Zeolite-Basalt powder, D) Porous lava rocks E) commercial Ceramic powder and F) ceramic Intalox saddles

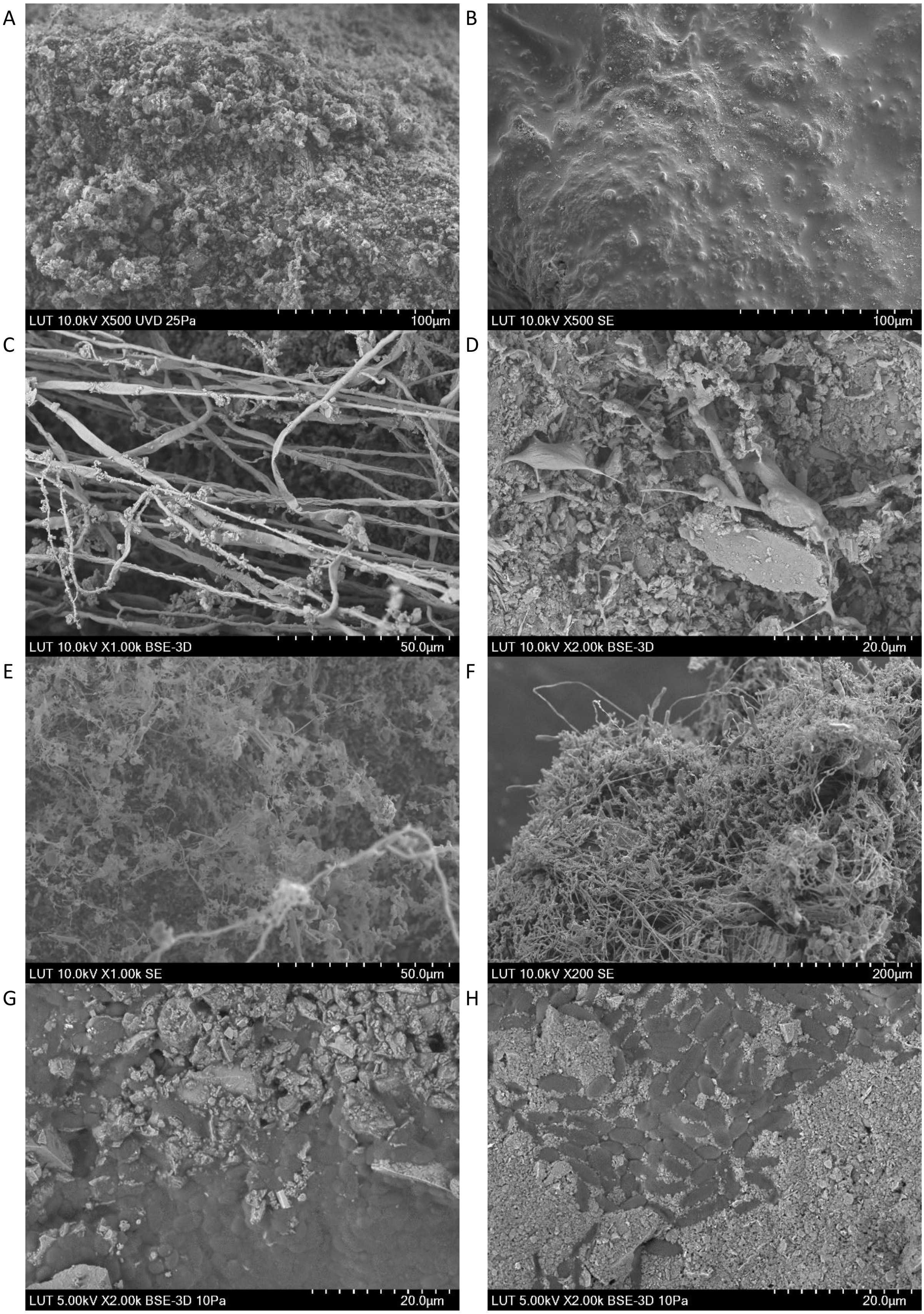


Figure 27 SEM images of microbial growth on surface of shungite rocks after 14 days exposure to EM solution. Collection of SEM images from the EM growing study. a: clean shungite surface, b: shungite surface with a possible biofilm growth on it, c: fibrous growth on shungite, d: possible bacterial growth on shungite, e: fine fibrous growth on shungite, f: fibrous growth on biochar, g: bacterial growth/film on zeobas granules, h: bacteria on ceramic powder.

EM concept for water purification filters

EM application combined to shungite filter would be most efficient for small and mid-size waterbodies for removal of nutrient, or to inhibit the growth of pathogenic and harmful bacteria through competitive exclusion, resulting in the dominance of beneficial species resulting healthier and improved water quality. The SHEM-WP filtering system focuses in 1) removal of solid material, 2) sophisticated filtering effect via e.g., sorption mechanisms, and oxidation (shungite), and 3) improvement in aquatic system and its biodiversity (EM).

The most common EM applications apply zeolite or zeolite-basalt-ceramic powder mixture as growth media (mudballs), or fermented EM is spread as liquid to soil. In the present concept EM is proposed to be implemented as an independent unit, namely as the last unit of the filtering system. Alternative to having it as the first unit would cause an increase in growth of the bio-population in shungite. Back flow from the EM unit to shungite unit would naturally boost this phenomenon.

The EM storage solution should be activated before utilization. Cultivation or fermentation period should be as minimun 7 d. Activation with various sugar compounds (molasse) is recommended, and the growth and activity of micro-organisms should be monitored. It can be done with an optic microscope or with a nutrient solution (for example with fertilized solution). Adding activated EM solution to fertilizer solution and measuring difference of it to original solution would give a reliable estimate on level of activity. Effects should be seen in 1-2 days (Figure 25). Alternatively, the activation of EM could be done with the fertilizer solution (this procedure was not applied or studied in SEM-WP). Depending on the case, pH and change in it can be applied as an indicator of activity.

Table 9 concludes basic concept and aspects.

The micro-organisms will grow on the surface of the growth media. Part of the bio-population is flushed to the recipient. The runoff water flow varies according to precipitation level, and seasonality. Too high flow might decrease flush most of bio-population out from the chamber. Too low flow rate might cause growth of algae inside the chamber until a critical concentration is achieved or the chamber dry, which might cause death of population. It would be critical that there is certain flow into the chamber, or the chamber volume is high enough.

Shungite unit before the EM unit would ensure the quality of incoming water. Shungite would pre-treat the contaminants in the runoff water. According to the field test results, the high phosphor removal rate might be even too high in the shungite filter for optimal EM growth. However, no clear effect due to the lack of nutrients was found. The filtering system was found efficient in phosphor removal.

Seasonality effects on water temperature. The natural uptake of nutrients by plants can be assumed to happen only when the temperature is over 10ºC. In laboratory conditions it was found that the EM growth was still strong even in 5ºC dark fridge for at least a week (7 d). The natural nitrogen removal and “growth season” at constructed wetlands in Lappeenranta ended in late September or early October, when the temperatures decreased near 10ºC. Also, the amount of daylight varies and effects on shallow waterbodies. It is recommended that EM unit’s maintenance is done at least in spring, when the highest melting water flow peak is over and water temperature is increasing over 10ºC. A typical time would be in May. The renewal and maintenance of shungite unit at the same time would be feasible.

Table 9 SHEM-WP concept for using EM in filter system. Storage, activation, cultivation/fermenting are required before EM together with its growth media is placed in filter.

Storage and maintenance	Activation	Growth	Filter chamber
• Liquids are stored in room temperature until open • pH of solution is indicator, if the ME can still be applied (e,g, pH<5) • There are concentrates that needs activation and ready-to-use liquids.	• Before adding EM to filters, it should be activated, and the activity should be checked with a nutrient solution • Manufacturer propose activation procedure with a special melassi mixture, but many sugar compunds can be applied • Original recipe contains fermentation in so called mudballs. The technology is not applicapble in filters since natural clay or commercial powders cannot be applied due to small particle size.	• Dilution ratio 1:1000 is recommended, but feasibility of dilution depends on amount needed. • Optimal fermentation time with suitable growth media would be 10-14 days. Minimum 7d and maximum 21 d. • The can be checked via discreased dissolved TP test or visually with microscopes.	• A separate filter chamber or tank is recommended • Inert and non-toxic growth media without any unknown bacteria or microbial population. • The growth media can be ceramic or natural stone material. Surface pore size and structure effects. • Too high or too low inflow might decrease the efficiency

2.3 COMBINING SHUNGITE AND EM

Shungite combined to EM technology can offer non-chemical and natural based alternative for in-situ purification system. It can be implemented into existing urban drainage systems or into water bodies. In SHEM-WP several field tests illustrated the innovation in relevant aquatic environment. Shungite has valuable properties for water purification: sorptional, bacterial, catalytic, and reduction-oxidation properties. It can address several pollutants in the urban runoff water. In the present innovation micro-organisms are applied to initiate positive changes in the ecosystem by means of excessive organic matter decomposition and increased uptake of nutrients (natural nutrient cycle). The runoff and snowmelt water contains emissions from anthropogenic activities, drainage surfaces, gardening, misconnections (water entering from sewage system), etc. The essential first step in filtering is removal of particles mechanically. Depending on the application, various nets, meshes, and foams (e.g., polyether (PE) foam filters with various pore size 30-60 ppi) can be involved. Namely in case of foam filters, this mechanical media also promotes the colonization of beneficial bacteria. There might be settlement tanks in modern drainage systems conveying runoff water, but still the floating solid particles need to be removed before the water can enter the filter system. Shungite unit can be designed to function as a mechanical filter and physically trap particles from the water.

Figure 28 and Appendix 3 illustrate the main schemes of shungite-EM filtering system. One of the research questions was, if shungite could be applied as growth media for EM. In the SHEM-WP field tests the EM is placed in its own chamber, that was either isolated last step in system, or in chamber that allowed the mixing of water containing EM to flow spread to shungite unit. For maintenance, it is advanceable to place EM into a medium that can be cleaned and renewal separately from the shungite unit. Another question was if the bacterial growth in shungite should be encouraged since this bio-population was unknown and heterogenous.

There are benefits in both designs: if influent is purified with shungite before it is introduced to micro-organisms, the clean water matrix is less likely toxic and contains less pollutants. However, shungite filter might also remove phosphor from the water and disturb the growth of EM. The aim is that the EM grows in the chamber over the summer season. If the biological unit is placed before the shungite unit, the influent is not cleaned and risk that the influent quality alters increases. However, if the EM can spread to shungite unit, the shungite will also serve as growth media for it. The flow rate influences efficiency of both units. This issue is to be optimized in future designs.

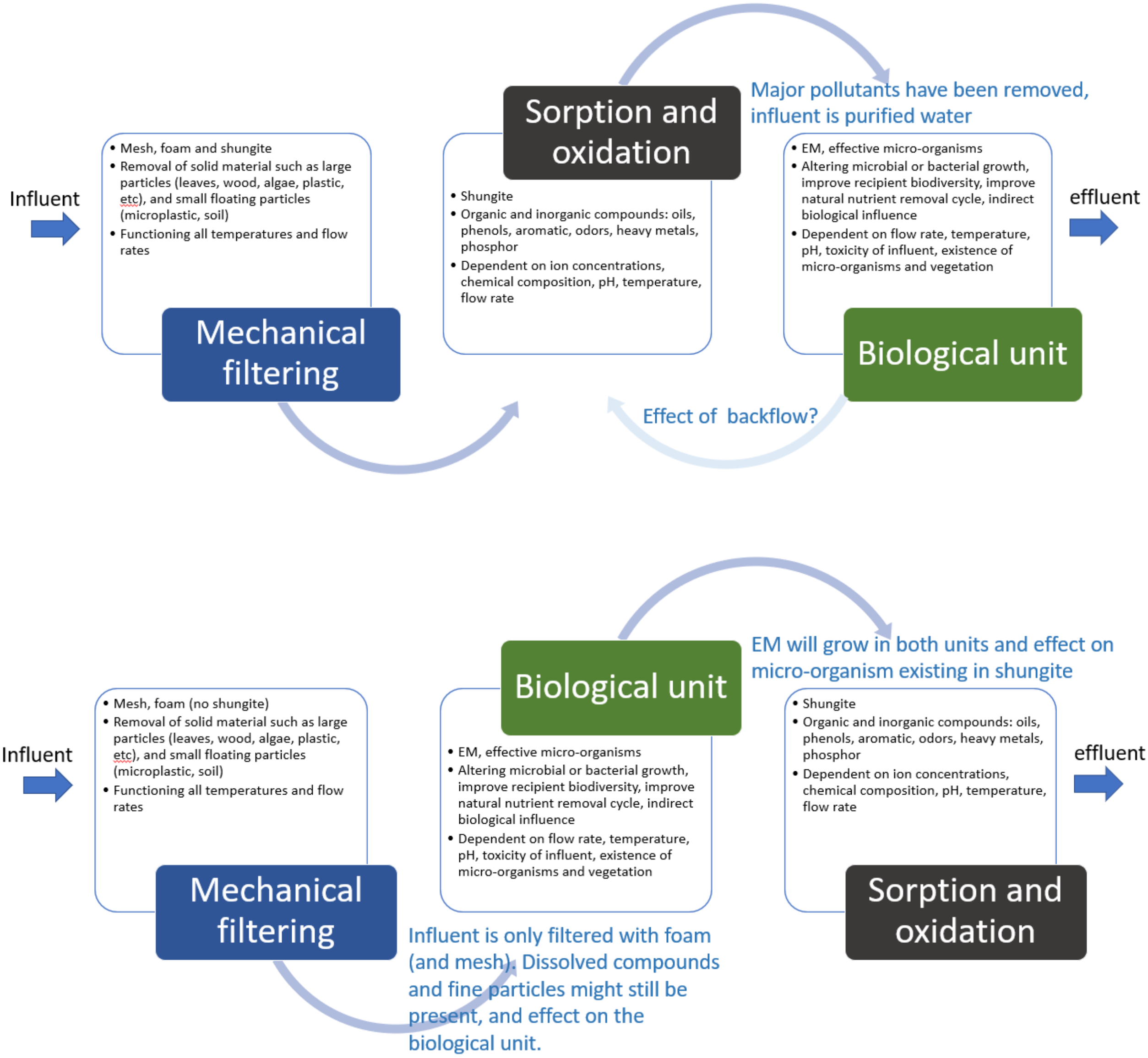


Figure 28 Two alternative concepts considered in SHEM-WP project. The first essential step is removal of solid particles, which already represent a major fraction in emission load. 2nd and 3rd step have special features. The shungite unit participates in removal of fine particles, but the main function is purification via sorption and other chemical mechanisms involved. The biological unit contains EM on growth media. Due to unknown bacterial content of shungite, inert ceramic particles without additional function were selected as growth media. When a biological unit is placed before the shungite unit, the influent still contains several urban emission compounds, but EM would spread to shungite unit and while filter system would serve as growth media. When the shungite unit is placed before the EM unit, the influent to EM is purified water, and less altered by the pollutants and external bio-populations.

The seasonality and flow rate affect the efficiency of the system. Seasonal fluctuation causes huge variation in temperature, daylight, and flow rate. Snow melting season or storms are the critical events when the highest flow and pollution load appears. The system functioning as mechanical filter at these events is crucial from an environmental point of view. With active SHEM-WP filters the variation in flow rate is controlled with a pump that defines the flow rate. In passive filters, the high flows exceeding the filter capacity were handled with bypass lines. In both cases, more R&D is needed to overcome the flow rate issues. It can be assumed that 25 % of the precipitation in this region is snow, and effect of melting can be seen mainly from mid-April to mid-May (shallow infiltration effect is seen until June).

3. Filters and purification concept

Filters were designed and constructed in Finland and in Russia for field tests of combined filtering effect of effective micro-organisms and shungite. Since tests had been supposed to be conducted on sites with different hydrological and chemical conditions, the design of filters constructed by project partners significantly differed. Also, depending on the conditions where the filters were used, they were designed to utilize natural water flow or were equipped with water pump providing constant flow through filtering media during a certain time period. Despite of some construction differences, all filters were based on similar basic principles and applied shungite sorption unit and EM cultivation unit. Thus, application of different technical solution in filter's design brings added value to the fiend tests and consequently to the project outcomes. See Figure 28 and "Appendix 3: Concepts of purification processes applying SHEM-WP system" for more details.

The pollution in urban stormwater and runoff water has different points of origin. Quality is directly affected by anthropogenic activities and land usage of the catchment area (Burant, Selbig, Furlong, & Higgins, 2018). There can be variation of several orders of magnitude in concentrations between different catchments. Runoff water contains a variety of substances: suspended matter, oxygen-consuming substances, nutrient salts, bacteria, viruses, other microorganisms, toxic heavy metals, and other environmentally harmful substances. These contaminants are either dissolved or particulate. The field test sites introduced in Chapter 4 were selected represent different urban catchment areas.

Urban rainfall-runoff transports a wide gradation of particulate matter (PM) which can play a role as reservoirs for many chemical substances by providing surface area for the partitioning (Baum, Kuch, & Dittmer, 2021). While coarser inorganic fractions (gravel and sand) in runoff are settled out by unit operations or in the upstream drainage system, the organic and small size inorganic particles are challenging due to their low particle settling velocity. The first essential step in purification of urban runoff water is removal of large or medium size solid particles from the influent flow to the SHEM system. This primary separation methodology depends on the implementation site and the existing conveyance system. Site features also defines the required hydraulic capacities and retention needed for proper treatment of excess the water flows. In field tests several fit for purpose prototypes were tested in real environment (2019-21). The six field tests contained on-ground and underground implementations into runoff conveyance systems and other urban waterbodies. In some filtering system there was an electronic pump to ensure constant flow to purification units. The biological cultivation unit was installed either as a separate unit after the shungite sorption unit, or as a mixed flow unit allowing backflow.

In the SHEM system the shungite sorption unit receives prefiltered water. The larger particles have been filtered out with the technical solutions, settlement tanks or ponds. In the SHEM system fiber filters and textiles might be included to improve the preliminary mechanical separation step before shungite unit. Shungite has a number of positive technical characteristics as filter medium: high mechanical strength and low abrasion; and high filtering capacity (processability, due to low pressure resistance). The amount of shungite needed depends on the influent flow (amount and quality). Shungite layer has a role in mechanical separation in addition to chemical sorption. The filters in field tests were pilot size prototypes that can be expanded to full size solutions.

In the SHEM system the biological cultivation unit was either placed as an independent unit or as mixed flow batch unit after the shungite sorption unit. The influent to biological unit was purified by shungite, and it could be assumed that the most toxic and harmful chemical substances had been removed. The EM was growing in ceramics or porous natural material (lava rocks or shungite). Before implementation into field the EM was cultivated in the fermentation chamber in the laboratory. The recipient water landscapes varied: in one site the EM was led via stony stream and path (soil) to network of three settlement basins, in other case it was led to a shallow settlement basin with functional vegetation, and the third typical solution was to spread the EM to natural flowing water network (Chapter 4). Several different concepts were tested and pilot size filters design for them to verify the proposed purification concepts (Appendix 3).

3.1 Design of filters used in Russia

A sorption filter for field testing of filtering capacity of shungite shale was designed by ITM-Geyser LLC (Saint Petersburg) in 2020. The filter combines two filtering technologies based on effective micro-organisms (EM) and shungite sand. A general scheme of the sorption filter is given in Figure 29. The filter is a three-chamber vessel. Body of the vessel and internal walls are made of polypropylene sheets and inlet and outlet pipelines are made of polypropylene.

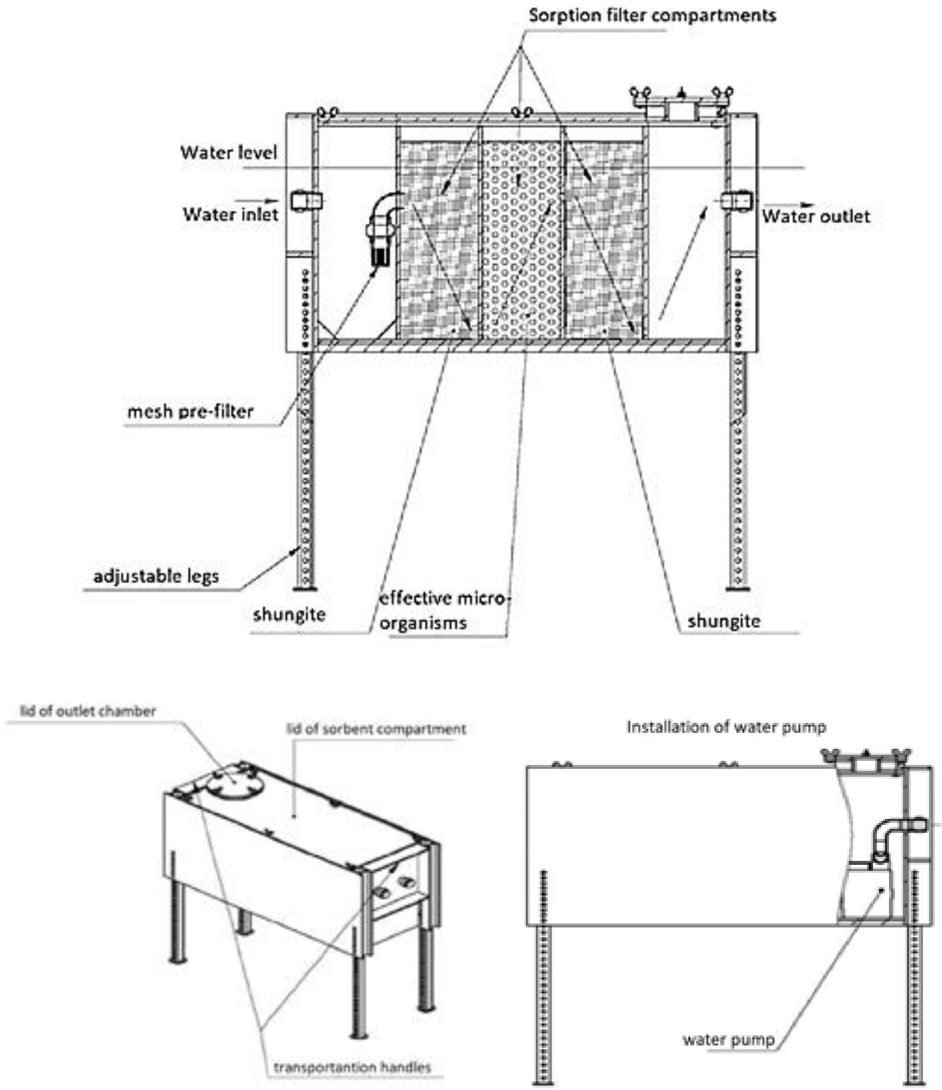


Figure 29 General scheme of sorption filter.

The design of the installation of sorption filters provides for: resistance of construction materials to corrosive processes; ensuring the tightness of the structure; the ability to remove / replace sorption materials from the filter installation; possibility of removing sediment / sludge from the filter unit (polymer filter); the ability to install an underwater filter at the bottom of a water reservoir; the ability to connect the installation of a flow-through filter with existing treatment structures (pipeline, dam, concrete blocks, etc.); possibility of autonomous operation of sorption filter installations.

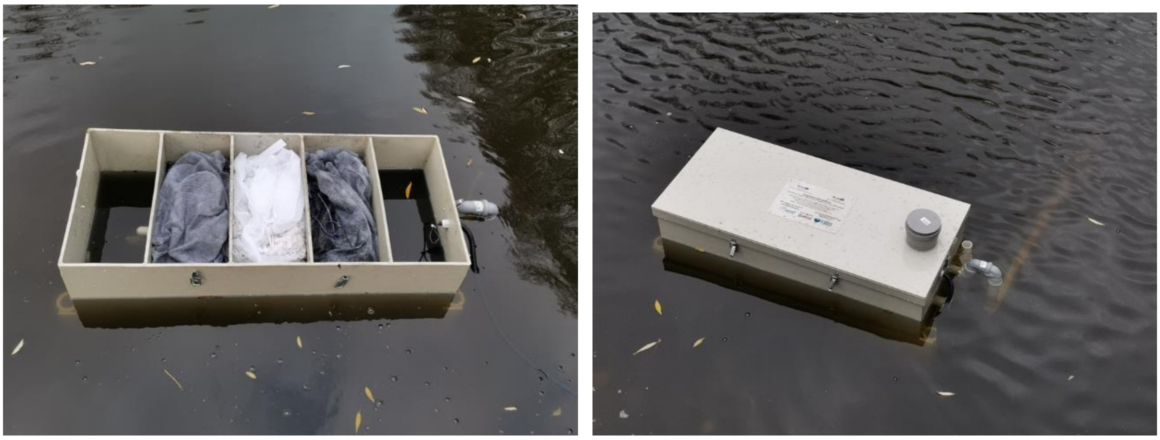


Figure 30. Installation of sorption filter equipped by water pump.

The sorption filter consists of 3 chambers. The first chamber contains mesh polymer pre-filter. The second chamber contains filtering materials in three compartments. The third chamber is designed for installation of a pump for treated water. The filter is equipped with adjustable legs, the design of the filter allows it to be installed in reservoirs at a depth of 1 m. The filter has a common lid for all three chambers, including chamber for filtering material and separate lid for sampling from the third (outlet) chamber. The filter can be made in two versions: passive and active. Passive filter is designed for installation in water streams where flows through it under natural pressure. Active filter is design for installation in water bodies without flow and equipped by water pump in outlet chamber, providing water flow through the filter. This type of filter can be installed in a submerged position.

The sorption filter with combined loading can be installed in a standard storm sewer outlet with a width of 500 mm without preliminary changes and additions to the structure. It is desirable to organize the outlet of purified water from the sorption filter in such a way that the sorbent is fully submerged.

Passive sorption filter can also be installed and fixed at the bottom of the reservoir, while the supply of purified water is organized utilizing natural pressure of water flow through pipes connected to the corresponding filter inlets. The filtration rate can be adjusted by a valve located in the first filter chamber. The productivity of the sorption filter can be regulated within 1-5 l/min interval.

A combination of mechanical, physicochemical and microbiological methods of water treatment is applied in the sorption filter. Mechanical method is designed to remove dispersed impurities from water; it is based on filtration of stormwater through a layer of filter media. The physicochemical method is based on the adsorption of emulsified oil products by sorption loads and the sorption of pollutants in the ionic form. The microbiological method of cleaning is provided by the activity of "Effective microorganisms" (EM) planted on a ceramic carrier.

The filter functions as follows: the purified water inflows by gravity into the first chamber, which acts as a sump that retains large particles and protects the sorption material of filter. A mesh filter in the first chamber accumulates leaves and large particles of soil, sand, dirt, etc., and has to be regularly manually replaced. The first chamber contains a valve, which can be used to regulate the inlet water flow.

The second chamber is divided into 3 compartments, which are filled with different loads. Loading is packed in mesh bags to ease handling when servicing filter. Filtering material in the first compartment performs the first stage of water purification. Further, water which has undergone preliminary mechanical purification and first stage of sorption enters the second compartment containing a ceramic carrier with effective microorganisms performing microbiological purification. The third compartment of the sorption filter is filled with a material that inhibits the growth of microorganisms and performs the function of additional treatment.

After passing through the sorption part of the filter, purified water enters the outlet chamber, where it outflows or is pumped to a water reservoir or city sewer. Samples of purified water are to be taken from the outlet chamber.

Shungite sand with grain size from 5-10 mm produced by NPK "Carbon-Shungit", Petrozavodsk was used as sorption material in the first and third compartments of filtering chamber. In the second compartment EM ceramics in the form of rings 15 * 15mm, produced by OOO PromKeramika, Tula, was used as carrier for effective microorganisms. Concentrate of effective microorganisms EM Active (EMa), manufactured by Multicraft (Austria), was cultivated in accordance with the manufacturer's requirements and planted on the ceramic rings.

Three passive filters and one active filter equipped by water pump were produced for field tests in SHEMWP project.

3.2 Design of filters used in Finland

Three different filters were applied in field tests. They are all passive filters without a pump and introduced here in detail.

1) Filter for testing the shungite and EM growth (filter to pretest the materials) contained two separate chambers with no back flow option.
2) Vertical flow passive filter where inflow was vertical (end-of-pipe solution)
3) Horizontal flow passive filter where the inflow was horizontal (double bottom pipe)

In laboratory environment adsorption tests were carried out in small colons with 25-100 mL volumes. In addition. pilot scale tests in laboratory environment were carried out with 50-250 L volumes. Basic principle and materials applied in field test filters are presented in Figure 31.

Even after the first mechanical separation steps with settlement systems, there are small solid particles in the suspension entering the SHEM system. Porous filter medium was applied to retain this solid fraction. Reticulated polyether open cell foams were used in Finland to the prevent particles to enter and exit the units. There are sponge and foam products commercially available for multiple purposes and applications (fishponds, industrial or oil containing wastewaters, garden ponds, etc.). In the field tests it was found out that the microorganisms attached into the sponges and are living in the material. Thus, the foam can be seen as an element of biological filtration in addition to mechanical separation. The significance of sponges as the biological filter could not be evaluated based on the field tests. Curled fiber sponges offered simultaneously sufficient flow of water through the filter without clogging. The mechanical filtering with sponges and foams should be optimized according to the flow velocity and the pollution substrates aimed to be removed. The mechanical separation with foams and sponges can be expected to alter mainly the particle fractions > 50 µm. In addition to sponge filters, there was a textile layer preventing particle transportation in the system. The mechanically filtered water entered the Shungite layer, which finalized the filtration, sorption and oxidation of pollutants.

The first field test in 2019 was aimed to test materials in field environment. The filter consisted independent chambers for shungite and EM to enable monitoring the materials and their behavior. In 2020-21 passive filters that could be implemented as on-ground or under-ground end-of-pipe solution in common urban conveyance systems or constructed wetlands. One vertical and one horizontal inflow systems were selected for the field tests.

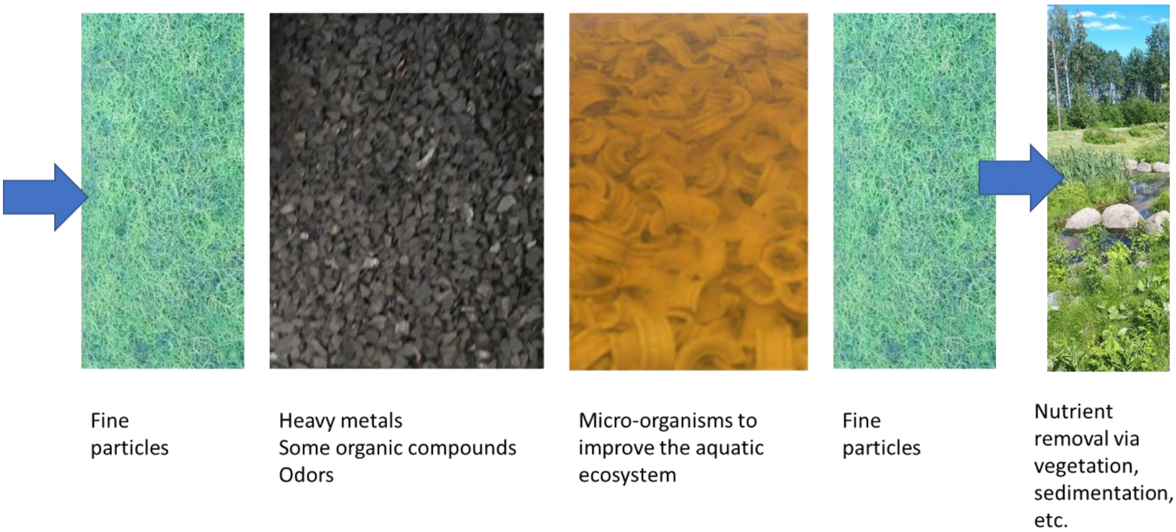


Figure 31 Filters consist of foam to filter fine particles, and two chambers: one for shungite and other one for EM growth media. The settlement pool(s) after the filter system are counted as essential part of the proposed purification system.

Filter to preliminary testing of materials

Figure 32 and Figure 33 illustrates the first filter applied in Sammonlahti CW in 2019. It consisted of independent chambers for shungite and EM. Samples were taken from shungite to study the adsorption and effectiveness of purification and activation cycles. The EM unit was monitored for biological activity. The effect on water quality was monitored comparing the influent and effluent water quality and making visual observations in the ecosystem and incoming flow. In addition, the filter system and materials, such as the foams, fiber textile, mesh filter, and various alternative growth media were tested.

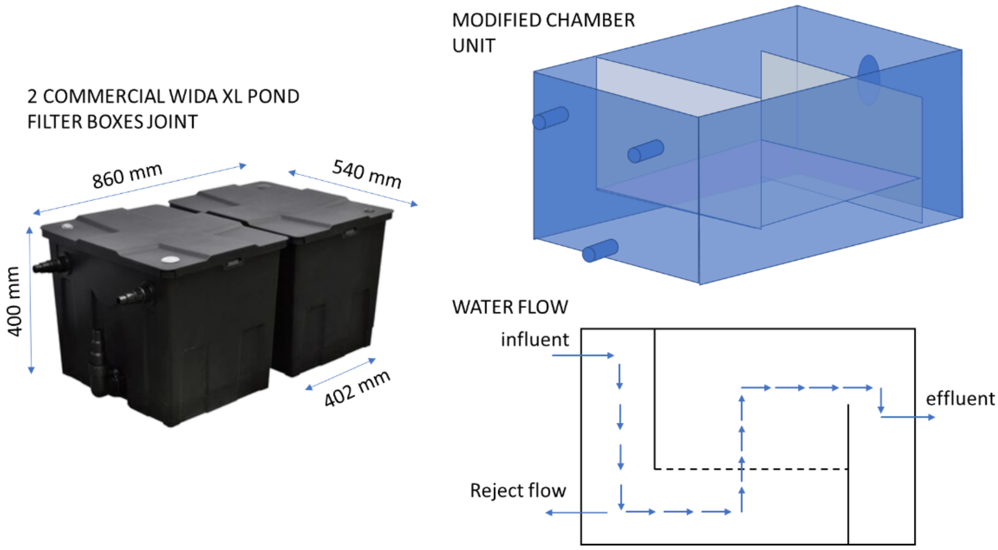


Figure 32 Modified Wida XL boxes were applied in pre-tests of filter media in Sammonlahti constructed wetland in 2019. The boxes were modified from original pond filter systems allowing higher flow rates through two chambers. The first box contained a foam layer and shungite, and second box foam layer and EM in growth media. fine particles were removed from boxes via a reject flow. preliminary filtration to remove large size particles were made with a net installed to water intake.

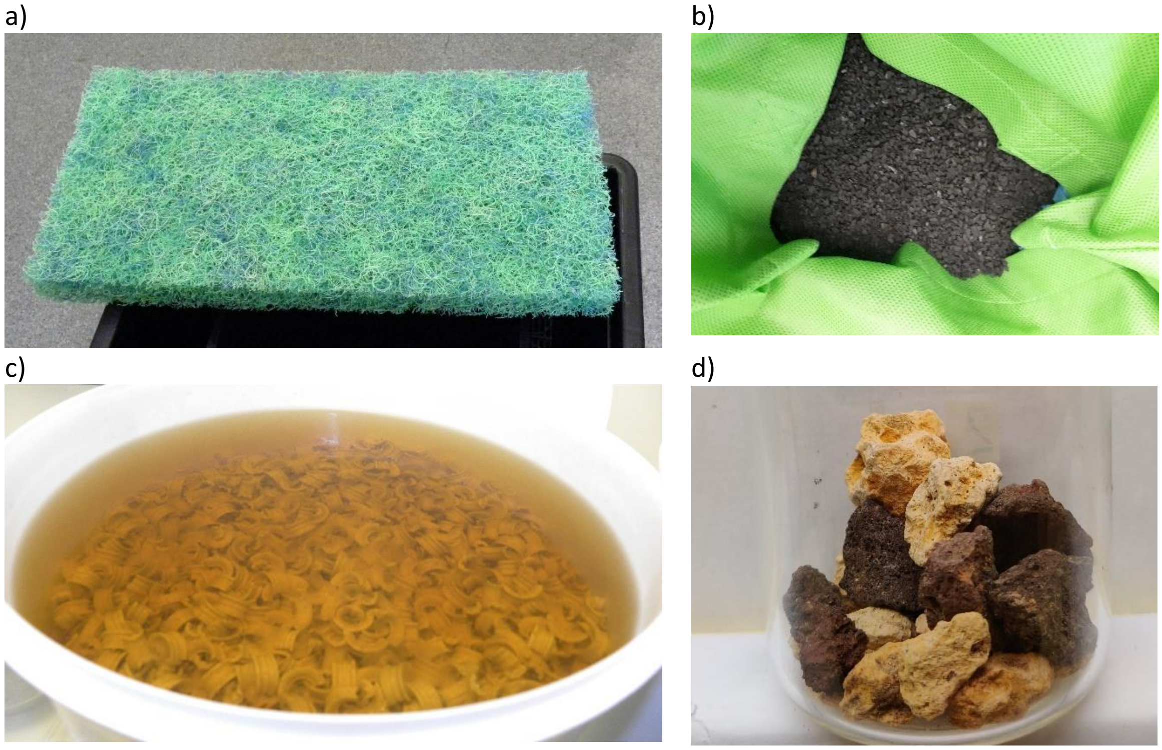


Figure 33 a) foam applied in removal of fine particles, b) shungite were in fiber bags (or geotextile bags), c) EM solution fermenting in laboratory with the ceramics, d) porous lava rocks were studied in field test 2019 as an alternative for ceramics.

Vertical and horizontal flow filters

Functionally different prototypes for filters were designed and two of the designs were applied in latter field tests: one with vertical and another with horizontal flow.

In a vertical flow filter water enters through a diagonal sieve, shown purple in Figure 34. The purpose of the sieve is to prevent leaves and other debris from entering the filter. Also, a sponge is placed below the filter 1 to prevent solid matter still remaining in the flow from entering the filters. Flow barriers are set in a way that enables the water to flow upwards through filter 1 and then downwards through filter 2. This design protects filters from being exposed to solid matter that descends to the bottom of the pipe and exits the pipe through the specifically designed hole. Inside filter 1 there is Shungite and inside the filter 2 is EM. Above the filters is a sealed lid for maintenance purposes. The pipe is made of PEH. Images of an installed vertical filter can be seen in chapter 4.1 in the Sammonlahti field test description.

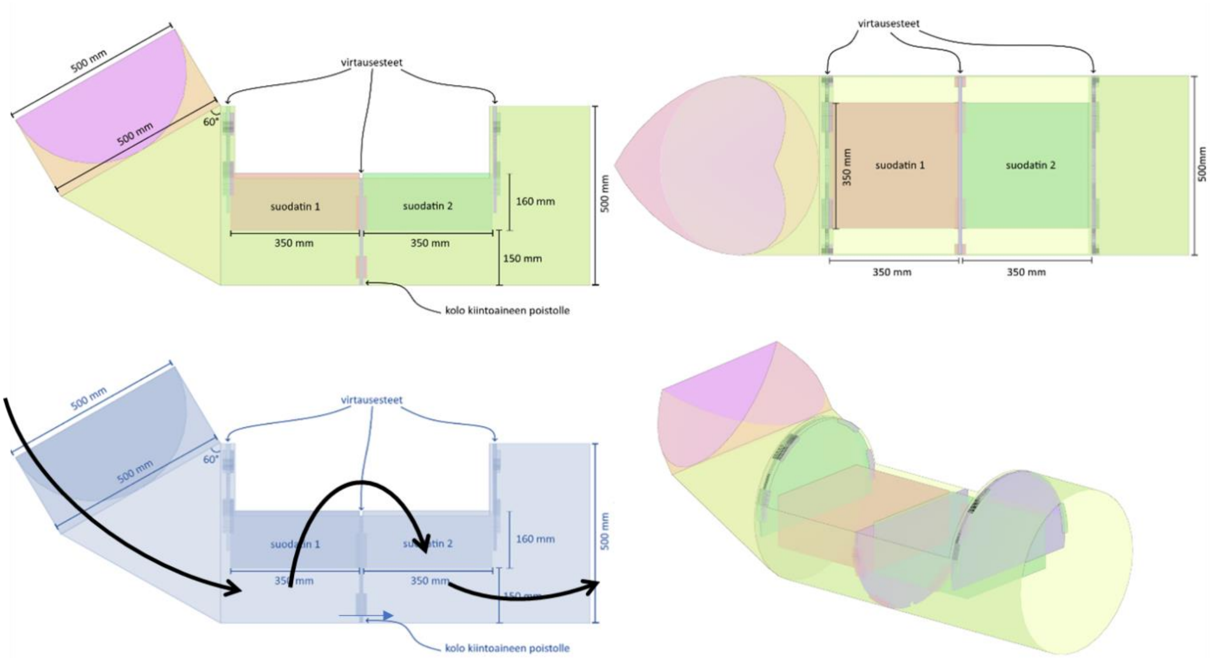


Figure 34 Technical drawings of the vertical flow filter. Filter was applied in Sammonlahti CW in 2020-21 field tests.

In the horizontal filter the filters are in a box at the bottom of a pipe as described in Figure 36. The water falls into the filter element through a ramp, which is covered with a fabric to prevent solid matter from entering the filters. The water then proceeds through the filters. Filter 1 is filled with shungite and filter 2 with EM. The box that contains the filters is on rails so that it can be removed for maintenance. Images of an installed horizontal filter can be seen in chapter 4.2 in the Highway 6 ramp field test site description.

Figure 35 Vertical flow filter applied in Sammonlahti CW at 2020-2021 field test.

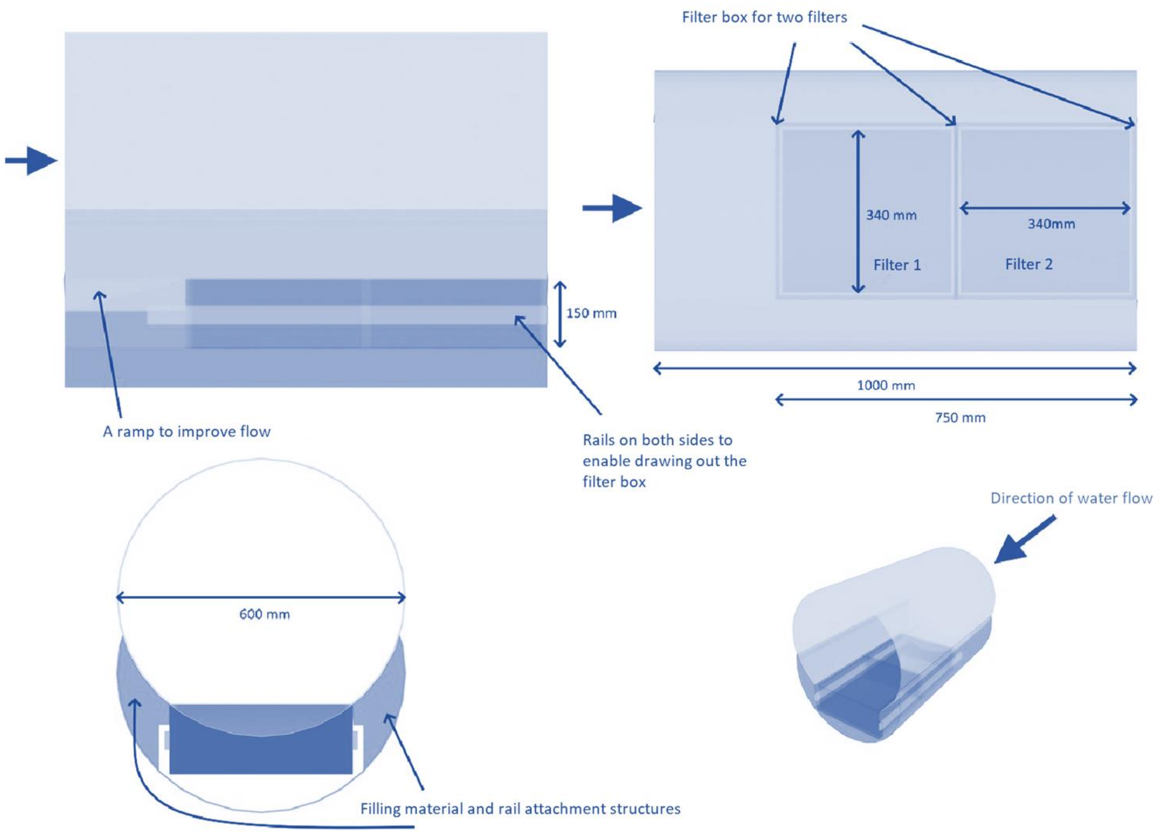


Figure 36 Technical drawings of a horizontal flow filter

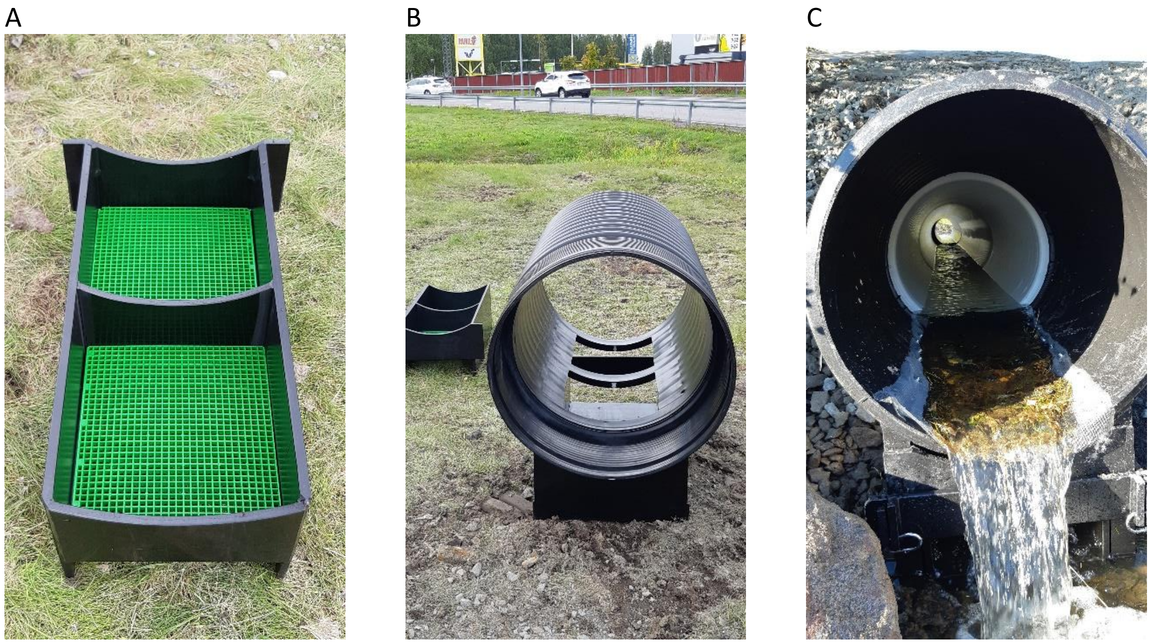


Figure 37 Horizontal flow filter implements at ramp of highway 6 site: A) sledge for filter media, B) pipe unit above the sledge, C) flow out from the pipe unit. Horizontal water flow pass grid above the materials and flows partially through the filter materials.

4. Field test sites and implementation of filters

To test the filter prototypes with real runoff waters, field tests were implemented. The filters were installed to two different sites at Lappeenranta: Sammonlahti CW and Highway 6 ramp CW. In addition to the tests in Lappeenranta, field tests at four sites were carried out in St. Petersburg. The field tests aimed to support 1) testing of filter media in real environment, 2) monitoring runoff water quality, 3) technical design of filters for commercial purposes, and 4) development of maintenance and re-use of shungite cycle.

4.1 Description of field test sites in Finland

Four sites at Lappeenranta were considered for field test sites (Table 10). The sites water quality was analyzed, and they were monitored for technical feasibility to test different filter approaches.

Sammonlahti CW is a site where previous EM research has taken place in 2016. The water quality of influent has been studied in SHEM-WP campaigns, but background information was available from the EM studies and annual follow up program. The installation of the filter was also considered to be feasible into basin 1 outlet, and it required no permissions. Sammonlahti CW was chosen as the site representing runoff from residential area. Monitoring of water quality started in May 2019. There were two field tests at outflow from first basin. In July-Aug 2019 a test to gain information about functionality of shungite and EM was carried out. The material studies continued over the winter season until May 2020. In 2020 a vertical flow filter was implemented and monitored for a year.

The second selected site, Highway 6 ramp CW, represents runoff from small-scale industrial activity and shopping malls. Tullitie pipeline outlet and Ratapuisto pipeline outlet were considered alternatives. Based on water quality these sites would have offered proper test sites, but from both of them the settlement basin was missing, and technically the basin was most feasible to build to Highway 6 ramp. Highway 6 ramp was feasible to implement a horizontal flow approach. The field test implementation required land construction work, since a new pipeline (containing the filter) had to be installed. The pipeline improved flow from main drainage system to settlement basin.

Both implementations at the selected test sites contained a basin after the filter, which functions as a growth medium for the EM. In Sammonlahti the EM from filter leached to stream and it could be expected the EM was spread to soil in downstream, where it was transported to secondary basin. In Highway 6 ramp CW the secondary basin was large, and the EM was directly fed from the purification system into it. Both secondary basins were shallow.

Table 10 Potential field test sites evaluated

Name	Description
Sammonlahti	Main test site: pre-test in 2019 for filter materials, vertical flow filter test 2020-2021, water and flow monitored 2019-2021. Minor renovation of basin 1 in spring 2020.
Highway 6 ramp	2nd field test site: land construction made in 2020 to change the recipient pool. Horizontal flow filter test 2020-2021.
Ratapuisto	Water quality monitored in 2019. Field test not carried out. Alternative to Sammonlahti.
Tullitie	Water quality monitored in 2019. Field test not carried out. Alternative to Highway 6 ramp.

Ratapuisto *Tullitie*

A

B

Figure 38 Drainage ends in Ratapuisto and Tullitie were among the evaluated alternatives for the field test sites. A) Catchment areas, and B) visualization of filter implementation site

Sammonlahti constructed wetland

One of the selected sites was Sammonlahti constructed wetland. It is located on a slope between Sammonlahti residential area and lake Saimaa. The catchment area – shown in Figure 39 – for the wetland is approximately 1 km^2 and consists of residential area, grocery stores, roads, and streets. There are no functioning gas stations or industrial activities in the area. The highest traffic in the area is in Helsingintie and Skinnarilankatu. The amount of traffic on these two roads is estimated in Lappeenranta city general plan. Key figures to describe the catchment area are shown in Table 11.

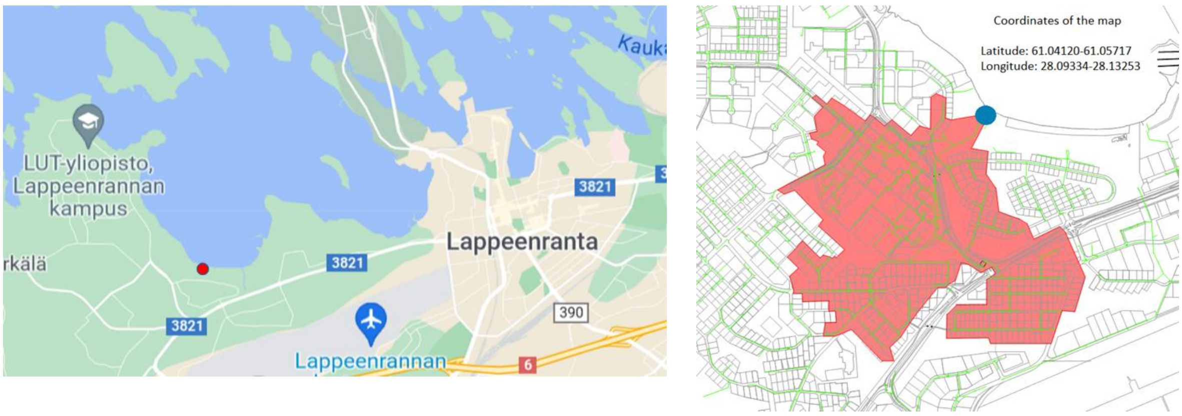


Figure 39 Catchment area of Sammonlahti field test site

Table 11 Key figures of Sammonlahti sites catchment area

Sammonlahti test site	
Total area	1 km2
Covered area*	39 %
Gas stations	0 stations
Helsingintie	5700-17000 cars/day
Skinnarilankatu	14000 cars/day

* Pavements and rooftops

The Sammonlahti wetland is formed by four basins connected by brooks (Figure 40). The wetland with its first three basins was constructed in 2012 and the fourth basin was added in 2020 as a part of a wetland renovation to enhance the run-off water treatment. From the last basin the water flows to Sunisenselkä of lake Saimaa. The wetland surface area is 1,1 ha and it has an average flowrate of 16,6 l/s.

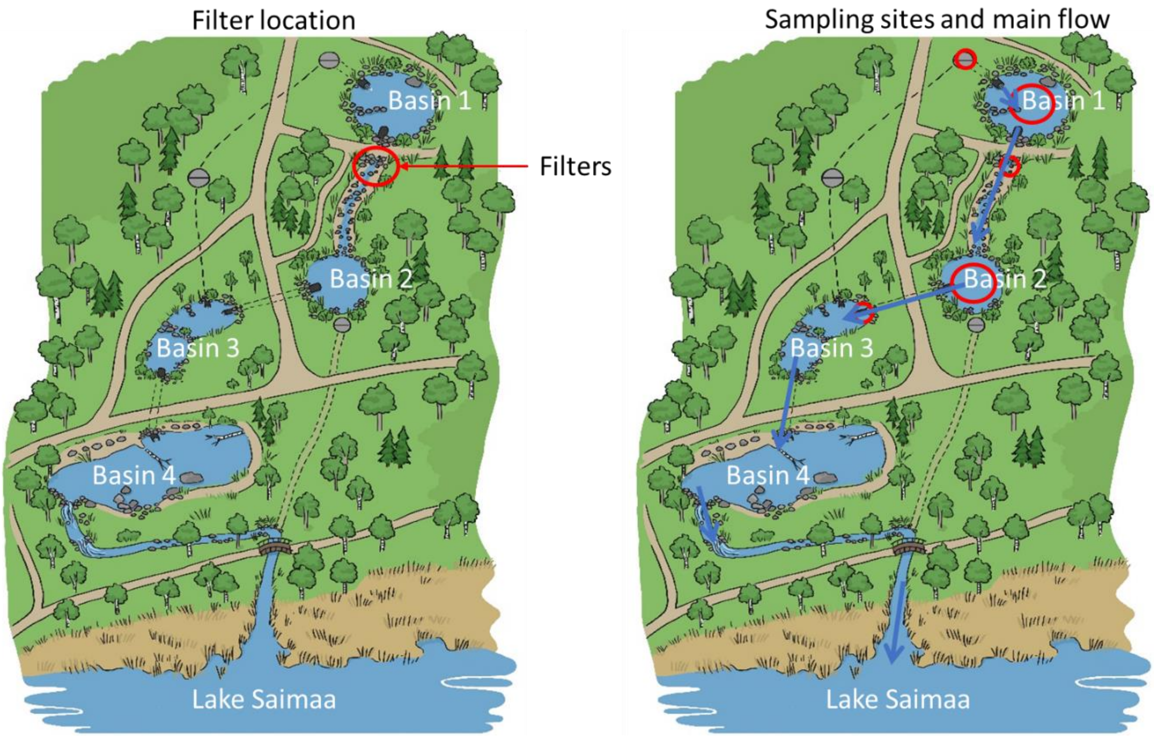


Figure 40 Sammonlahti CW in 2020. Basin 4 was built in 2020. Filters were implemented in 2019 and 2020 at outflow from basin 1. Water quality was monitored as composite samples from Basin 1 and 2, and their out flows.

Sammonlahti constructed wetland was the selected site for pre-tests from July to August in 2019. The goal for pretesting was to gather preliminary information for designing the filter prototypes for latter field tests. Figure 42. shows the pretest filter, which is described in further detail in chapter 4. The results of the pre-test are explained in detail in Chapter 6.

Basin 1: influent from drainage system (2019). Water quality was monitored as taking a composite sample. Settling tank in drainage system is located near influent pipe.

Outlet from Basin 1: filter location, water quality and flow monitored as single weekly samples

Stoned water pathway (stream) to Basin 2

Basin 2: water quality monitored as composite samples

Outlet from Basin 2: water quality monitored in 2019

Basin 3: renovated in 2020

Basin 4: build in 2020

Effluent to Saimaa

Figure 41 Photos from Sammonlahti CW

Figure 42 Pre-test filter located at outlet of 1st basin at Sammonlahti constructed wetland

Field tests of 2020 at Sammonlahti started in July, when the filter was installed. Between the pre-tests of 2019 and field tests of 2020 a major renovation took place at the site. Figure 43 shows how the settling of solid matters in the 1st basin was not optimal and this was improved by constructing stone walls to prolong the duration of water in the basin. Also, the water level of the 2nd basin was raised, and similar structures were placed to prolong the duration of the water. 4th basin was added to the wetland. Especially changes in 1st and 2nd basin affect the comparability of the field test results with the older data.

Figure 43 The 1st basin before and after renovation.

Figure 44 Outlet pipe from 1st basin before and after the filter installation.

The EM-shungite filter was installed in July of 2020 following the outlet pipe of the 1st basin and the field test ended in September of 2021. The 1st basin of the wetland serves to remove solid matter from the flow entering the filter. To enable the installation, the pipe had to be extended with an additional pipe section.

The pipe extension was installed on a bed of rocks and the EM-shungite filter was installed right below the pipe outlet. The filter model used at Sammonlahti wetland is a vertical model described in detail in chapter 3. This installation did not require permission.

Highway 6 ramp CW

The other selected site is located in connection with a highway ramp between highway 6 and Vanha Viipurintie. The test site has a catchment area of approximately 2 km^2. The estimated catchment area is shown in Figure 45.

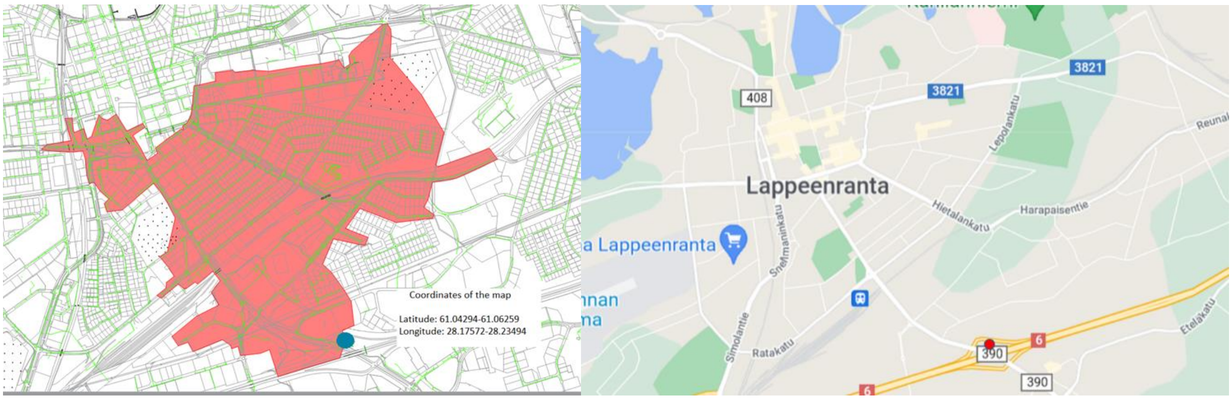


Figure 45 The catchment area of field test site at highway 6 ramp

The catchment area is a slope on the southern side of Lappeenranta city center. It contains large residential area of mostly detached houses in Alakylä. The northern side of the catchment area extends to Kauppatori, shopping malls Galleria and Iso-Kristiina and the Armila wellbeing center. In the southern parts of the catchment area there are areas of commercial services and small-scale industry. These areas contain two supermarkets, car dealerships, car workshops and a car inspection centre. There is also a railway with both passenger and cargo traffic passing through the catchment area. Small section of highway 6 belongs to the catchment area. Key figures describing the catchment area are shown in Table 12.

Table 12 Description of highway 6 ramp sites catchment area

Highway 6 ramp site	
Total area	2 km2
Covered area*	47 %
Areas of commarcial services and small-scale industry**	18,6
Gas stations	6 stations
Railway - passenger trains	30 per day
Railway - Cargo trains	40 per day
Highway 6	12000-40000 cars/day
Highway 6 - Vanha Viipurintie ramp	3000-6000 cars/day

* Pavements and rooftops
** Of Reijola and Harapainen as stated in general plan of Lappeenranta city

A flood pool for runoff waters was constructed at the site in 2011-2012. The EM-shungite filter was installed at the site near Highway 6 ramp in September 2020 as the structures were renovated to suit the purposes of water protection. Figure 46 shows the site before (upper) and after (below) the renovation. As shown in Figure 46 the run-off water coming from east (left) passed through the area through a ditch, except in the case of flood. The ditch was blocked with drowned weir and a new pipeline was installed to bring the water to the settlement pool. An adjustment well enables the usage of the ditch in case of malfunction and enables maintenance of the flow field and the filter. These changes prolong the duration of water at site and enable the settlement of solid matter, nutrients, and contaminants. Also, the collection basin was renovated to function as a primary settlement pool to mitigate the solid matter entering the filter. A permission for the construction was required. Construction was outsourced to Maansiirto Vammas Oy.

A) Highway 6 ramp and sampling sites before 2020 construction and filter implementation.

B) Highway 6 ramp CW and sampling sites after filter were implemented.

Figure 46 The highway 6 site aerial photo before renovation (A) and a functional illustration of the site after renovation (b).

Figure 47 Highway 6 ramp CW and construction: A…B) CW before implementation, C…G) construction, and H... I) CW site after modification. H) influent to settlement pond before the filter, I) secondary settlement pond and outflow pipes from filter.

EM-shungite filter is installed to the outlet of another of the new pipelines between the primary settlement pool and the settlement pool. The field test started in September of 2020 and lasted until September of 2021. The filter in use was a horizontal filter described in detail in chapter 3. The second pipeline is built slightly higher as a backup line in case of cloggage to prevent flooding. The filter is installed as an extension to the pipe. Water falls from the pipe extension through a fabric into a box containing shungite and EM, and the box can be drawn out for maintenance as shown in Figure 48.

Figure 48 Highway 6 ramp CW: A and B) Outflow EM-shungite filter installed at the end of the black pipe. The upper "white pipe" is backup pipe for flood water. C and D) influent from the small upper pond to the filter.

The water exiting the filter can be seen in Figure 37 and in Figure 48. The fabric covering the inlet of the filter was found to be clogged by solid matter namely after heavy rains, which significantly could reduce the flow rate through the filter without maintenance. Technical development to would be required in commercial solution on preventing the solid material cumulation. More discussion on issues in maintenance is in chapter 4.3. The horizontal flow filter did function very well, even better than expected. There was a small settlement pond and outlet from the pond was led to a settlement tank in the drainage pipeline before the filter sledge. This mechanical separation of solid material worked well, and removed main larger particles from the water suspension. Only when the flow rate increased, the solid material flooding in strong flow did not settle and even 5 cm diameter stones were found from the top of the filter. Coarser materials were flushed with the flow, if not settled or entered the filter sledge. Organic matter was less problematic in this site, since there was less vegetation, and influent arrived from underground conveyance pipelines to the primary settlement pond.

4.2 Description of field test sites Russia

Four sites were selected for field test of filters in Saint-Petersburg. Two test sites are lakes. They constitute a natural but regulated water system, located in the south-east outskirts of the city of Saint-Petersburg (Krasnoselsky district). The system consists of two lakes, Dudergof and Dolgoe separated by a water dam with two waterways (spillways). Another site is a closed pond, located in Pionersky park of Primorsky district and the last one is a water retention pond of road network storm water management. Selection of these sites serves for testing filters in different hydrological conditions and for various water quality.

Lake Dudergofskoe

Lake Duderhofskoye is located in the Krasnoselsky district of St. Petersburg, in the Krasnoye Selo town, and occupies a vast territory on the right side of the railway in the vicinity of the Mozhayskaya railway station (Figure 49). The area of the lake is 627,942 m2. According to this parameter, oz. Duderhofskoye is one of the largest in the city of St. Petersburg among the reservoirs of this type. The perimeter of the coastline of is 3923 m, the volume of water mass is estimated as 710,000 m3 and the average depth is 1.3 m. The catchment area is about 17 km2 with about 5 km2 of urban area.

The lake has an oval shape with a winding, sometimes indented coastline. The reservoir is stretched in north-south direction. The lake is about 1.30 km long and about 600 m wide (Figure 49). Dudergof lake is the upper reservoir in the lake system which serves as waterhead of Dudergofka river which enters the Gulf of Finland through the system of channels.

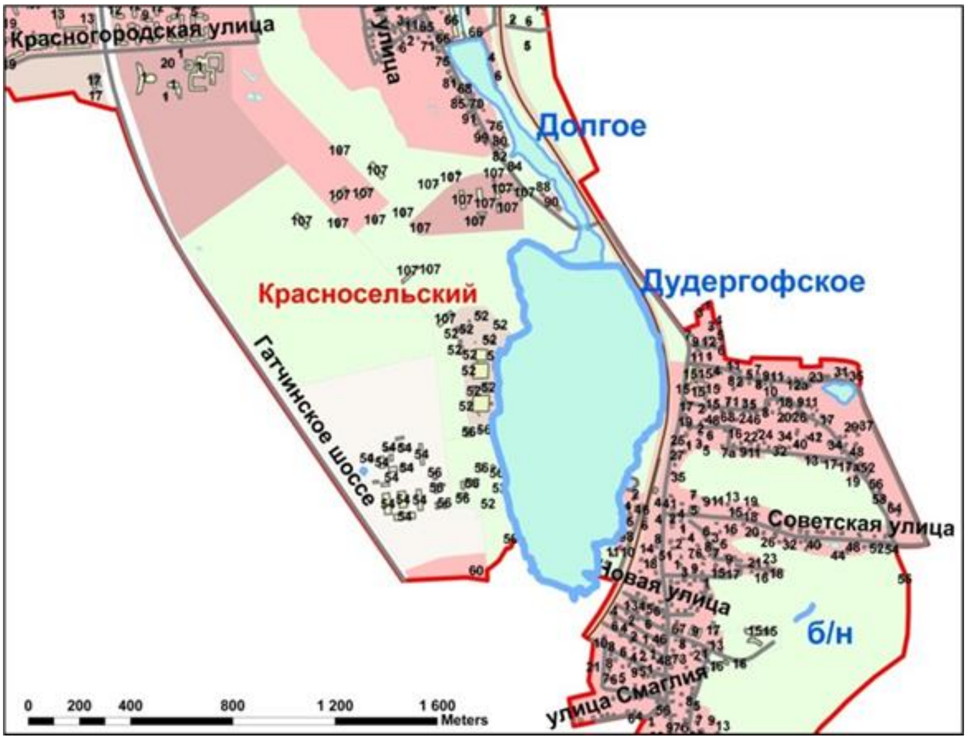


Figure 49 Scheme of Dudrgofskoe lake and surrounding area.

The basin of the lake is developed in Pleistocene sediments of Ostashkov age. These sediments are represented by loams of glacial origin. Duderhofskoe is open lake with water discharge to lake Dolgoe which is also one of the test sites for this study. Water supply for Dudergof lake is provided by small streams and springs, slope and soil runoff, precipitation to the water area. From the lake, water is discharged to Dolgoe lake through two spillways in the dam. Water level fluctuation in the lake is 15-40 cm.

The width of the earth dam separating lakes Dudegrof and Dolgoe reaches 15-20 m (Figure 50). Height above the water surface is about 0.5-0.7 m. Most of the shoreline along the dam is overgrown with dense thickets of reeds, often extending far into the water area. Two spillways lined with concrete blocks are arranged in the body of the dam. Above both spillways two bridges are built. Both of them are in good condition: automobile reinforced concrete, and pedestrian wooden with a metal frame.

Figure 50 Earth dam separating Dudergofskoe and Dolgoe lakes.

Coastal slopes of the lake are steep, eastern with a height of 12 to 64 m, southern - up to 25 m, western 8-15 m. Western slopes, closely adjacent to the shoreline are sometimes steep with traces of abrasion and land sliding in the vicinity of groundwater outsprings. There are also ravines overgrown with meadow grass. The soil of the coastal slopes is sandy and sandy loamy. On the western slope in some places there are outcrops of limestone and springs. The slopes of the basin are covered mainly with foliaceous forest: willow, maple, oak, elm. The eastern and southern slopes are built up with private houses with vegetable gardens. Wastewater treatment plant is located to the west from the lake in the near a peninsula in the middle part of the catchment area. Railway runs along the east coast of the lake in some places forming 2 m high embankment with steep slopes covered with meadow vegetation. The distance from coastline to the railway varies from 1 to 50 m.

Bottom of the lake along the coastline is covered with plant residues and within sight by attached aquatic plants. The bottom of the lake is sandy with gray silt, which is about 30 cm thick next to the shoreline reaching thickness of about 1.5 m in the central prat of the lake (Figure 51). The water in the reservoir is transparent, light brownish in color. Ducks nests have been observed in the reed thickets, and, according to local residents, reeds are inhabited by muskrats.

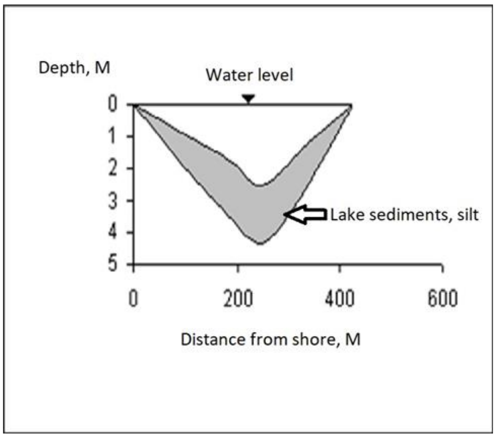


Figure 51 Bottom profile across Dudergofskoe lake.

Dolgoe lake.

Lake Dolgoye is located in Krasnoselsky district of Saint Petersburg. It is a narrow water basin extending in north-northwest direction (about 0.8-0.9 km) with greatest width is 0.13 km (Figure 52). The area of the lake is about 0.090 km2, and average depth is 1.2 m with 3.5 m maximum. Macrophytes cover the entire bottom of the lake. The lake has no inflowing water streams. Dolgoe and Dudergofskoe lakes are separated by dam with two water spillways. Water flow from Dudergofskoe lake serves as the major water supply. Water flow rate through spillway 2 is 1.5 m3 per second. A dam at the northern end of the lake separates it from lake Bezymyannoye which belongs to the same water system. Contribution of groundwater and precipitation in the water balance of Dolgoe lake is insignificant.

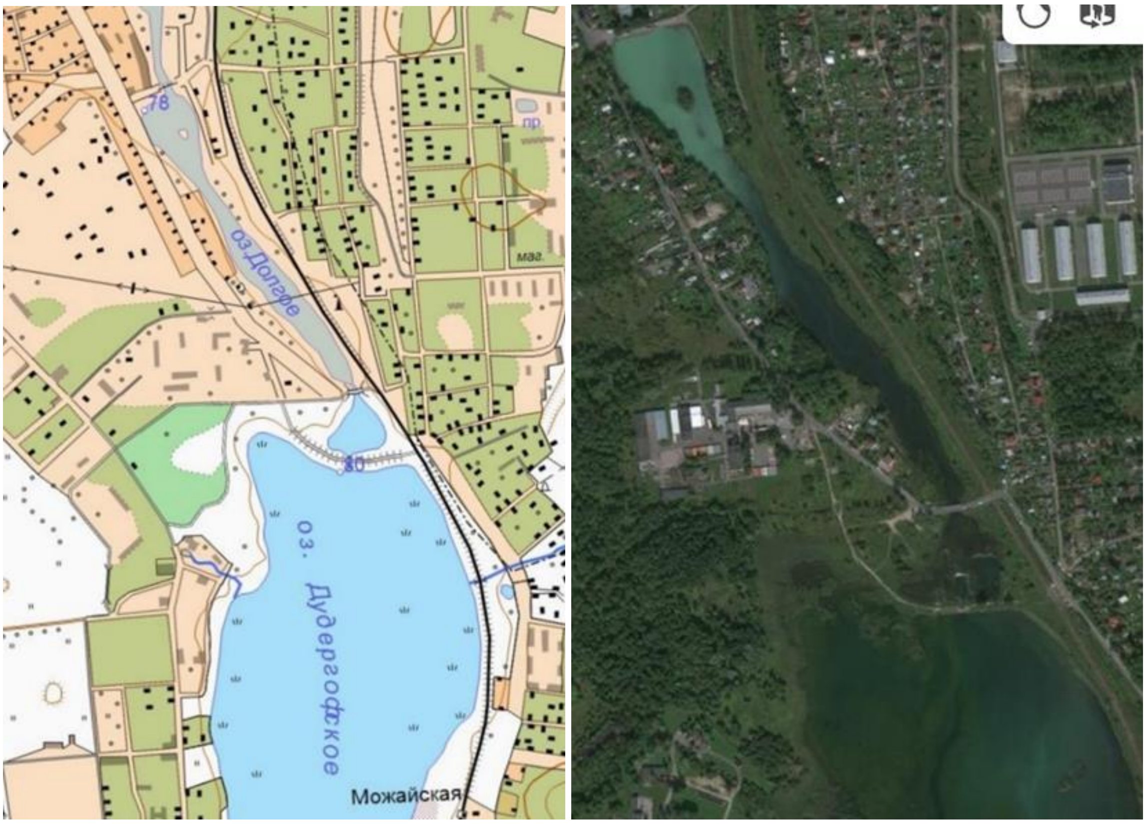


Figure 52 Map and satellite image of Dolgoe lake.

The shores of the lake are low in its southern and northern ends. In the central part shores are formed by an elevation to the west and railway to the east of the lake. In the northern dam zone, in the middle part of the lake, and, especially, in the southern part of the lake, there are areas intensively overgrown with higher aquatic vegetation.

There are no significant sources of pollution on shores of Dolgoe lake, except for possible minor input from private land plots along the lake shore and run off from railway. In general, all kinds of contaminants enter the lake with water from Dudergofskoe lake.

Pond in Pionersky garden.

The pond is located in the Primorsky district of St. Petersburg at the intersection of Serdobolskaya and Studentskaya Streets. Despite the pond is situated in Pionersky Garden, its location can be characterized as urban environment (Figure 53). Walking paths are laid along the shores with benches and small containers for garbage. However, an industrial area and garages are situated about 60 meters to the south of the pond and an unpaved car parking lot is just 5 meters from shoreline to the east of the pond. There are also several residential buildings in the vicinity of this test site. Also, an electric transformer is placed within 5 meters from shoreline as well as 2, likely stormwater, sewage wells.

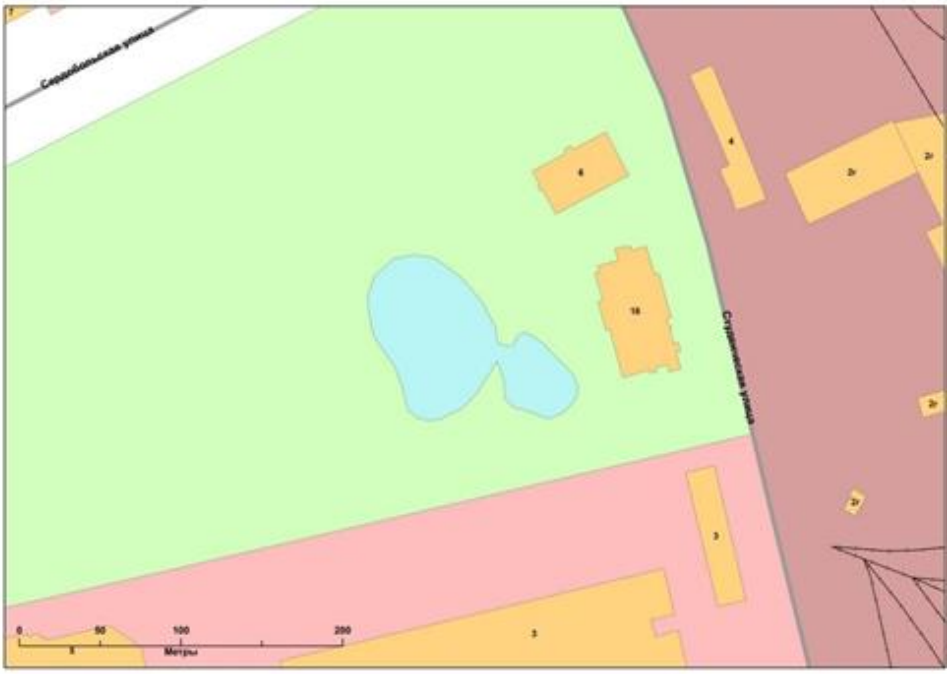


Figure 53 A general scheme of the Pinersly pond surroundings area.

The pond consists of two parts connected by a canal lined by two concrete slabs. A pedestrian bridge about 2 meters wide 8 meters long is thrown over the canal (Figure 54). The bridge has an iron frame and railings with wooden floors.

Figure 54 Pedestrian bridge and canal connecting two parts of the pond.

Coasts of the pond are gently sloping with angle of about 30 °. The coast of the pond is covered by meadow grass. Some traces of household originating litter were spotted around pond coasts. However, there were no significant sources of potential contamination observed.

Figure 55 General view to the pond in Pionersky garden.

Stormwater retention pond.

Storm water cleaning system is a system of small (one, two, sometimes three) low-flow, small natural or artificial reservoirs (ponds) overgrown with aquatic vegetation (e.g. reeds) to retain nutrients and other contaminants released from rad network and prevent their release into the aquatic environment. Natural sorbents are used to be applied in the system in addition to biological treatment. This test site consists of one retention pond. Schemes of the site is given Figure 56.

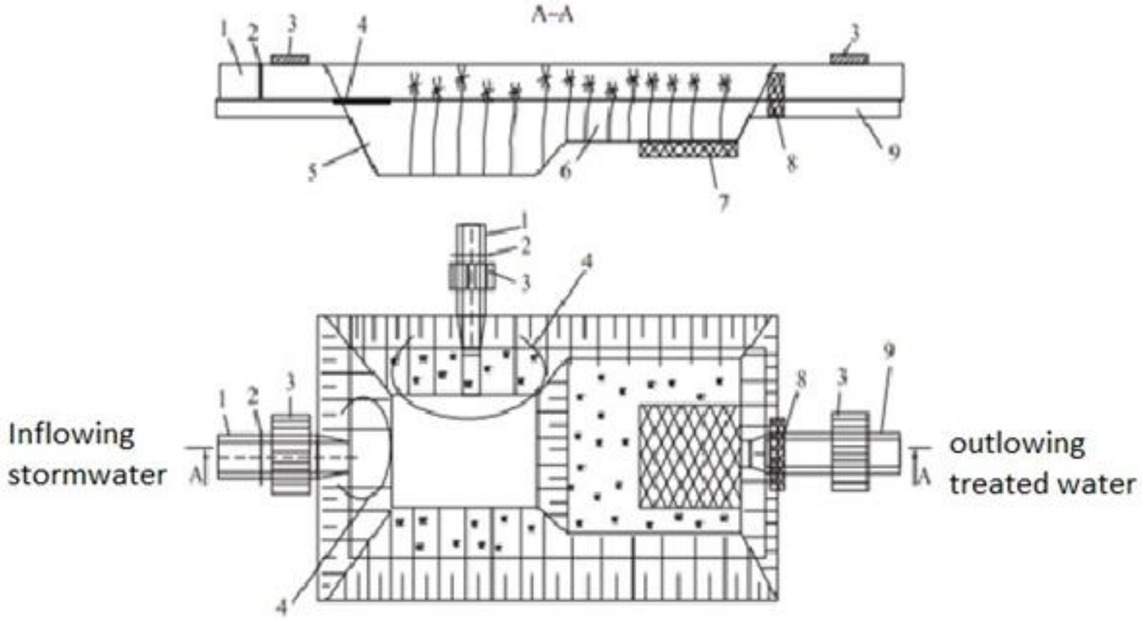


Figure 56 General scheme of the retention pond. 1 – supply ditch; 2 – grate for floating debris; 3 – bridges; 4 – floating boom for absorption of oil products; 5 – buffer pit for deposition of large fractions of suspended solids; 6 - part of the reservoir with aquatic plants; 7 - natural sorbents on the bottom of the pond; 8 – outlet filter with sorbent; 9 – outlet ditch.

Construction of retention ponds is recommended for roads of the third category and above with heavy traffic and sufficient side areas.

The grate is design to retain large pieces of liter from the runoff and prevent their entering the retention pond Figure 57. Booms for absorption of floating oil products form stormwater are installed at the entrance to the retention pond Figure 58. The buffer pit in the front part of the retention pond serves for sedimentation of large particles entering the pond with contaminated stormwater. After the buffer pit stormwater enters the main part of the retention pond, where smaller particles are sedimented and retained by natural sorbents on the bottom and nutrients are retained by aquatic plants Figure 58. Purified stormwater is released from the retention pond through an outlet filter filled with natural sorbent such as zeolites, shungites, black shist etc. The filter provides final stormwater cleaning before the release to the environment.

Figure 57 Supply ditch with grate and oil booms

Figure 58 The main retention pond and outlet with final filter.

4.3 Technical feasibility and maintenance

Active and passive filters were tested. Active filter can control the flow rate and would be feasible in urban areas where electricity supply can be arranged. Finnish filters were all passive filters where volume flow depend on precipitation and seasonal variation. Installation of these filters as part of rainwater drainage system might be more flexible. High influent variation alters the filter for clogging with solid matter flooding in high flow, or in dry season by organic material growth inside the filter chambers. Table 13 concludes issues to be considered between active and passive filter system.

Urban rainwater contains man-made contaminants or natural forms of pollution (such as rotting leaves). They have to be filtered with prefilters. Active filter allows prefilter installed to inlet pump. Passive filter without a pump has to contain a settlement tank or pond. In high flow season or rain peaks the rainwater contains solid material and items that might not settle as expected in the rainwater drainage system. There are plastic items (such as plastic packs) or leaves that are light and can float long distances in the system. It is essential to prevent solid material of this type entering the filters. The passive filters contain a filter mesh or net in addition to preliminary settling tanks and ponds. These prefilters filtered out the light particles and natural flow flushed the filter mesh. However, clogging of filter due to algae and small branches occurred. Even stones with 5 cm diameter were found from the meshes. It is likely that there was some vandalism or children playing with the flow. In public places the vandalism factor always has to be considered. Table 13 concludes considerations found in SHEM-WP field tests. The filters applied in field tests were small-scale prototypes and the innovation will require more development to become a commercial purification system.

Table 13 Issues in active and passive filter solutions.

Technical issues	Active filter	Passive filter
Implementation and integration	Requires electricity supply for pump. Offers more options in controlling, monitoring, and automation Partial intake of flow unless all water is pumped via the filter from resin basin	Does not require electricity supply. Simple technical structure that can be adjusted to horizontal or vertical inflow Might require land construction
Maintenance and operating	Electricity demand increases maintenance costs namely if huge water volumes are pumped Monitoring and operating system could be easily automated. In-situ maintenance recommended at least twice a year. Requires visit to the site	Monitoring system for material clogging the filter or vandalism might be an issue in distance locations. In-situ maintenance is recommended as minimum twice a year. Maintenance and operating require visiting the site.
Clogging with solid material	Influent to pump can be filtered and floating solid material is not a critical issue. Foams utilized in removal of small particles and oil compounds might cause clogging. Automated removal of small solid particles is required.	Prefilter mesh may be clogged. Foams utilized in removal of small particles and oil compounds might cause clogging. Automated removal of small solid particles is required. In dry season the influent may stop, and algae start growing inside the filter
Flow rate variation	Pump equalizes the variation in influent. High flow rates require either high-capacity filters or flood ponds Less sensitive for dry seasons if water volume is adequate	Natural variation effects the flowrate and retention time may vary Have to be designed as flood safe with bypass opportunity or flood pond solution Gravity based purification systems may dry
Winter season	Freezing in wintertime may be a risk	Freezing in wintertime is low risk to system

Figure 59 Visualization of common clogging and flow issues in field tests: a) organic matter clogging the pre-filter mesh, B) too tight mesh as pre-filter blocks the flow, c) melting water brought stones into filter, D) floating material is a problem, F) filter opened after winter is functioning without problems.

5. Monitoring the water quality at test sites

5.1 Monitoring campaigns for water quality in Lappeenranta

Dates and aims of sampling campaigns in Lappeenranta are presented in *Table 14*. In this chapter only the results from the water quality campaigns are addressed. The aims of sampling campaigns varied

1. Water quality for field test site selection was carried out in Sammonlahti CW, Highway-6 ramp CW, Ratapuisto outflow, and Tullitie outflow. Sites are presented in previous chapters.
2. Water quality fluctuation was monitored to gain information about the concentration levels and variations of the urban pollutants.
3. Shungite material was monitored to gather information about the pollutants it had sorpted.

Table 14 Sampling campaigns in Lappeenranta

Site	Aim	Date
Sammonlahti	Data originating from previous studies. Wetland water quality was monitored during EM research. Applies as reference data for water quality.	15.6.-26.10.2016
Sammonlahti	Weekly monitoring for water quality of basins 1 and 2.	17.5.2019-19.8.2019
Sammonlahti	Short campaign for testing shungite and EM with natural run-off water started 4.7.2019 and ended in mid-August. The test could not be continued due to the lack of influent flow from basin 1.	4.7.-13.8.2019
Sammonlahti	Monitoring water variation in water quality, filter installed on July 22nd, 2020.	22.7.2020-10.8.2020
Sammonlahti	Monitoring campaign continues	5/2021-7/2021
Highway 6 ramp	Monitoring water quality, filter implemented on Sep 15, 2020	4.6.2020-10.8.2020
Highway 6 ramp	Monitoring campaign continues	5/2021-7/2021
Tullitie 1 pipe outlet	Water sampled for selection of field test site	14.6.-24.7.2019
Ratapuisto pipe outlet	Water sampled for selection of field test site	14.6.2019

Sammonlahti CW has several ponds or basins Figure 42). The filter was located at the basin 1 outflow of pipe. As the EM effect can be assumed to be seen mainly indirectly in the catchment aquatic system, the water quality in basin 2 was monitored. Sammonlahti CW water quality has been monitored before the project in 2016, and the data were applied as reference. In May August 2019 the Sammonlahti 1 and 2 basins and their outflows were sampled weekly. A short field test with filter was carried out in July-August 2019, and filter outflow and shungite material were sampled. The Sammonlahti CW basin 1 and 4 were renovated in spring 2020, and sampling campaign had to be postponed from May to July. Filter was installed to information about the technical feasibility and effect of seasonal fluctuation. Shungite in filters were sampled. Monitoring continued in 2021.

Highway 6 ramp required land construction work. The existing recipient basin was taken into more efficient use and the main flow was directed into it. Influent quality was monitored in 2020, and filter was implemented in autumn (15.9.2020). The technical feasibility and shungite testing continued during the winter season. Water quality before the filter (influent to the CW), outflow from filter, and outflow from the catchment basin were sampled in May-July 2021.

Tullitie and Ratapuisto outflows from pipelines were sampled in 2019 for general water quality information. The Tullitie sampling site leads run-off water flow to Highway 6 ramp CW, and water quality in these two sites were found very similar. Ratapuisto site has run-off from city center, and it was found to be the most contaminated. However, for testing EM technology the site was not optimal because the recipient basin was missing.

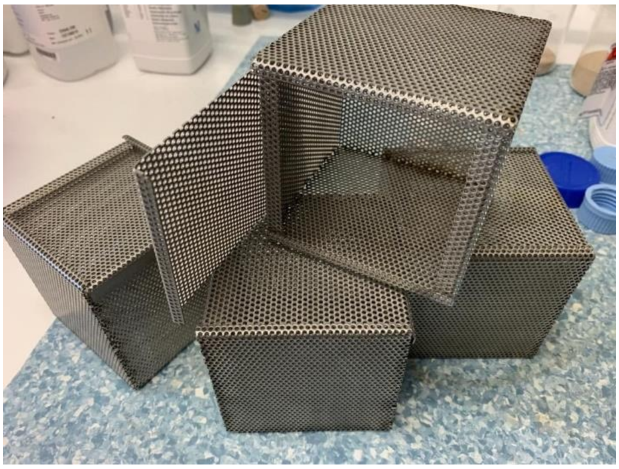
Table 16, Table 17, and Figure 62 and Figure 63 show the median, mean and maximum concentrations measured from these 4 sites.

Sampling

Sampling and analysis of Lappeenranta sites were carried out by LUT university. Reference measurements and sampling for nutrients, and oil (furans) were made by Saimaan vesi- ja ypäristötutkimus Oy, which is an accredited body. Appropriate sampling guides and standards were applied in primary and secondary sampling. Sampling equipment was made of plastic, and they were washed with the incoming water before taking the real samples. Sampling at sites was performed from downstream to upstream to avoid causing disturbances in the sampling targets. Composite samples taken with a sampling basket were mixed before taking the secondary samples. The whole flow profile was taken into sample from pipe flows. In sampling the ponds, the solid material from bottom and surface were avoided. The ponds were shallow (30-80 cm) and it set challenges for the sampling. Samples were transported to laboratory for further handling immediately or within 1 h. For visual observations photos of sites were taken, and in sampling diary the weather conditions, amount of precipitation (during the previous week), other remarks on the site and weather were reported. Flow rate at sampling time, pH, conductivity, temperature and in some cases nitrogen compounds with ion selective electrode were measured immediately. The samples were stored according to the standards for further analysis. Microplastic sampling differed. The shungite was held in metal cages to prevent plastic contamination from the sampling equipment. Detailed sampling reports are not included in the final report due to their length.

A) Sammonlahti Basin 1 and 2 water samples were taken as composite samples of 5-10 subsamples. The depth of water was typically 50 +/- 20 cm.

B) Samples from pipe outflow were collected with instruments that allowed the whole profile across the cross flow to enter the sample.



C) Microplastic analyses: metal cages were filled with shungite and placed in filters for a month. Mesh 2 mm.

D) Shungite samples from filters were collected for adsorption studies.

Figure 60 Sampling was carried out according to sampling standards and guides.

Analysis and analytes

The majority of samples were taken and analyzed by LUT laboratories. The aim of monitoring was to provide information supplementary to the field tests. Several sampling campaigns were carried out (*Table 14*).

2019-21 the sampling campaign had different targets. The variables determined in all sampling campaigns were nitrate, phosphor, pH, and 25 metals. For nitrogen cycle sample sets were checked for total nitrogen, nitrate (nitrite), and ammonium. The nitrogen analytics were made immediately from non-filtered samples with an ion-specific electrode for nitrate and ammonium. In addition, TOC (Total Organic Carbon) analyzer was applied to determine total solved nitrogen. The concentrations depend on solid material content. The CWs (Constructed Wetlands) were shallow, and samples taken from ponds contained more fine particles and even algae than those taken from flows. Therefore, the total nitrogen with digestion of solid material was not carried out. Samples for TOC analyzer, ion chromatograph (IC) and ICP-MS instrument had to be filtered through 45 µm laboratory filter (45µm syringe filter). IC with anion colon were applied to define chloride, sulfate, fluoride, nitrate, and nitrite concentrations. IC with cation colon were applied to ammonium. ICP-MS were applied to analyze 25-45 chemical elements (metals) from the samples. Many concentrations were under analytical detection limit or uncertainty were too high to be reported. In literature, it is often suggested that the bioavailable fraction of smallest particles is the most contaminated one. It can be expected that the concentrations of many toxic urban associated heavy metals, such as Cu, Zn, Cd, and Pb, is high namely in the particle fraction are the highest in the <45 µm bioavailable fraction (Baum, Kuch, & Dittmer, 2021) (Burant, Selbig, Furlong, & Higgins, 2018). In the present study, the purification efficiency of main nutrients and heavy metals as total concentrations and as the dissolved and smallest size particle fraction (< 45 µm) were monitored at the Lappeenranta field tests.

Conductivity and pH were measured right after sampling. Oil compounds were determined with an external laboratory (also sampling for the oil index were made by certified personnel of this external body, Saimaan vesi- ja ympäristötutkimus Oy). Unfortunately, no oil compounds, phenols or COD demanding components were found from CW samples. TOC (inorganic and organic), suspended solids (SS), COD and phenol compounds were made from few samples. The aim of sampling campaigns was to provide information relevant to filter field tests. Table 15 shows list of analytes. Appendix 1 contains the instrument and analytical procedure specifications.

Table 15 Analytes applied in describing runoff water quality in CWs (Appendix 1 contains information on all analytical procedures applied in SHEM-WP project)

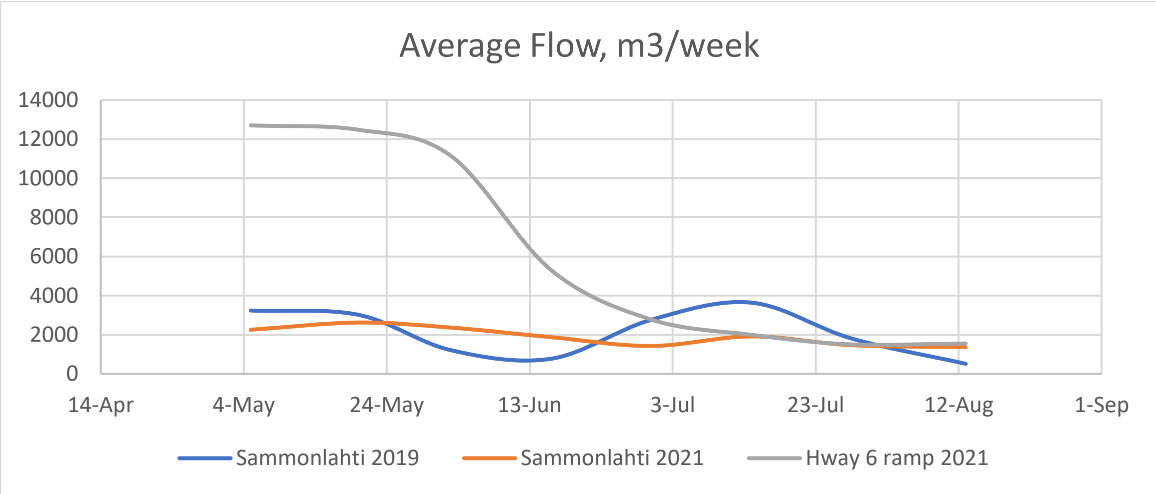
Analytes
IC: Cl^-, NO_3^-, SO_4^{2-} (cation: NH_4^+). Phosphates and fluorides were under detection limit
Ion selective probe: NH_4^+ (NO_3^-)
TOC: Total nitrogen, TN, TOC
ICP-MS: Metals: Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Te, Au, Hg, Pb, Bi, U, P
pH, conductivity
External laboratory: Oil compounds
Suspended solids
Raman: microplastics

Average concentrations and variance

Average or median concentrations are presented in the following tables and figures. During the sampling campaigns there were found high sudden values after the storms or in melting water. Due long sampling intervals, it cannot be evaluated real effect of the values in the average. The average values represent different flow volumes, and it causes bias on results, if they are applied in defining the quality. Median values together with the maximums can be expected to describe the quality in a more realistic manner.

To compute the real mean values the concentrations should be weighted with flow. Flow rates on sampling day were measured. Examples of variation in flows are presented in Figure 61. They are applied in environmental assesment and feasibility study in latter chapters (to compute cumulative mass of zink removed).

A practical example on Zink concentration: Median and mean values were often close to each another, but Zink is one of the elements, which increase during the heavy rain and snow melting season. If one takes the average value directly from the results measured from "basin 1" before the filter: c(Zn) = 9.2 mg/L. When the current flow is considered and values weighted with it: c(Zn) = 11.8 mg/L. Neither of these values represent the typical concentration in the influent. Median value (50 % fractile) is 6.4 mg/L. The correct conclusion would be that typical concentration in the influent if 6.4 mg/L, but it can occasionally increase to even 30 mg/L in season of high flow rate. Table 16 and Table 17 shows median and maximum values measured during the sampling campaigns 2019-21. Figure 62 and Figure 63 visualize the results.



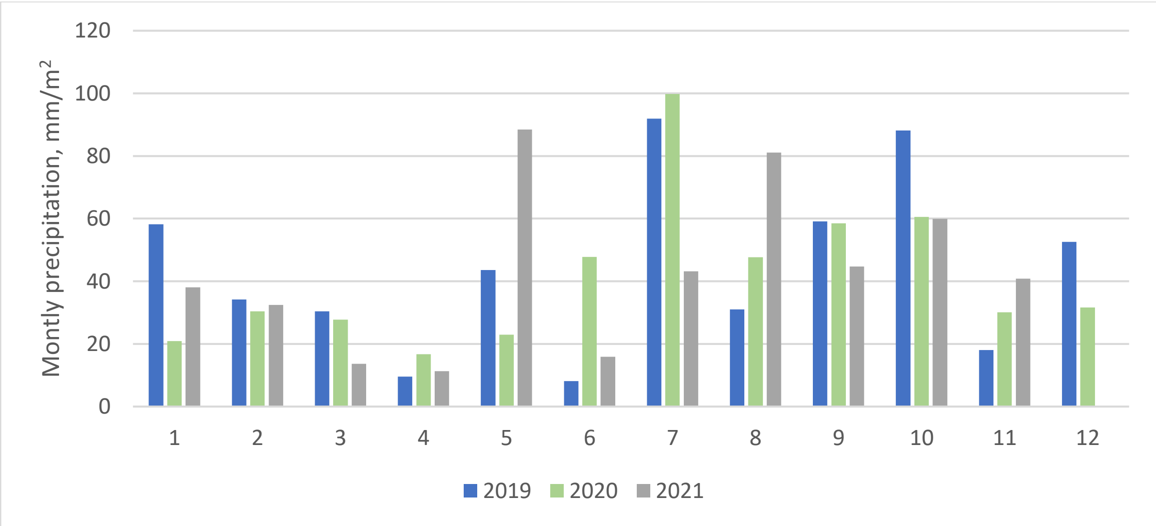


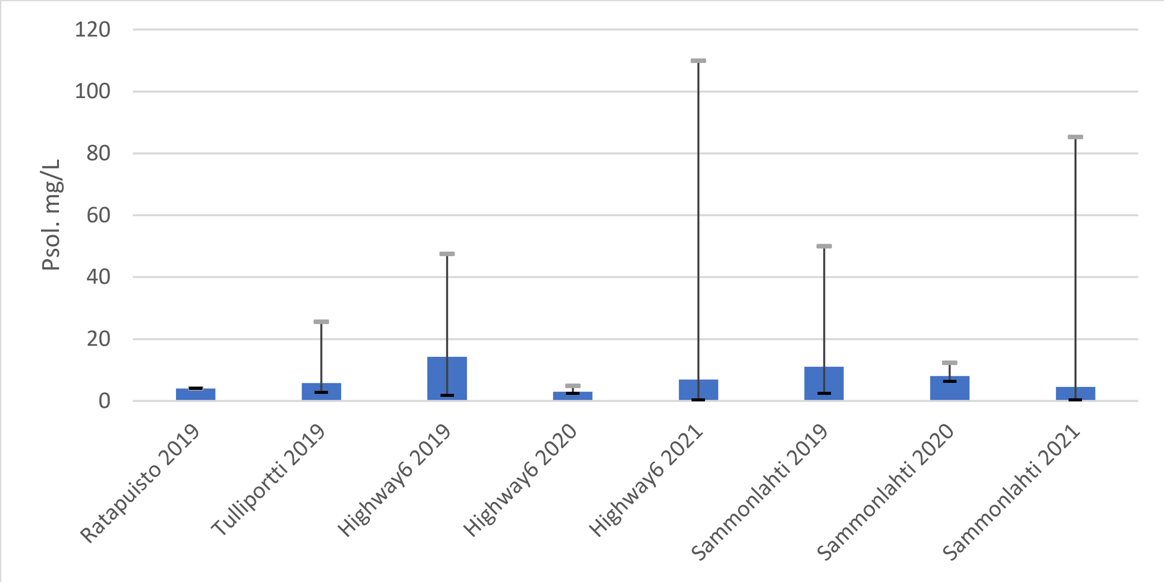
Figure 61 Flow rates were monitored at two field test site. The flow depends on precipitation and amount of snow. Flow volume of Sammonlahti: effect of snow is still seen in May. in 2019 the flow clearly reflects the amount of rain. In mid-august 2019 there were no out flow from basin. in 2020 there were structural renovation in basin 1 and as the result flow seem to be less effected by the precipitation since there is less variation. Highway 6 ramp collects runoff and shallow in-filtration water from larger area. It seems that the effect of smelting snow together with high precipitation is seen in CW still in the first week(s) of June. That corresponds also to the time frame, when the lake Saimaa surface level is affected by the snow in-filtration. The flow in May (13,000 m3/week, 80,000 L/h) is almost ten times higher than flow in August.

Table 16 median nutrient content and maximum values

	Ratapuisto, 2019		Tulliportti. 2019		Highway 6: 2019		Highway 6: 2020		Highway 6: 2021		Sammonlahti: 2019		Sammonlahti: 2020		Sammonlahti: 2021	
Conc	median	max	median	max	median	max	median	max	median	max	median	max	median	max	median	max
P_{sol}, µg/L	4.1	4.1	5.8	26	9.1	47	3.0	4.9	6.9	109	11	303	8.1	12.3	7.0	85
TN, mg/L	11.2	11.2	3.1	7.9	2.7	4.1	3.3	5.9	2.5	4.7	3,7	16,7	4.1	19.7	3'.5	18.4
N_{sol}, mg/L	8.7	8.7	1.6	4.3	1.4	2.1	1.7	3.0	1.3	2.5	1.8	3.8	2.0	3.7	1.9	2.7
NO3-N_{sol}, mg/L	8.5	8.5	1.6	3.5	1.4	2.1	0.7	1.0	0.9	1.1	1.7	3.7	2.1	2.4	1.8	2.3
Cl, mg/L	36	36	25	29	17.5	26.2	17.1	24.7	16.3	21.4	7.2	9.0	6.8	8.3	7.3	7.6
SO4, mg/L	126	126	63	116	50	84	36	42	37	46	24	39	24	25	23	28

Table 17 median concentrations of metals and the maximum values (ICP-MS). Limit of Determination, LOD = 0.05 µg/L.

	Ratapuisto	2019	Tulliportti	2019	Highway 6	2019	Highway 6	2020	Highway 6	2021	Sammonlahti	2019	Sammonlahti	2020	Sammonlahti	2021
Conc. µg/L	median	max	median	max	median	max	median	max	median	max	median	max	median	max	median	max
23 Na	26677	26677	14388	23453	14217	26719	11591	14245	11816	15920	6738	15395	4480	7287	6500	13546
24 Mg	14569	14569	9447	15850	8871	14556	7476	8306	6839	8320	5535	11034	3387	5237	2900	8109
27 Al	1.32	1.32	0.97	1.64	1.14	2.79	1.04	1.69	2.14	12.03	3.77	13.73	16.44	21.45	5.43	68.03
39 K	14845	14845	4934	10588	4841	9117	4334	4983	3795	6625	2130	4394	1579	2114	1166	4608
44 Ca	98096	98096	45458	75558	48938	60330	42137	46539	34808	52737	24362	39401	17571	25033	13460	41875
51 V	0.10	0.10	<LOD	<LOD	<LOD	<LOD	0.21	0.23	0.09	0.18	0.12	1.22	0.56	0.66	0.24	0.47
52 Cr	0.11	0.11	<LOD	<LOD	<LOD	0.09	0.13	0.19	<LOD	0.23	<LOD	0.27	0.29	0.30	<LOD	0.27
55 Mn	49.5	49.5	61.1	75.7	23.8	47.4	42.7	52.6	53.7	131.4	7.0	357.7	5.2	7.2	12.7	38.4
56 Fe	7.59	7.59	5.17	11.54	5.73	14.65	2.51	9.51	5.04	1291	7.53	85.16	36.69	55.06	6.01	262.29
59 Co	1.77	1.77	0.29	0.60	0.19	0.24	0.20	0.26	0.18	0.47	0.12	0.98	0.07	0.08	0.24	3.71
60 Ni	5.38	5.38	0.94	2.05	0.85	1.24	0.79	0.83	0.93	3.03	0.52	3.20	0.48	0.63	0.61	26.11
63 Cu	3.58	3.58	8.24	35.52	9.83	45.75	1.25	2.11	6.91	22.05	1.66	78.25	2.51	7.99	4.28	31.49
66 Zn	6.41	6.41	2.02	3.87	2.92	8.72	3.31	7.70	3.91	56.34	3.09	120.63	36.50	47.50	1.49	37.09
75 As	0.58	0.58	0.19	0.49	0.20	0.31	0.18	0.23	0.15	0.26	0.14	0.47	0.14	0.16	0.09	0.32
78 Se	0.25	0.25	0.15	0.37	0.12	0.20	0.10	0.14	0.12	0.21	0.15	0.35	0.11	0.17	0.13	0.24
98 Mo	2.11	2.11	0.68	1.63	0.91	1.71	0.97	1.09	0.94	1.84	0.66	1.39	0.48	0.60	0.67	3.63
107 Ag	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
114 Cd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.21	0.07	0.09	<LOD	0.06
123 Sb	0.19	0.19	0.06	0.51	0.07	0.12	0.11	0.19	0.06	0.18	0.07	0.32	0.07	0.09	<LOD	0.08
125 Te	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.20	<LOD	<LOD	<LOD	<LOD	<LOD	0.20
197 Au	<LOD	0.47	<LOD	1.04	<LOD	0.69	<LOD	1.31	<LOD	1.43	<LOD	1.83	<LOD	0.90	<LOD	1.99
202 Hg	<LOD	0.08	<LOD	0.11	<LOD	0.08	<LOD	0.12	<LOD	0.39	<LOD	0.42	<LOD	0.18	<LOD	0.12
208 Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.25	<LOD	0.17	<LOD	<LOD	<LOD	0.27
209 Bi	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.11	<LOD	<LOD	<LOD	0.05
238 U	0.86	0.86	0.70	1.48	0.94	1.25	0.72	0.84	0.69	1.17	0.47	1.03	0.25	0.32	0.45	0.73



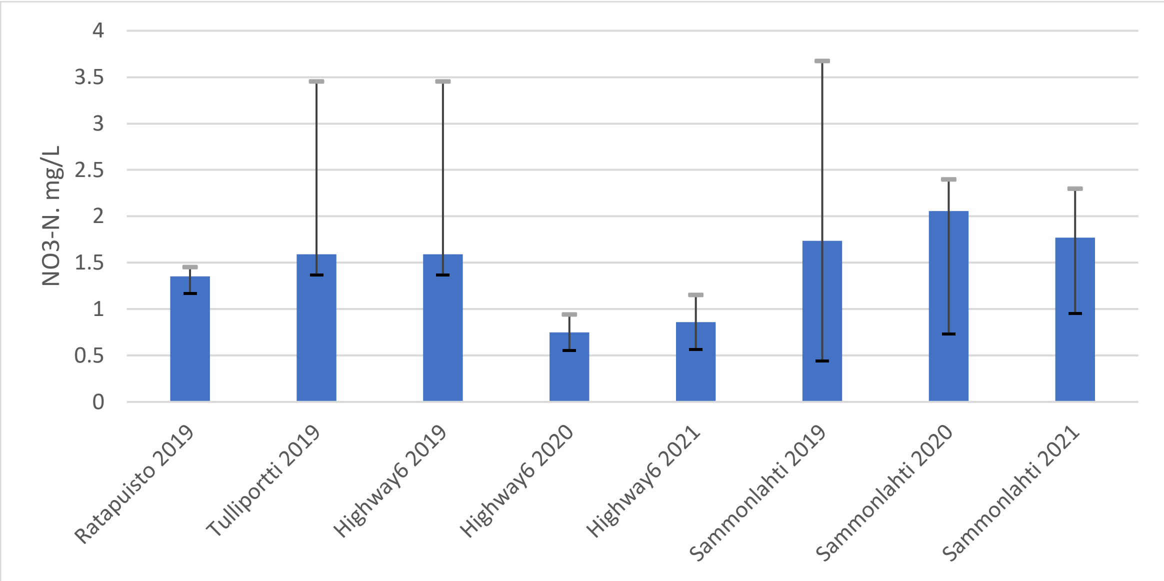
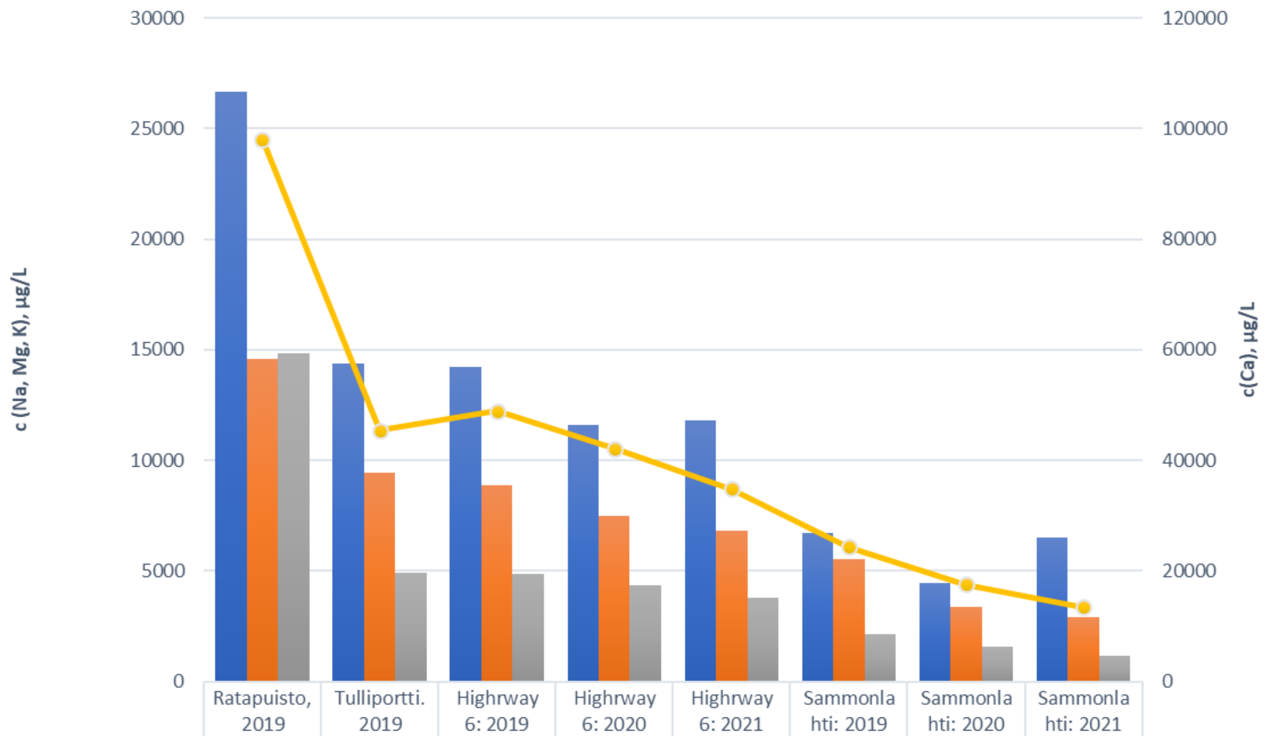
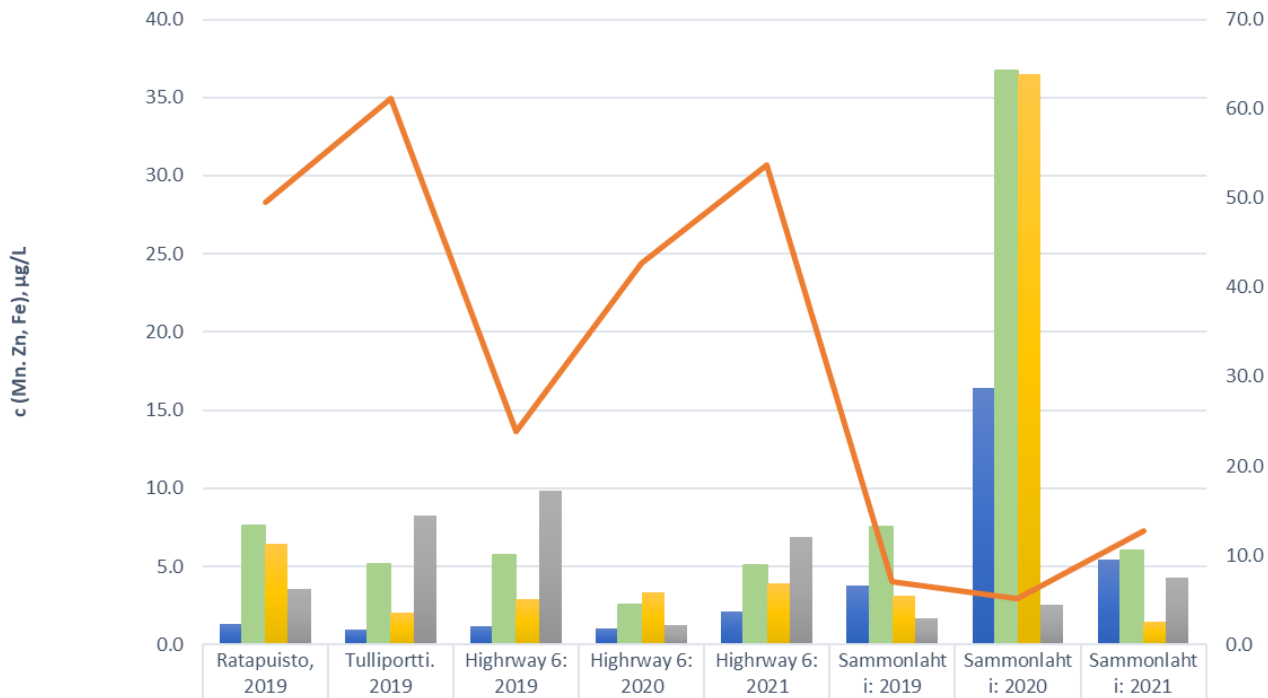


Figure 62 Nutrients: Median concentrations with minimum to maximum variation range, A) P_{sol}, and B) NO3-N. Sammonlahti 2019 and 2021 and Highway 6 2021 represent variation over 3 months summer- period. Ratapuisto and tulliportti were sampled in 2019 June-July. Sammonlahti 2020 captures only variation in August. Number of samples = 7 … 61. Phosphorous values from the exceptional emission event detected on May 20, 2019, were removed from the plot due to the visualization (The most extreme high value in Sammonlahti basin 1 were >300 µg/L).



	Ratapuisto, 2019	Tulliportti. 2019	Highrway 6: 2019	Highrway 6: 2020	Highrway 6: 2021	Sammonlahti: 2019	Sammonlahti: 2020	Sammonlahti: 2021
23 Na , µg/L	26677	14388	14217	11591	11816	6738	4480	6500
24 Mg , µg/L	14569	9447.0	8871.2	7476.4	6838.8	5535.0	3387.3	2899.6
39 K , µg/L	14845	4934	4841	4334	3795	2130	1579	1166
44 Ca , µg/L	98096	45458	48938	42137	34808	24362	17571	13460



	Ratapuisto, 2019	Tulliportti. 2019	Highrway 6: 2019	Highrway 6: 2020	Highrway 6: 2021	Sammonlahti: 2019	Sammonlahti: 2020	Sammonlahti: 2021
27 Al , µg/L	1.3	1.0	1.1	1.0	2.1	3.8	16.4	5.4
56 Fe , µg/L	7.6	5.2	5.7	2.5	5.0	7.5	36.7	6.0
66 Zn , µg/L	6.4	2.0	2.9	3.3	3.9	3.1	36.5	1.5
63 Cu , µg/L	3.6	8.2	9.8	1.2	6.9	1.7	2.5	4.3
55 Mn , µg/L	49.5	61.1	23.8	42.7	53.7	7.0	5.2	12.7

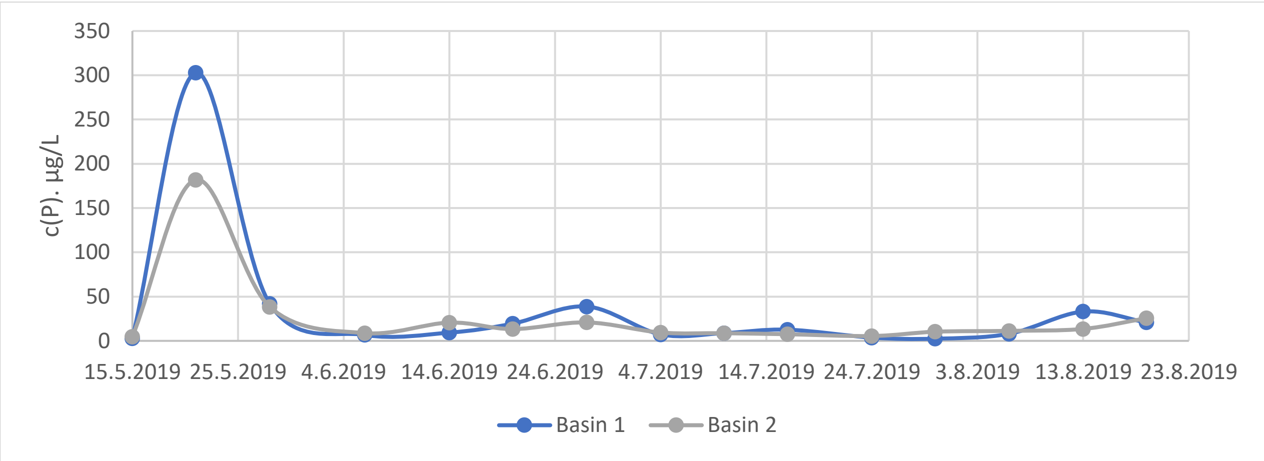
Figure 63 Median metal concentrations at potential test sites. a) Major elements, B) Minot elements, C) Selected Trace elements.

Water Quality and fluctuation at Sammonlahti

Sammonlahti constructed wetland has been monitored in a previous EM study in 2016. The results are included here as background or reference information about the site. At the beginning of the SHEM-WP, in 2019, Sammonlahti wetland were analyzed weekly to define variation of metal and nutrient concentrations. A small flow from the outflow from basin 1 was led via a test filter in (July-Aug). In 2020 and 2021 the monitoring continued after a new filter was implemented (filter 22.7.2020 – 27.8.2021).

Figure 64, Figure 65, Figure 66, and Figure 67 shows examples of variation in concentrations and quality over the 2019 sampling campaign. Findings are discussed in the figure captions. More time series are visualized in chapter 6 with discussions on the effect of filters on water quality.

A)



B)

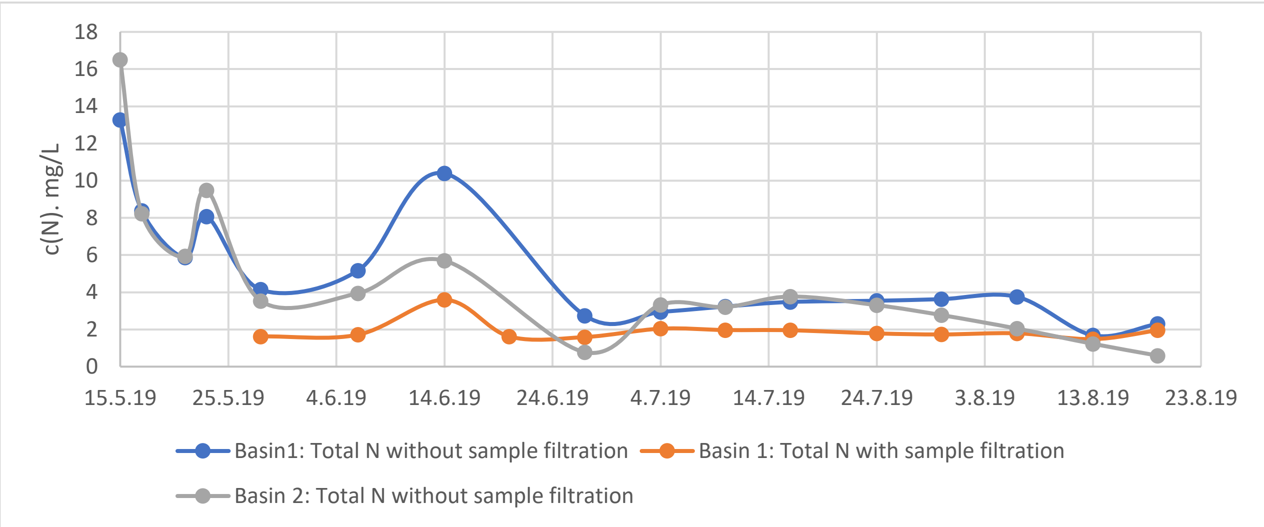
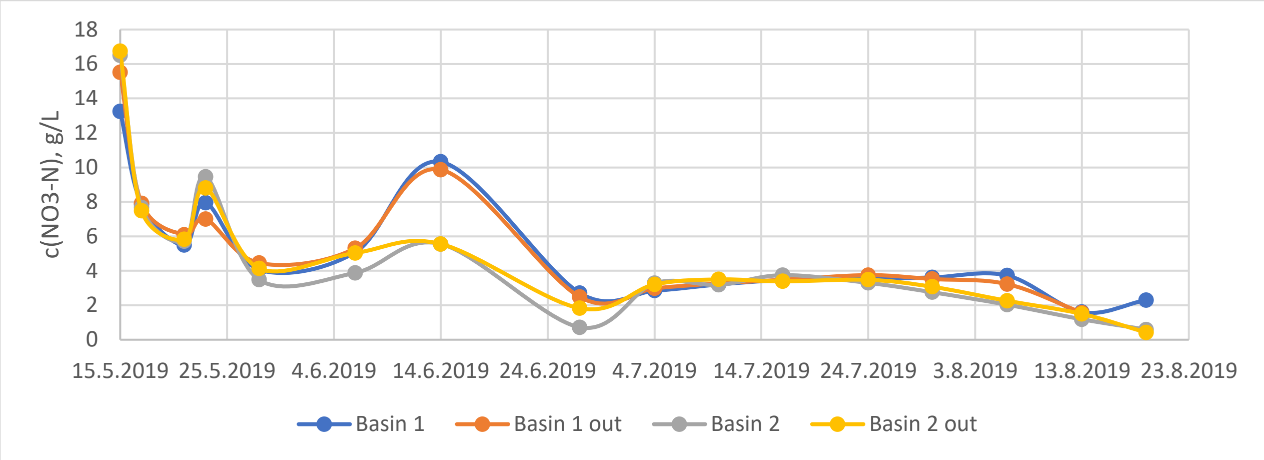
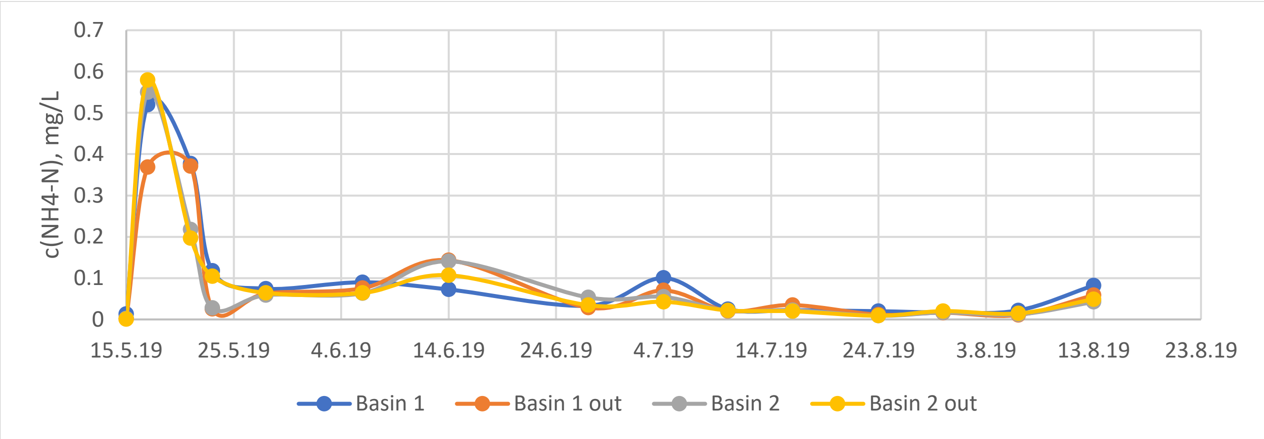


Figure 64 Sammonlahti CW Basins 1 ND 2: Phosphor and nitrogen concentrations measures with ICP-MS (TP), TOC Analyzer (TN from syringe filtered samples) and ion specific sensor (TN without sample filtration). The events seen in data: smelting snow arriving in May, heavy rains and flooding in mid-June, rain diluting runoff in July, and the inflow vanishing in mid-August. The focus of study has been in fraction available for plants. filtering small particles out with syringe filters also remove particles containing nutrients.

A) Nitrogen in nitrate form is 80-95 % of TN



B) Nitrogen in ammonium



C) Nitrogen in filtered samples

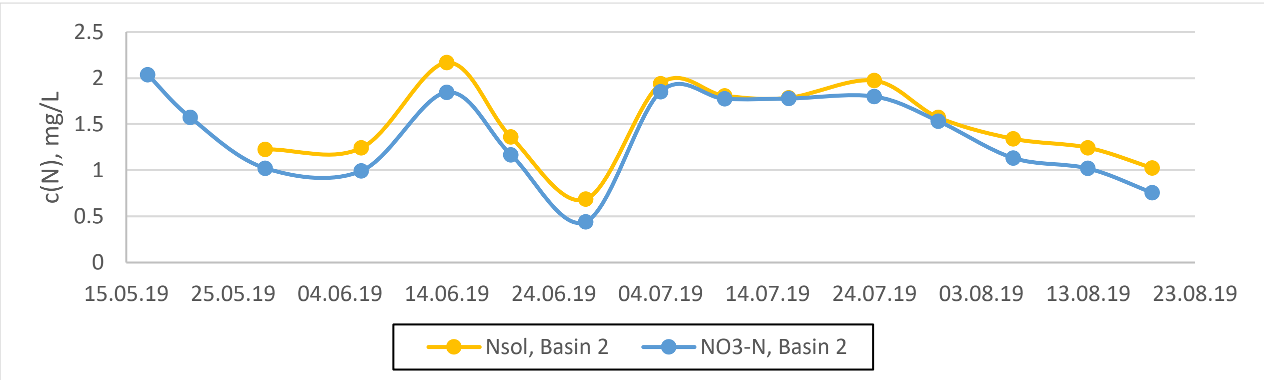


Figure 65 Nitrogen in 2019 at Sammonlahti CW. In 23.5. there are high values detected in several analytes. This one could not be explained by a flood. on June 14th, the reason is flooding in city after exceptionally heavy storm. Ammonium fraction increases also at the end of campaign when water flow ends but nitrogen removal still continues.

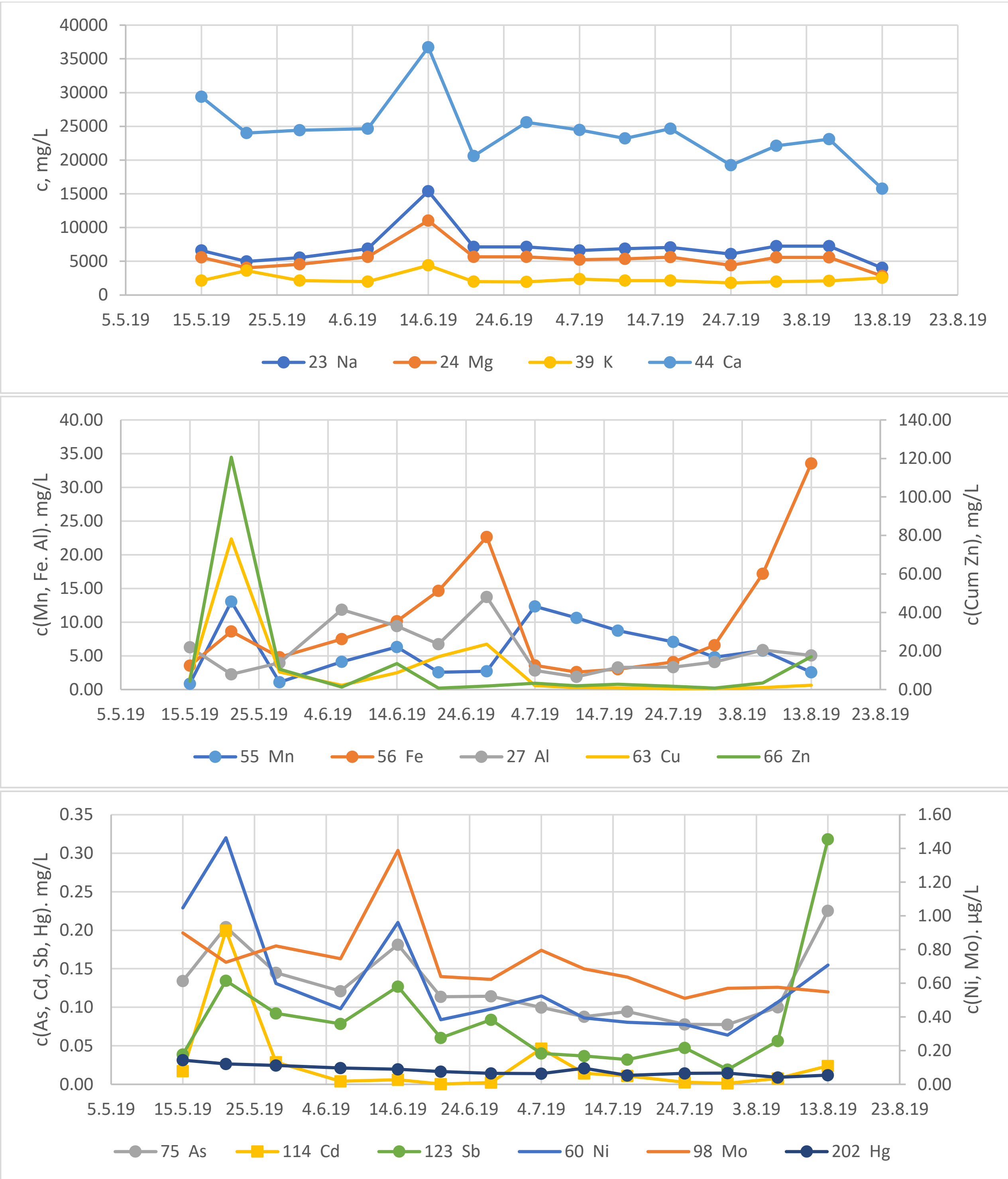
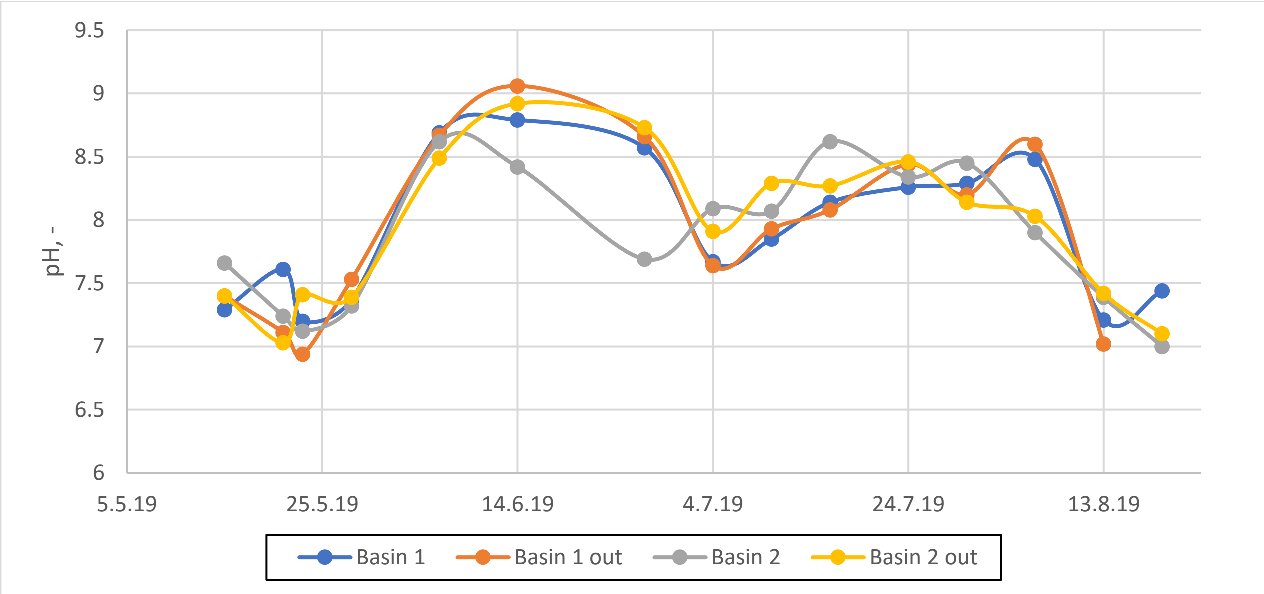


Figure 66 SAMMONLAHTI CW: Basin 1 (composite sample): variation of metal concentration in summer 2019. The events seen in data: smelting snow arriving in May, heavy rains and flooding in mid-June, rain diluting runoff in July, and the inflow vanishing in mid-August.



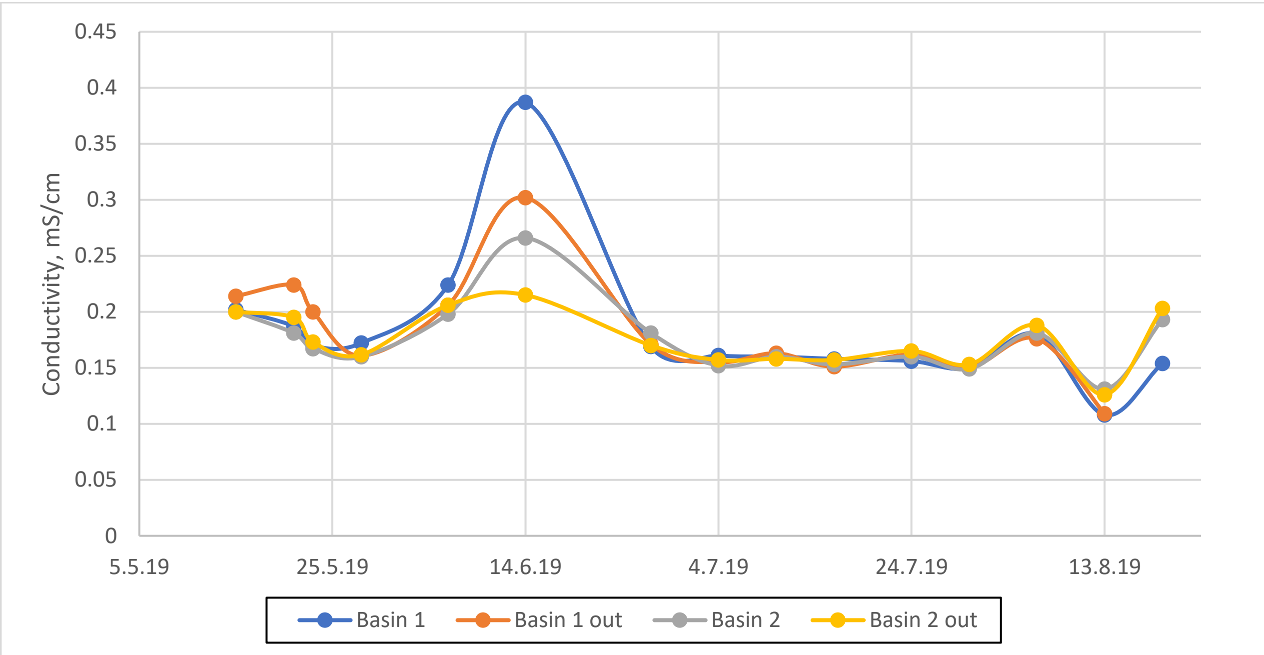


Figure 67 Example of pH and conductivity variation in Sammonlahti CW. Conductivity reacts to the discharge in mid-June and correlates with high metal concentrations detected. Good quality natural inland water conductivity (e.g., in the recipient Lake Saimaa) is typically 0.03-0.15 mS/cm. The pH values are typical for biologically active water bodies. In May the water is still relatively neutral, but the biological activity, namely in June, increases the pH. In August, the inflow ends, and biological activity decreases. The discharge detected in June has affected also to the pH.

Water Quality and fluctuation at Highway 6 ramp

Figure 68 and Figure 69 presents examples of variation in concentrations in 2020 and 2021 sampling campaigns. Findings are discussed in figure captions,

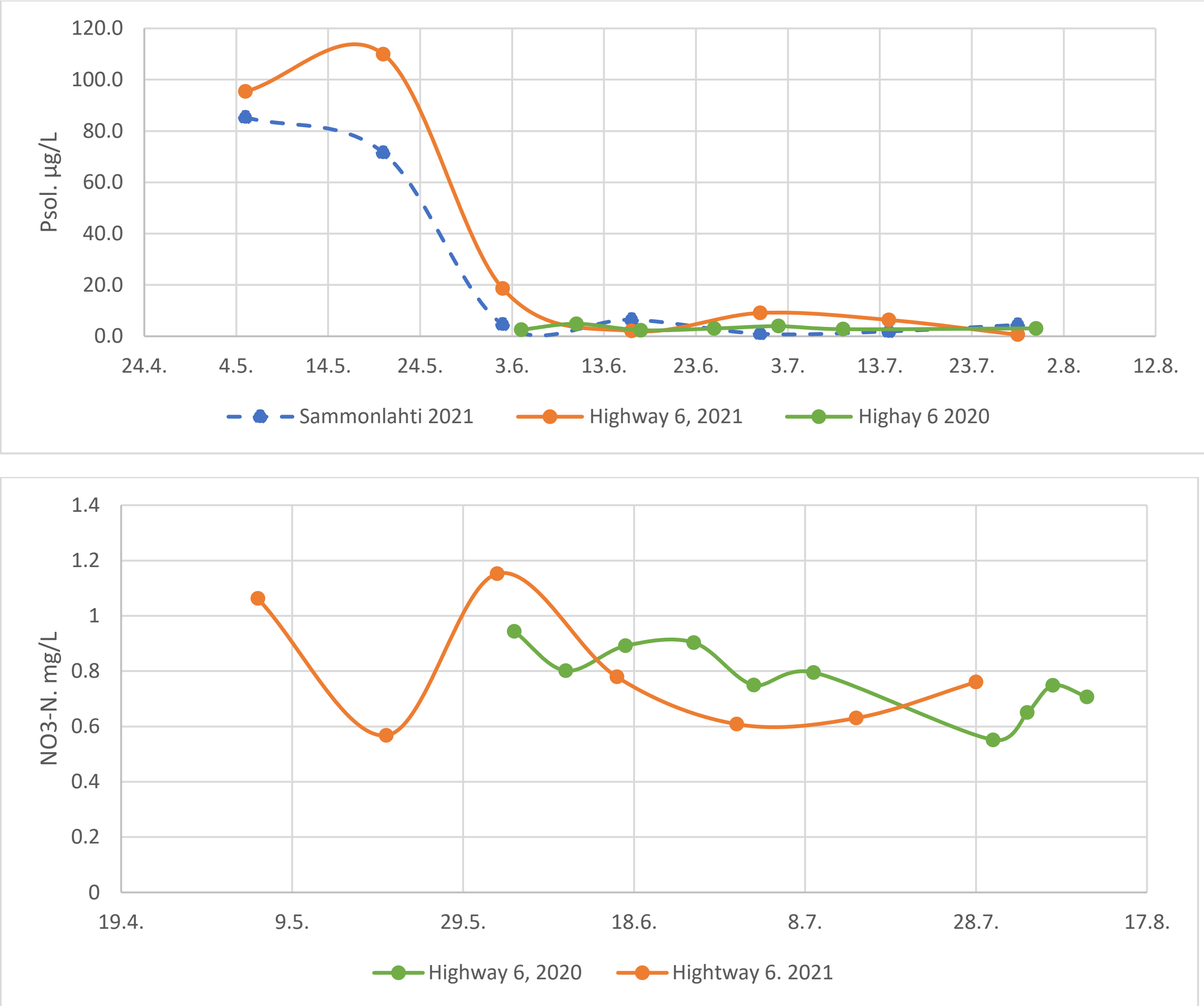
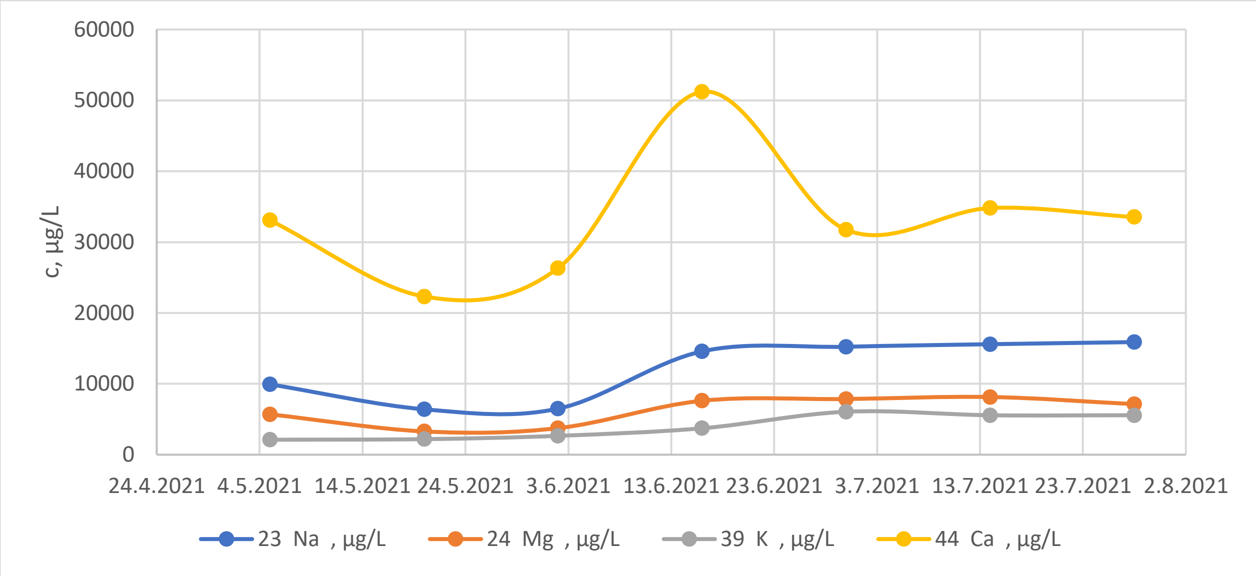


Figure 68 Phosphorus and nitrogen (bonded into nitrate) at Highway 6 ramp CW: namely phosphor content in runoff water correlates with the flow. In early May the nutrient removal has not started, and nutrient content is high. it decreases towards the end of summer season.



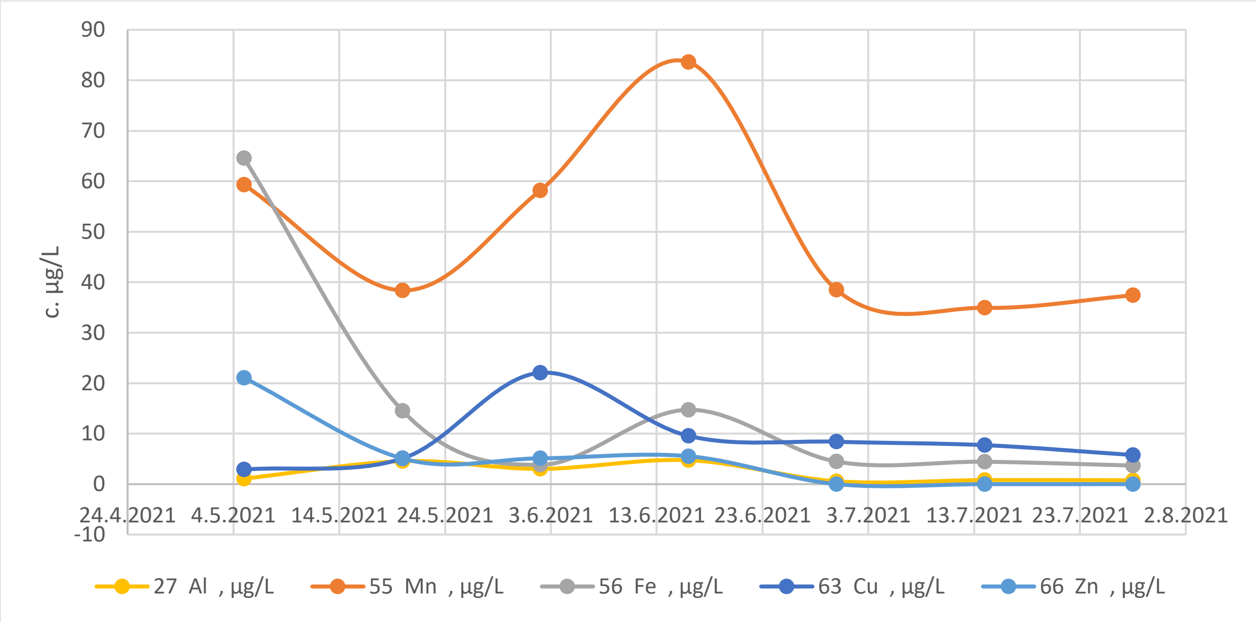


Figure 69 Influent to Highway 6 ramp: concentrations of main and minor metals in May-July, 2021. Several metal concentrations are higher in May, when also the flow level is also still high. in beginning of May the metal concentrations seem low, but the flow rate is high, and dilution of influent is significant. The amount as mass is higher in May compared to July. Heavy metals often related to urban emissions, such as Fe, and Zn (Mn) have even higher concentrations in snow melting residues than in the latter period. In mid-June there has been a rainy week and Mn, Fe and Ca concentrations have increased.

5.2 Water quality monitoring on test sites in St. Petersburg.

SHEM project working programme included water quality monitoring at the sites selected for field test of the filters. Sampling campaigns were organized for one year period at all testing sites. Altogether 66 water samples were taken at eleven observation points at all field test sites. An overview of the monitoring campaign at all sites is given in Table 18.

Table 18 Overview of the monitoring campaign.

Test site	Sampling points	Sampling dates
Dudergofskoe lake	T1 – 5 meters from water spillway 1	07/10/2021; 10/12/2021; 25/03/2021; 11/08/2021; 08/09/2021; 30/09/2021
	T2 – 5 meters from dam between water spillways	07/10/2021; 10/12/2021; 25/03/2021; 11/08/2021; 08/09/2021; 30/09/2021
	T3 – 5 meters from water spillway 2.	07/10/2021; 10/12/2021; 25/03/2021; 11/08/2021; 08/09/2021; 30/09/2021
Dolgoe lake	T4 - 5 meters from water spillway 2	07/10/2021; 10/12/2021; 25/03/2021; 11/08/2021; 08/09/2021; 30/09/2021
	T5 - 5 meters from dam between water spillway	07/10/2021; 10/12/2021; 25/03/2021; 11/08/2021; 08/09/2021; 30/09/2021
	T6 - 5 meters from water spillway 1	07/10/2021; 10/12/2021; 25/03/2021; 11/08/2021; 08/09/2021; 30/09/2021
Pond in Pionerski park	T1 small part	07/10/2020; 02/04/2021; 09/04/2021; 27/08/2021; 16/09/2021; 07/10/2021
	T2 large part	07/10/2020; 02/04/2021; 09/04/2021; 27/08/2021; 16/09/2021; 07/10/2021
Storm water retention pond	T1 – storm water inlet	07/10/2020; 02/04/2021; 09/04/2021; 27/08/2021; 16/09/2021; 07/10/2021
	T2 – storm water retention pond	07/10/2020; 02/04/2021; 09/04/2021; 27/08/2021; 16/09/2021; 07/10/2021
	T3 – outlet from the pond	07/10/2020; 02/04/2021; 09/04/2021; 27/08/2021; 16/09/2021; 07/10/2021

Water quality in the Dodrgoffskoe-Dolgoe lake system

Monitoring of water quality in the lake system consisting of Dodrgoffskoe and Dolgoe lakes was arranged at six sampling points Figure 70. These points were in Dudergoffskoe lake – stations T1, T2 and T3. Two of the stations were placed in front of water spillways from Dudergoffskoe lake to lake Dolgoe at a distance of about 5 meters from the dam. One monitoring station was between these two spillways at the same distance from the dam. Three other monitoring stations – T4, T5 and T6 - were located in lake Dolgoe following the same scheme. Two stations were in front of the water spillways, and one was in between. All were in about 5 meters from the dam. Due to high water flow rate through the two water spillways in the dam between the lakes (Figure 71), in this chapter both lakes are considered as one water system.

Figure 70 Monitoring stations in the lake system Dudergofskoe-Dolgoe.

Figure 71 Water spillways in the dam between Dudergofskoe and Dolgoe lakes (spillway 1: points T1 and T6; spillway 2: point T3 and T4).

Six samples were taken at each station during the period from October 2020 to September 2021 with the intention to reflect seasonal variations of water quality in the lake system. Sampling was not done in winter period when the lake was under ice cover. Sampling was carried out simultaneously at all points. Sampling dates are given in the Table 18.

Water quality monitoring involved several parameters: pH, BOD5, suspended matter, nutrients, organic contaminants, and heavy metals. Most of the parameters were identified for non-filtered samples. For heavy metals filtered samples were also analyzed to assess the proportion of dissolved metals and in the form of solid particles. Methodology of sample preparation is given in Appendix 1. Measured parameters are given in Chapter 6.3. The table reflects average, median, max and min measured values. Empty sells indicate that concentration was below the detection limit. Detection limits for these parameters are given in Table 19.

Table 19 Detection limits (LOD) for concentrations reported as below LOD.

Parameter	Unit	Limit of detection
Suspended solids	mg/l	<2,0
COD	mg/l	<10
Phenol	µg/l	<0,5
Total iron*	mg/l	<0,01
Total iron	mg/l	<0,01
Copper*	mg/l	<0,001
Copper	µg/l	<0,001
Zink*	mg/l	<0,005
Zinc	mg/l	<0,005
Led*	mg/l	<0,001
Led	mg/l	<0,001
Mercury	µg/l	<0,01

Potential hydrogen and biological oxygen demand.

In general water quality in the lake system is characterized by relatively low contamination. However, concentrations of some of the compounds reflect significant seasonal variation. Potential hydrogen is one of the relatively stable parameters throughout the whole year of observations. Median value was slightly about 7 variating between 7.9 in winter season and 8.5 in summer Figure 72.

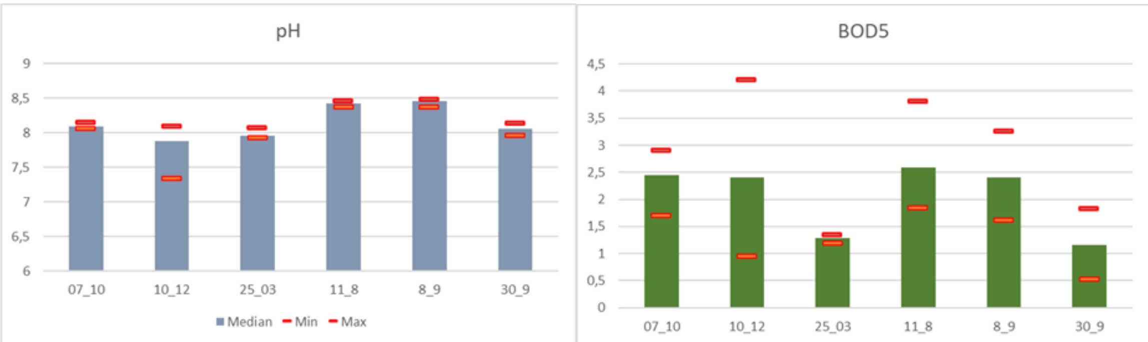


Figure 72 *pH and BOD5 in the water of Dudergofskoe-Dolgoe lake system.*

Mean values for biological oxygen demand also vary in a relatively narrow interval from 1.1 to 2.5 mgO_2/l with lowest values in March and late September and stable level of about 2.5 mgO2/l in all other months. However, the parameter demonstrates much higher dispersion between individual samples, varying in range of almost one order of magnitude from 0,5 to 4 mgO_2/l. Both parameters in general fall within the interval identified as quality standards for water bodies used for the water bodies used for potable water (75/440/EEC). Just a few individual samples demonstrate exceedance of the BOD5 quality standard (3 mg/l) set for A1 class.

Suspended solids

Concentration of suspended solids in water of the lake system was rather stable during the year of observation Figure 73. Medians for almost all months are close to 3 mg/l except for one observation in the beginning of august, when median concentration of particles in water increased twice and the highest value reached 34 mg/l. Thus, in general, except for this single measurement, water quality meet standards (25 mg/l) set by the EU DIRECTIVE 75/440/EEC.

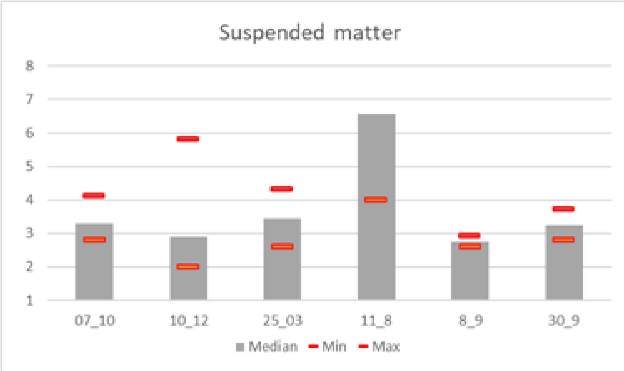


Figure 73 Concentrations of suspended solids in the water of Dudergofskoe-Dolgoe lake system.

Nutrients.

Nutrients play a crucial role in functioning of aquatic ecosystems. Concentrations of total nitrogen (TN) and total phosphorus (TP) depend not only on their inputs from external sources but also from internal fluxes affected by vegetation cycles, redox conditions, and other parameters. Thus, thresholds for identification of good environmental status broadly vary for different types of water bodies. Thus, for the European lakes, threshold concentrations of TN for good/moderate environmental status vary from 0.25 to 4 mg/l and TP from 0.005 to 0.5 mg/l. In general, the lake system Dudergofskoe-Dolgoe is characterized by elevated concentrations of total nitrogen and moderate concentration of TP. Both nutrients demonstrate significant seasonal deviations. Concentration of TN grew in winter period achieving the highest values of almost 7 mg/l and dropped down in summer period of active vegetation up to 3.5 mg/l. Median TP concentrations remained below 0.05 mg/l throughout the year, except for December when an abrupt growth of TP concentrations was observed, and median value exceeded 0,3 mg/l with individual concentrations exceeding 1 mg/l. In general, median TP concentrations are almost three times higher in august and the beginning of September that in October and March.

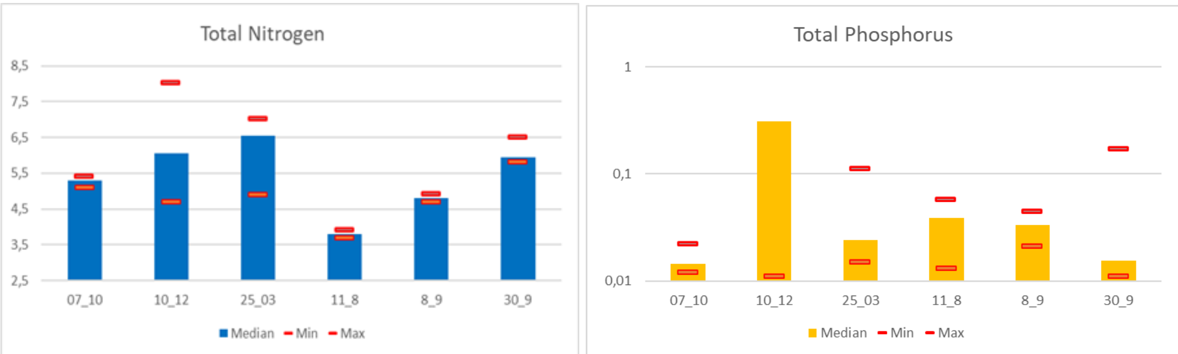


Figure 74 Concentrations of total nitrogen and total phosphorus in the water of Dudergofskoe-Dolgoe lake system.

Organic contaminants.

Two organic contaminants were monitored in the lake system: oil products and phenols. Median, maximum, and minimum concentration observed during the monitoring period are given in Figure 75. Concentrations of these organic pollutants were in general at a relatively low level throughout the whole observation period and do not demonstrate any systematic seasonal variations.

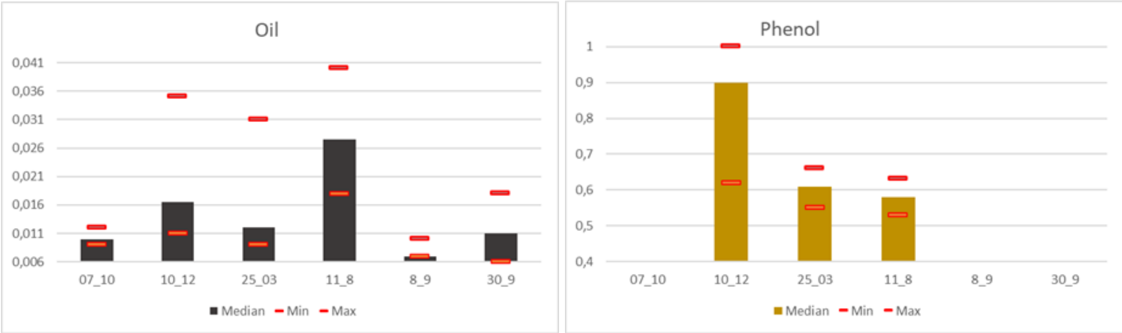


Figure 75 Concentrations of oil products (mg/l) and phenol (μg/l) in the water of Dudergofskoe-Dolgoe lake system.

Slightly elevated concentrations of oil products occurred in December and in August but there were no systematic seasonal variations observed. Medians for concentrations of oil products were mainly at the level of 0.001 mg/l with maximum values in individual samples as high as 0.04 mg/l. These concentrations do not exceed thresholds established for water bodies used for drinking and recreational purposes by both the EU – 0,05 mg/l (75/440/EEC) and Russian – 0,3 mg/l (ГН 2.1.5.689-98). Phenol was detected in limited number of samples demonstrating concentrations below 1 μg/l. Most of the measurements did not identify occurrence of phenol in concentrations above the detection limit 0,5 μg/l. Observed concentrations are below the threshold (0,001 mg/l) set by respective EU and Russian guiding documents (75/440/EEC, ГН 2.1.5.689-98).

Heavy metals.

Seven heavy metals were measured in filter and non-filtered water samples from the lake system: iron, manganese, aluminum, copper, zinc, lead, and mercury. But only three of them were detected above the respective detection limits in the majority of samples. Concentrations of detected heavy metals are illustrated by Figure 76. Elevated levels of iron and manganese concentrations are typical for the region. Elevated natural background provided by ground waters from inter glacial aquifers characterized by high concentrations of these metals. Both metals demonstrate similar seasonal variations of concentrations with highest median values in winter. It might be explained by prevailing of ground water supply over surface run-off in this period. Observed concentrations vary in a wide range of almost two orders of magnitude for manganese and one for iron. Concentrations of these heavy metals in non-filtered samples were expectedly higher than in filtered, especially, it concerns iron which concentrations in non-filtered samples were n some month five times higher than in filtered. Concentrations of aluminum did not demonstrate any seasonal variations. Mean values remained at the level between 0.01 and 0.02 mg/l almost throughout the whole year except for October 2020. There were only a few samples where concentrations of copper, zinc and lead above detection limit were measured (LODs see Table 19). These concentrations either in filtered or non-filtered samples vary in relatively narrow intervals: Cu 0,012-0,039 mg/l; Zn 0,005 -0,015 mg/l and Pb 0,0012-0,0032 mg/l. All these concentrations are significantly below environmental quality standards set by the EU and Russian regulations. There was not any mercury detection in the lake system during the observation period.

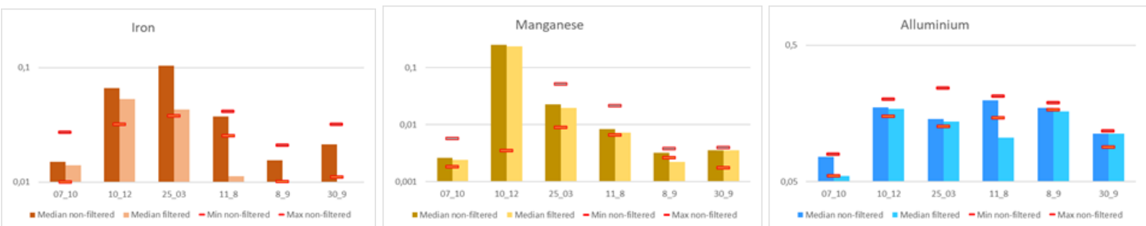


Figure 76 Concentrations of heavy metals in the water of Dudergofskoe-Dolgoe lake system.

Water quality in the pond of Pionerski park.

Monitoring of water quality in the relatively small pond located in Pionerski part included sampling in both small and large parts (basins) of the pond. Location of sampling points is given in Figure 77. Six samples were simultaneously taken from sampling points in different seasons of the year starting from October 2020 till October 2021. Sampling dates are given in Table 18. Since water freely circulates between these two basins of the pond through a channel, the average of concentrations measured in samples from both sampling points was applied to characterize water quality and its variation in the pond throughout the year.

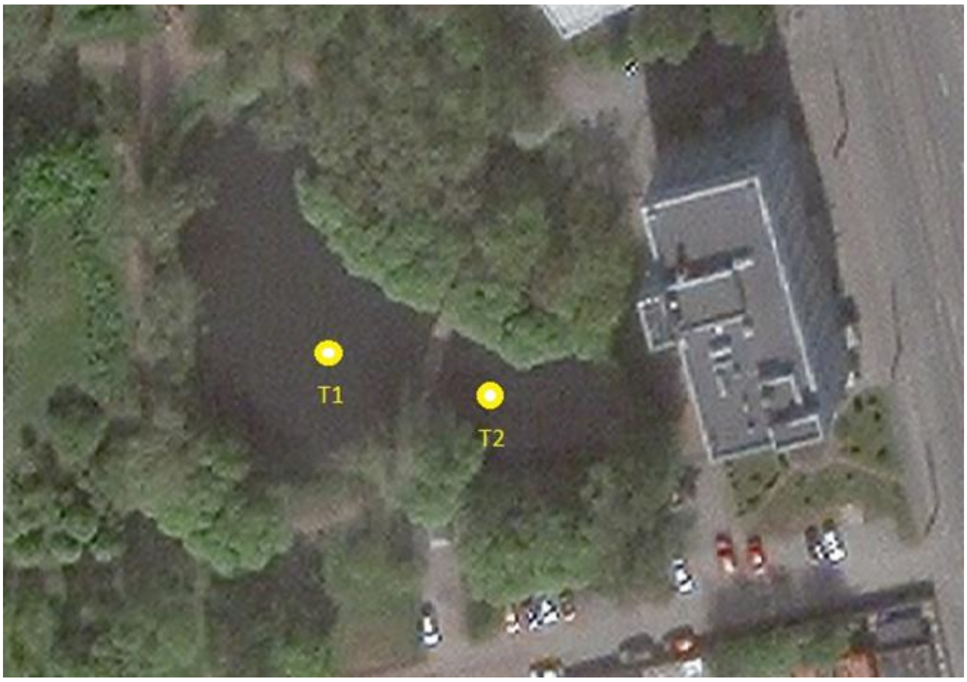


Figure 77 Monitoring stations in the pond in Pionerski park.

Water quality monitoring involved several parameters: pH, BOD5, suspended matter, nutrients, organic contaminants, and heavy metals. Most of the parameters were identified for non-filtered samples. For heavy metals filtered samples were also analyzed to assess the proportion of dissolved metals and in the form of solid particles. Methods of sample treatment are given in Annex 1. Monitoring results are compiled in Annex 4. N.D. indicates that the substance was Not Identified since concentration was below the detection limit. Detection limits for these parameters are given in Table 19. All diagrams in this section reflect average, minimum and maximum values for parameters measured in both basins of the pond. Measuring units are mg/l in all diagrams except for phenol which is given in µg/l.

In general, water quality in the pond is characterized by relatively elevated levels of contamination by organic pollutants, nutrients, and heavy metals. Since the water regime in the pond is mainly controlled by surface run off, variation of water quality also highly depends on precipitation. That is why available data does not seem sufficient to reflect any seasonal variations.

Potential hydrogen and biological oxygen demand.

Potential hydrogen is one of the parameters which remained relatively stable throughout the year of observations. Average value was slightly about 7 variating between 7.3 and 8.1 Figure 78. This parameter in individual samples varied slightly broader but remained withing the interval 7.5-8.5.

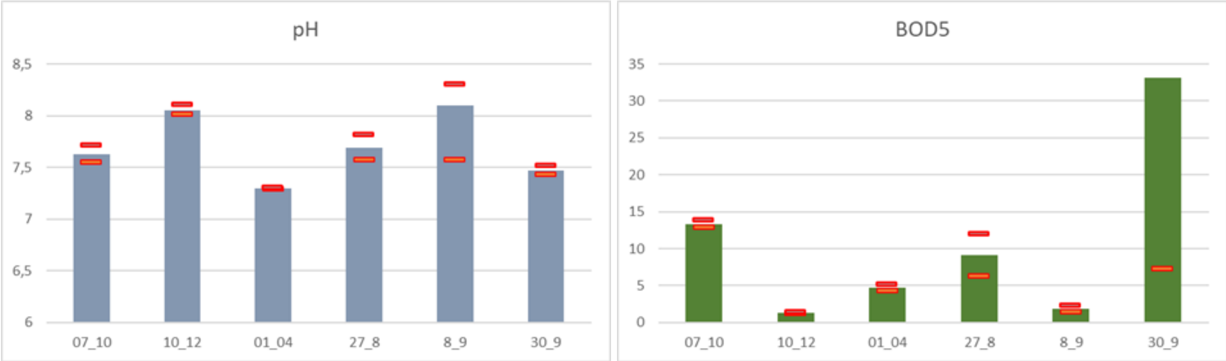


Figure 78 pH and BOD5 in the water of the pond in Pionerski park.

Biological oxygen demand varied broadly from first mg to several tens' mg per liter. Average value in December and the beginning of September was in the interval between 1 and 2 mgO2/l, while in late September average BOD5 was as high as almost 35 mgO2/l with individual sample demonstrating BOD5 almost 60 mgO2/l. General elevated level of BOD5 with extremely high concentrations in some months, likely connected with heavy precipitation, demonstrate significant organic contamination of water in the pond, which remarkably exceeds BOD5 quality standard (3 mg/l, 75/440/EEC).

Suspended solids

Average concentration of suspended solids in water of the pond varied in rather broad range from 2 mg/l to almost 30 mg/l Figure 79. I most months average value did not exceed 10 mg/l but in early and late September average concentrations of suspended solids were as high as 18 and 30 mg/l with individual measurement demonstrating 45 mg/l. Thus, in general, except for several single measurement water quality meet standards (25 mg/l) set by the EU DIRECTIVE 75/440/EEC.

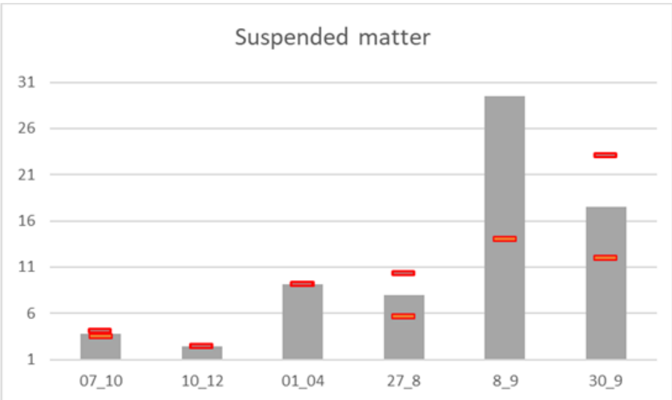


Figure 79 Concentrations of suspended solids in the water of the pond in Pionerski park.

Nutrients.

Since the pond does not have any specific hydrological regime, it is highly likely that concentration of nitrogen and phosphorus in the water is controlled by surface run off. Most of the samples demonstrate rather high concentration of nutrients (Figure 80). Average values for total nitrogen exceed 3,5 mg/l except for one sample taken in April 2021. In some months concentration of total nitrogen exceeded 6 mg/l, which is extremely high value compared to values for good environmental status of lakes (0,25 to 4 mg/l). There are no seasonal variations of total nitrogen concentrations in water which proves that precipitation and respective surface run off is the major source of nitrogen to the pond. Concentration of total phosphorus remains extremely high in the water of pond throughout the whole year. Only in December it lowers below 0,01 mg/l. All other months it is as high as almost 1 mg/l which demonstrates exceedance of total phosphorus concentrations in lakes in good environmental status (0.005 to 0.5 mg/l). As said above, the lowest concentration of total phosphorus was observed in December 2020. Then, it steadily grew until August 2021 and remained at the highest level until October 2021.

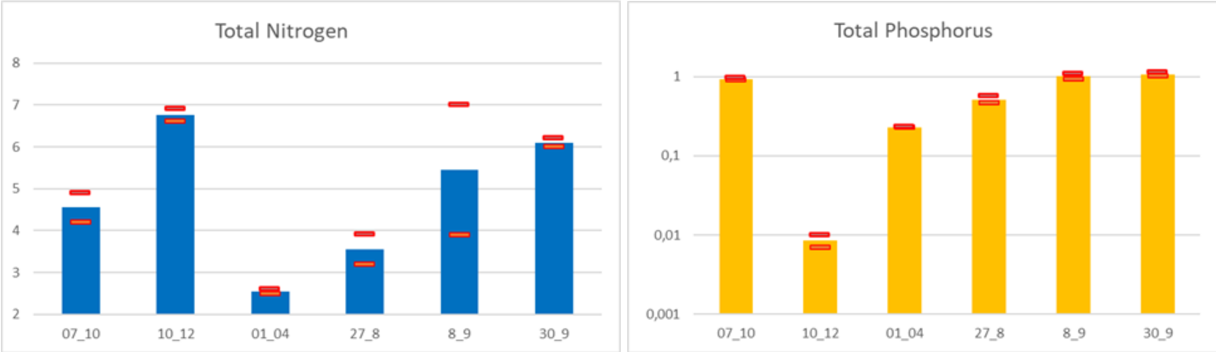


Figure 80 Concentrations of total nitrogen and total phosphorus in the water of the pond in Pionerski park.

Ammonium constitutes a significant part of total nitrogen content in water samples taken from the pond. In October 2020 and in late September 2021 the concentration of ammonia was about 3 mg/l. In other months ammonia also demonstrated elevated concentrations around 1 mg/l with minimum 0,2 mg/l in December 2020. EU directive on drinking water sets limit values for ammonium concentrations for A1 class water as 0,04 mg/l and for A2 0,8 and 1.2 mg/l. Concentrations observed in the pond significantly exceed these thresholds as well as softer limit values set by Russian standard for drinking waters (2 mg/l).

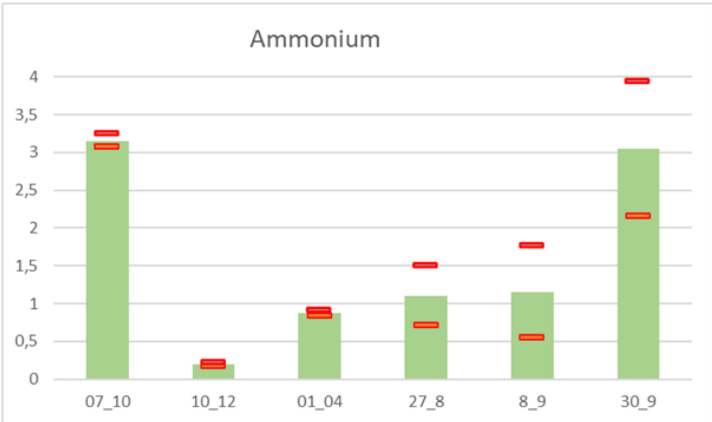


Figure 81 Concentrations of ammonium in the water of the pond in Pionerski park.

Organic contaminants.

Two organic contaminants were monitored in the pond: oil products and phenols. Average, maximum, and minimum concentrations observed during the monitoring period are given in Figure 82. These organic pollutants demonstrate elevated concentrations in all months without any seasonal variability.

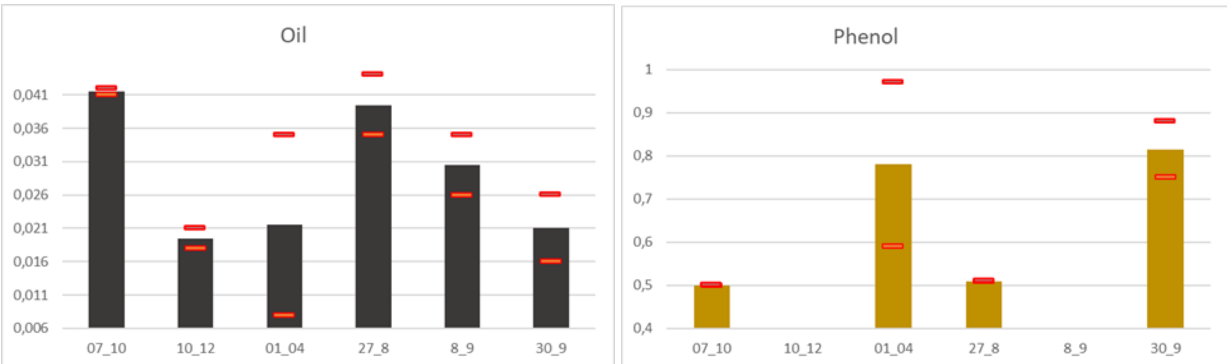


Figure 82 Concentrations of oil products (mg/l) and phenol (μg/l) in the water of the pond in Pionerski park.

Elevated concentrations of oil products occurred in October 2020, August 2021 and beginning of September 2021 with the highest observed concentration of 0,044 mg/l in August. In other months average concentration was around 0.02 mg/l. Concentration observed in two parts of the pond did not demonstrate large variation except for March where the difference was more than four times. However, observed concentration do not exceed thresholds established for water bodies used for drinking and recreational purposes by both the EU – 0,05 mg/l (75/440/EEC) and Russian – 0,3 mg/l (ГН 2.1.5.689-98). Phenol was detected in limited number of samples demonstrating concentrations below 1 µg/l. However, in April and in the end of September phenol was detected in samples taken from both parts of the pond with average concentration about 0,8 µg/l. In October 2020 and August phenol was detected only in one sample at the level slightly above 0,5 µg/l. Observed concentrations are below the threshold (0,001 mg/l) set by respective EU and Russian guiding documents (75/440/EEC, ГН 2.1.5.689-98).

Heavy metals.

Seven heavy metals were measured in filter and non-filtered water samples from the pond: iron, manganese, aluminum, copper, zinc, lead, and mercury. Concentration of mercury above detection limit was not detected in the samples. And lead was detected in only one non-filtered sample taken in August 2021. Concentration of lead was 0.003 mg/l. In general, concentrations of heavy metals in non0filterewd samples were expectedly higher than in filtered. Concentrations of detected heavy metals are illustrated by Figure 83. Iron and manganese demonstrate elevated level of concentrations mainly varying in the interval between 0,1 and 1 mg/l. Only in December 2020 concentrations these metals were significantly lower – iron about 0.01 and manganese even below 0,01 mg/l. In filtered samples iron was not detected in December 2020. Concentrations of aluminum vary in almost one order of magnitude. The lowest average value was in was in April (below 0.05 mg/l) and the highest in August (almost 0,7 mg/l for non-filtered sample). In other months, average concentrations were close to 0.1 mg/l. The highest average concentration of zinc (0,08 mg/l) was observed in August in non-filter samples. In other months, average concentrations of Zn were either slightly below or slightly above 0.01 mg/l. Copper also demonstrated the highest average concentrations exceeding 0.01 mg/l in non-filtered sample in August. Average concentrations of Cu in October 2020 and September 2021 were at a level slightly exceeding 0,001 mg/l. And in December 2020 Cu was not detected. The highest concentrations of almost all heavy metals except for manganese were observed in August. For comparison, concentrations of iron, manganese and aluminum in several samples exceed Russian quality standards for drinking water which are 0.3, 0.5 and 0.1 mg/l respectively. At the same time, quality standards for Zn and Cu (1 mg/l for each metal) were not exceeded. Standards set for drinking waters by the EU directive 75/440/EEC significantly differ from Russian. These values are comparable for iron and manganese for which the EU directive establish standards as 1 and 0.1 mg/l respectively. But standards set for Zn and Cu are much lower than Russian constituting 0.5 and 0.05 mg/l respectively. But anyway, concentrations of neither Zn nor Cu demonstrate exceedance of these standards.

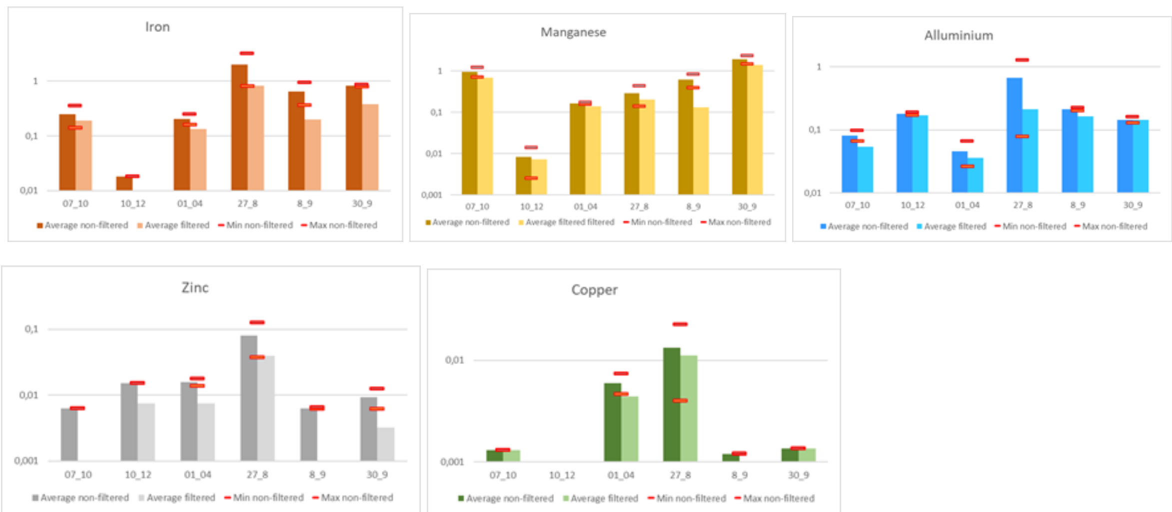


Figure 83 Concentrations of heavy metals in the water of the pond in Pionerski park.

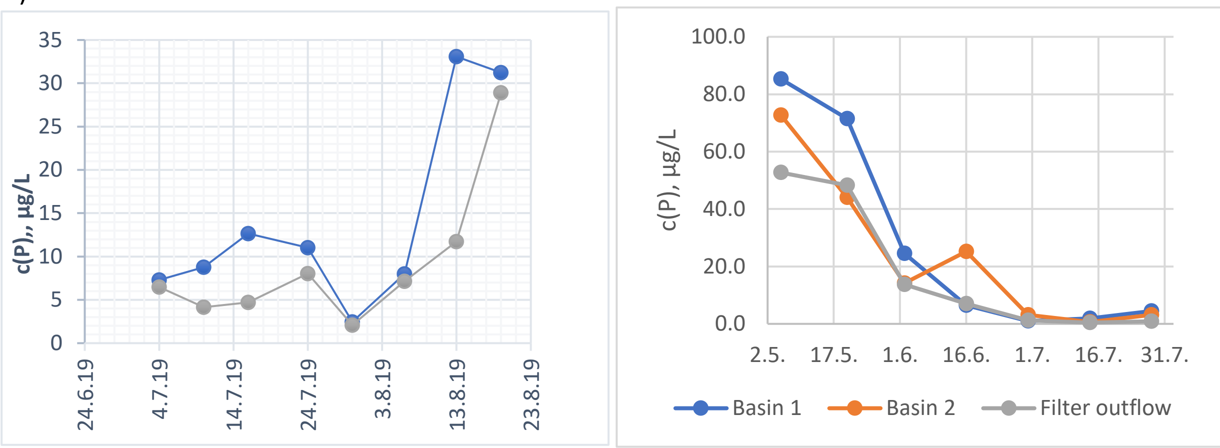
6. Effect of filters

Urbanization has led to the disruption or replacement of natural hydrological processes due to the sealing and degrading of natural soils. The impact of stormwater runoff quality on the environment was under consideration. Sealed surfaces cause the transport and accumulation of pollutants originating from traffic areas, building materials and other impervious surfaces. A range of pollutants can be found, such as sediments (including particle-bound pollutants), bacteria, oil and grease, heavy metals, nutrients, and trace organic chemicals. SHEM-WP purification system is aimed to mitigate the effect of these pollutants, and the impact on water quality was estimated. The main focus was on nutrients, heavy metal, and some organic compounds, such as oils and furans. Very limited visual evaluation on aquatic environment were made during sampling campaigns. For long-term impacts longer research periods and full-scale filters would have been required. This chapter presents the results supporting the main findings and conclusions. Removal of various solid particles fractions with the system was obvious, however the content of the extracted or sedimented fractions were not investigated. Environmental feasibility assessment in chapter 7 completes the conclusions on removal rates of the main contaminants.

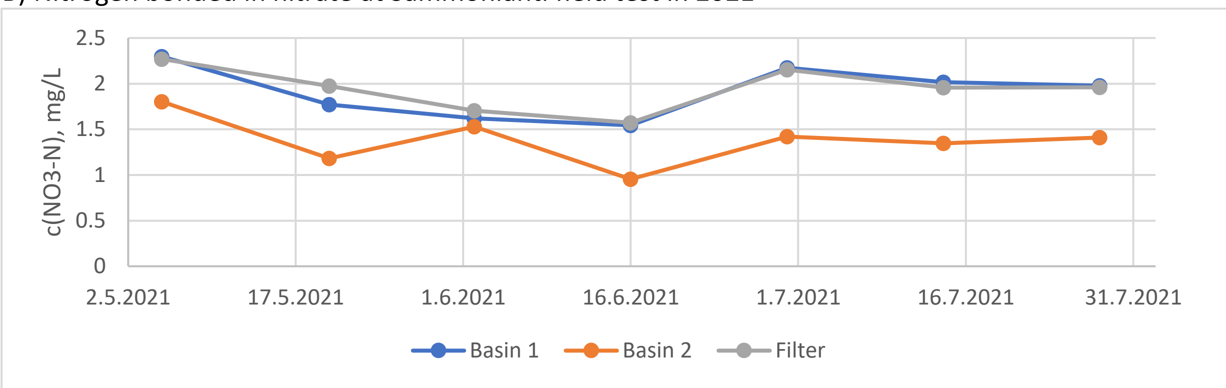
6.1 Effect of filters in Sammonlahti CW

Sammonlahti CW had two different filters installed. In the short test in 2019 there was a filter with two separate chambers. The first chamber contained only shungite and the second EM in growth media. The growth media contained ceramics and porous lava rocks. Lava rocks applied are a commercial mixture for small ponds. Shungite were activated with chemical and thermal treatment. The water quality of basins 1, basin 2, and filter outflow were sampled. In addition, the shungite rocks were sampled, and examined in laboratory for sorpted metal ions. Concentrations of oil compounds and furans were analyzed occasionally by external certified laboratory. However, the concentrations were below the detection limit and conclusions from field test samples could not be drawn. Conductivity or pH between basin 1 and filter outflow did not differ. For example, in July-Aug. 2019: average Cond(Basin 1) = 0.154 mS/cm and Cond(Filter outflow) = 0.156 mS/cm, and average pHs = 7.9 (in both sets). High pH indicates biological activity and removal of nitrogen in the system.

A) P in Sammonlahti CW in 2019 and 2021 field tests



B) Nitrogen bonded in nitrate at Sammonlahti field test in 2021



C) Sulphate and chloride concentrations in 2021 field test

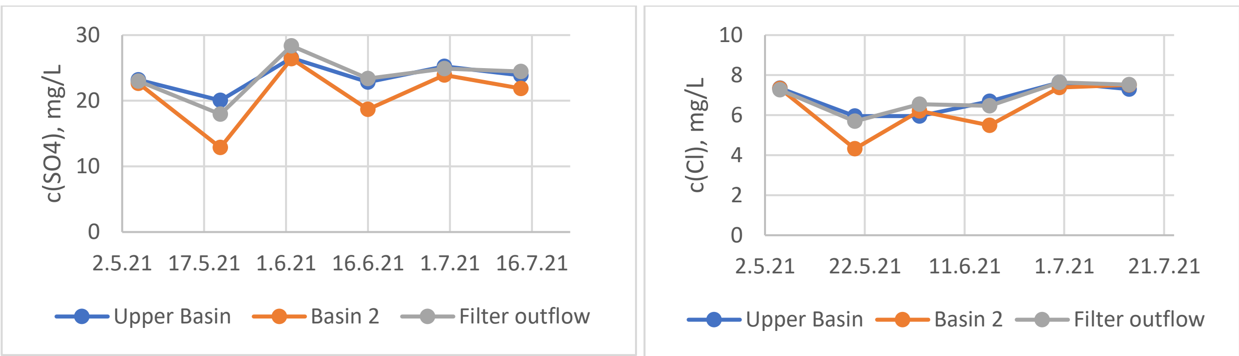


Figure 84 P and NO3-N (nitrogen bonded into nitrate) in Sammonlahti CW. Filter was installed into Basin 1 outflow. Samples taken from Basins 1 and 2 are composite samples. Filter samples were taken from filter outflow.

- *A) Filter has decreased phosphorous: In Sammonlahti 2019 pre-test the P concentration decreased immediately when filter was implemented in July. In August, the flow from Basin 1 decreased and there was only minimal inflow to filter. P concentration started to increase in mid-August due to filter drying. in May-June 2021 the P concentration decrease close to detection limit due to natural removal mechanisms. P concentration correlates with Fe and Al concentrations indicating the formation of phosphates. However, heavy rains increase variation in the results and relation is not clear.*
- *B) Nitrate decrease only in Basin 2. The effect of EM can be expected to be seen in Basin 2, and not in the filter. Nitrate concentrations are low, and it represents about 88-95 % of the total nitrogen concentration in water.*
- *C) Sulphate and chloride concentration decrease 10-30 % in the settlement basin (Basin 2).*

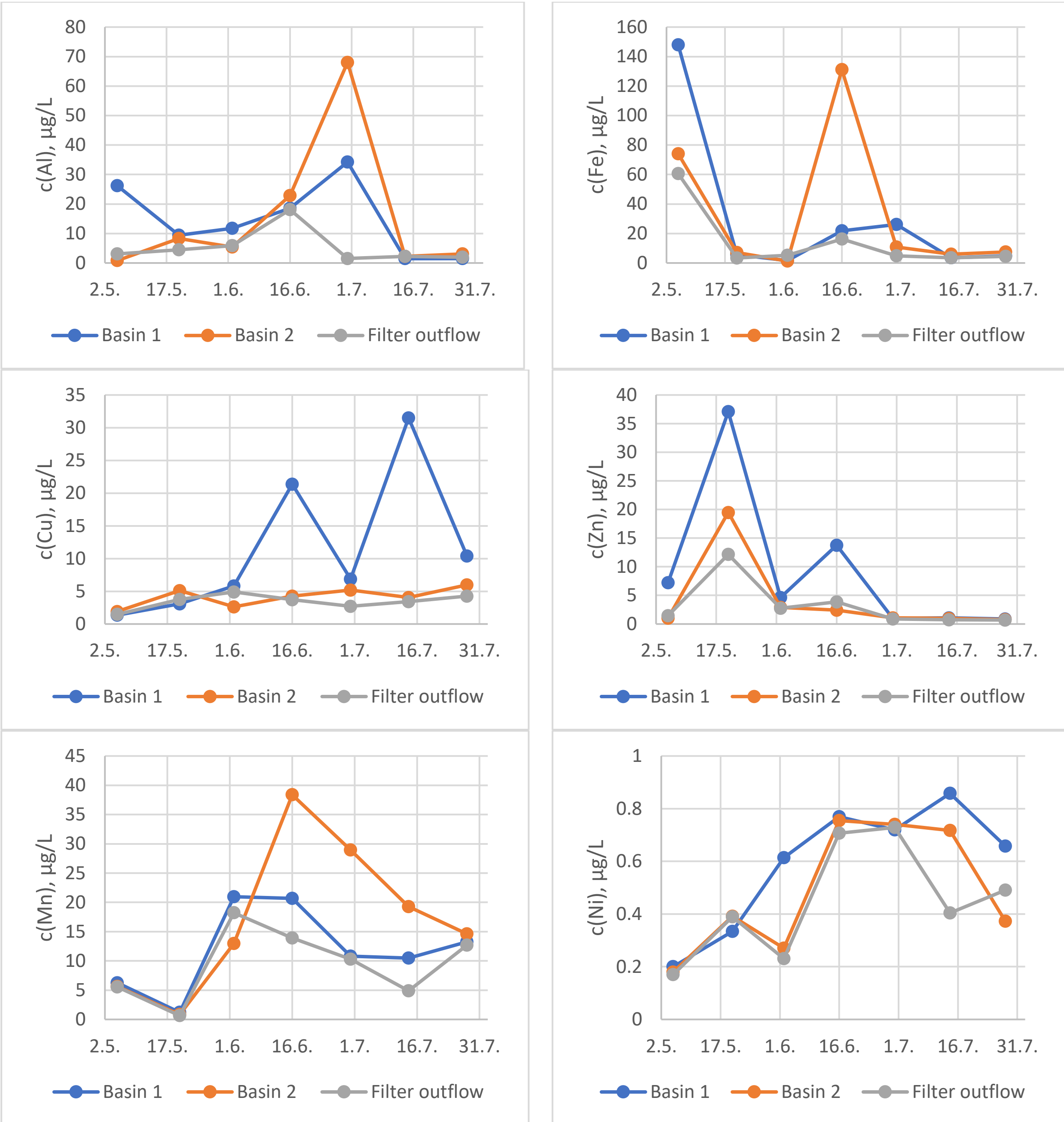


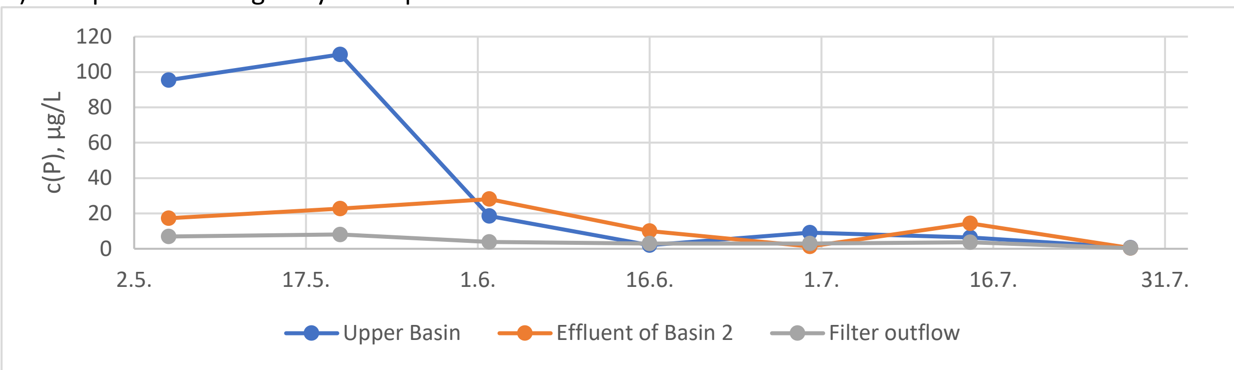
Figure 85 Sammonlahti CW: filter has decreased concentrations of Al, Fe, Cu, Zn, Mn, and Ni. Total 26 metal concentrations were determined. No systematic change in level of most of them were detected. Influent to filter (Basin 1) was run-off from residential area. in May 2021 there was high flow due to rains and smelting snow, and even small concentrations might correspond to higher loading than concentrations in June.

Concentrations in water are not directly describing the emission load to catchment area. The real load as mass can be estimated via volume flow. The natural water bodies also contain certain amounts of metals and nutrients, and the target values should be on the level of natural freshwater bodies. To illustrate the effect of filters, also estimates of emission as mass were computed and compared to tap water requirements or Lake Saimaa reference site (Ilkonselkä) contents (SVSY, 2021). Results and discussion are in the environmental feasibility chapter.

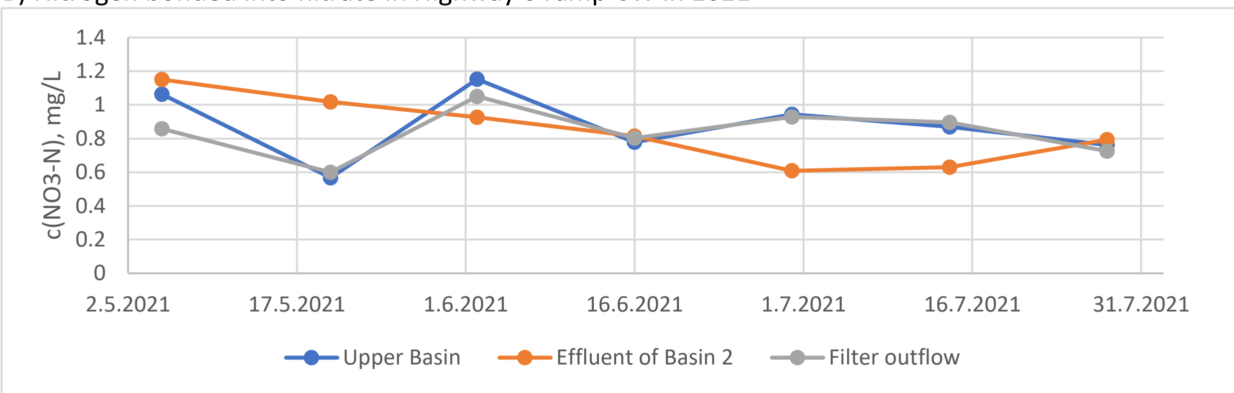
6.2 Effect of filter in Highway 6 ramp CW

A double bottom "underground" system was tested in Highway 6 ramp. It was a passive filter with horizontal inflow. Backflow from biological unit to shungite unit was enabled. Location at the bottom increased capture of smallest solid particles into the filter. Results revealed high sorption of phosphorus, aluminum, iron, zinc, copper, and manganese. Nitrogen removal took place only at the settlement basin. Microplastics study was carried out on this site in 16.6.- 9.8.2021.

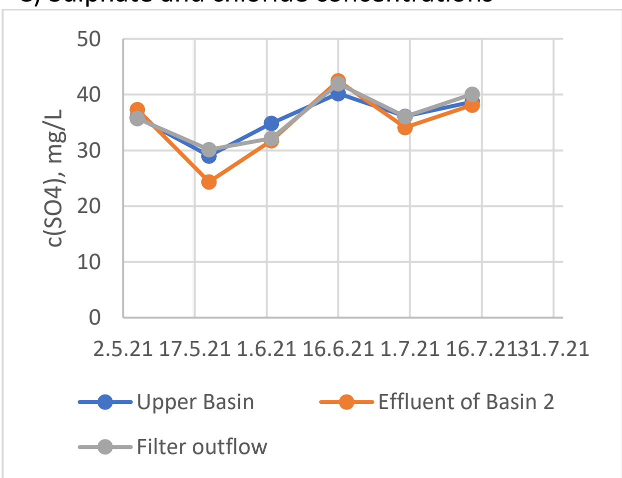
A) Phosphorous in Highway 6 ramp CW in 2021



B) Nitrogen bonded into nitrate in Highway 6 ramp CW in 2021



C) Sulphate and chloride concentrations



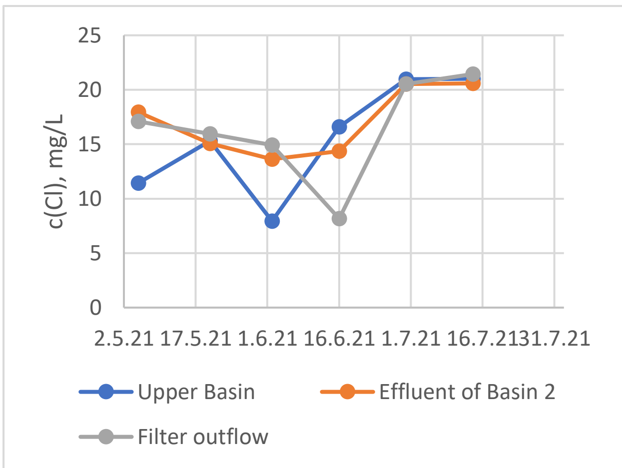


Figure 86 Highway 6 ramp: Phosphorus and NO3-N concentrations in May-July 2021. Samples were taken from 1) the upper basin, which is influent to filter, 2) outflow from the filter, 3) outflow from Basin 2. Basin 2 was too shallow that representative samples could have been taken from it. P concentrations in filter outflow are near analytical detection limit in all samples. Thus, the filter and shungite in it removes phosphorus and organic matter from the run-off water. P concentration tends to slightly increase in Basin 2 due to plant growth cycle. Nitrogen concentrations are low in influent, and filter has no clear effect on it. In the Basin 2 the N concentrations are even too low, and it can be assumed the nitrogen to be the growth limiting nutrient in this aquatic system. Filter has no effect or very minor effect on nitrate concentrations. Nitrogen in nitrate represents about 90-99 % of total nitrogen. The purification system has now a clear effect on sulphate and chloride concentrations.

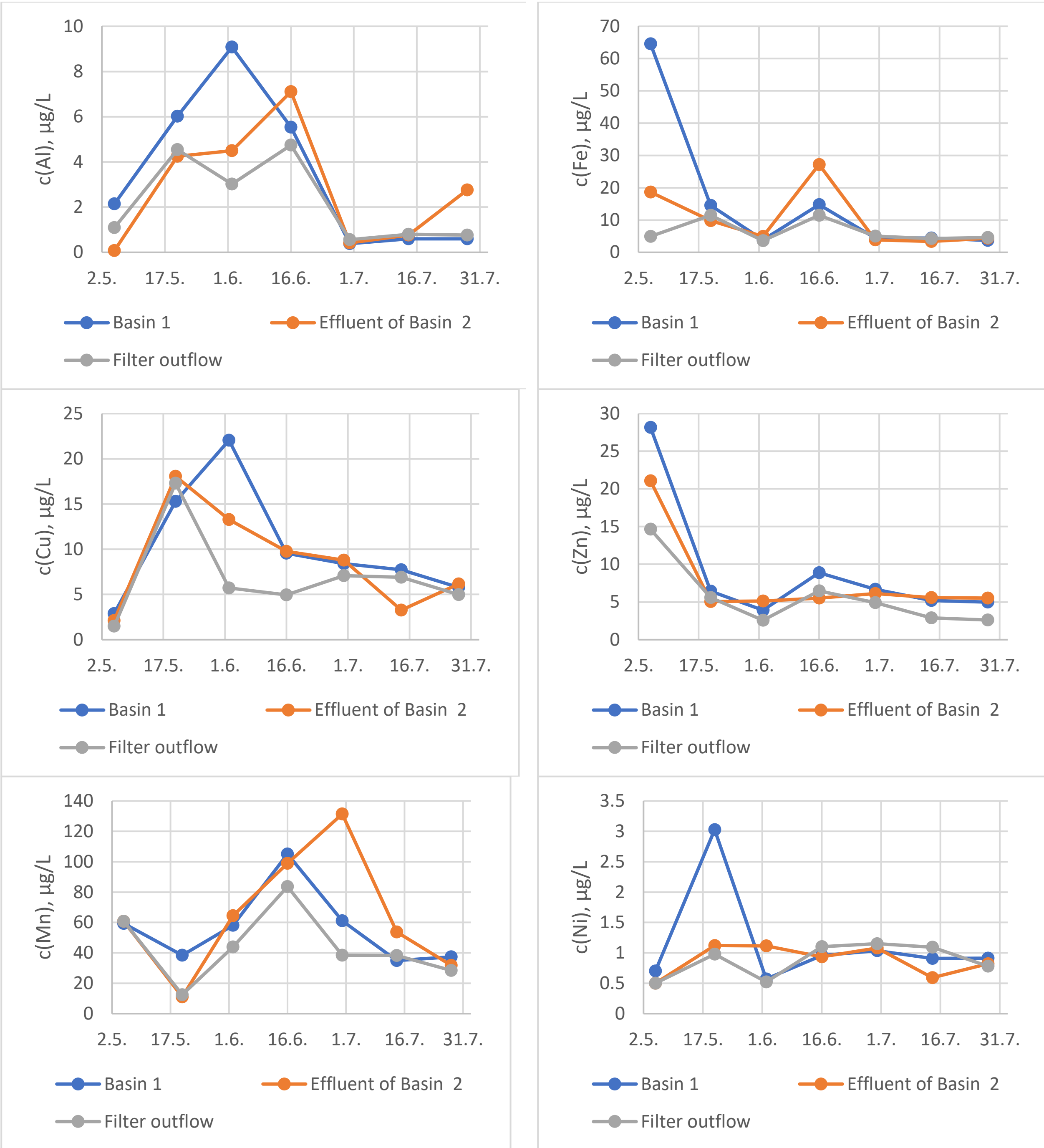


Figure 87 Metal concentrations in Highway 6 ramp CW in 2021: concentration of 26 metals were analyzed from the samples. Filter had no effect on most of them since the concentrations were close to detection limit- or since the amount and variation of major chemical elements such as Na, Ca, Mg and K naturally higher than what can be affected with smallish filters.

Microplastics in shungite filter

Shungite has properties that support promote assumption of microplastic compounds retention in it. It can be expected that filter removing suspended solids would also decrease the number of microplastics particles in the flow. In Highway 6 ramp CW, total six 10 x 10 x 10 cm3 stainless cubes were filled with shungite and placed into the filter (Figure 60). The cubes were in two rows. Sample cubes in the first row show microplastic retention in them while the second row samples were almost clean from the microplastics.

Analysis of the samples was done by LUT research group specializing in microplastics (Mikkeli campus). Shungite was collected in pre-rinsed beakers on 9.8.2021. Beakers were covered with aluminum foil and transferred to the laboratory. One of the boxes was slightly opened during filtration, which probably allowed more organic material to enter the shungite. Three subsamples were collected from each shungite sample for microplastic analysis. Roughly 50 g of shungite was collected from the middle of the beaker from four layers with a rinsed stainless-steel spoon and placed on aluminum foil. Excess shungite from each layer was discarded into another beaker. All four collections were combined, mixed, and layered evenly on the foil. Sample was dived into four equal portions, three of which were poured into pre-rinsed glass beakers, weighed, and covered with foil. The fourth subsample was used for dry weigh analysis.

Samples were treated with Fenton's reaction to remove excess organic material and to allow possible MPs to be detached from shungite before density separation. Density separation with sodium tungstate (Na_2WO_4) solution was conducted for separating MPs from denser shungite before analysis of MPs.

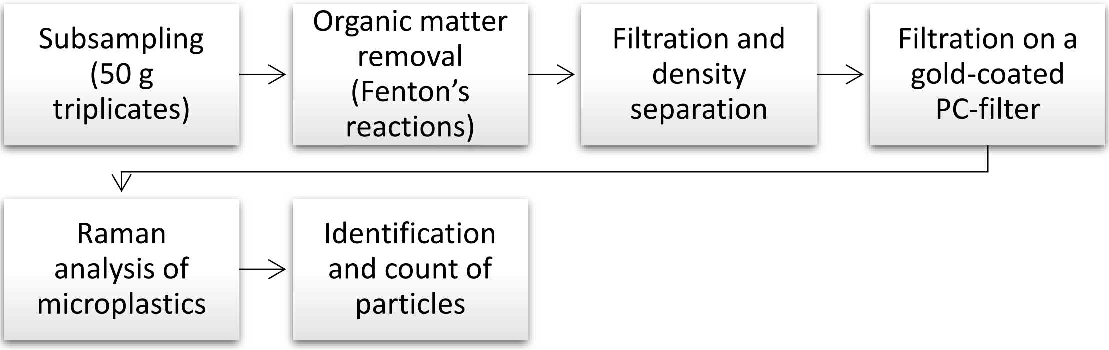


Figure 88 Microplastic analyses: sample treatment for Raman analysis is a multistep process that contains several extraction and filtering steps. To avoid contamination special instruments and laboratory hoods have to be applied.

For MPs analysis, the replicate of each sample type was subsampled before the final filtration on gold-coated PC filter. Analysis of microplastics was performed using Raman imaging microscope (Thermo Scientific, DXR3xi with OMNICxi software). Two replicates of each sample types were analyzed using 785 nm laser, 0.1 s exposure time with 10 scans and 50 µm pinhole aperture. Spectra were recorded within 600-1800 cm-1 and compared against polymer libraries including 13 commonly found polymer.

Results are shown in Table 20. 1 PE was observed in the procedure blank (PB1) that indicate contamination has occurred during the handling of shungite samples. Mean MPs concentration in shungite samples exposed to the stormwater in filtration units was 0.29 MPs/g dw and 0.02 MPs/g dw in the shungite sample before exposure to stormwater. According to these preliminary tests with lower size limit at 100 µm, microplastics (PE, PP and POM) seem to be retained in the shungite. Due to the analytical arrangement the smallest (< 100 µm) and largest (> 2 mm) fraction could not be studied. Due to the material properties, there might still be MP particles that retained in the shungite after the Fenton extraction step.

Table 20 Over 100 µm microplastic particles extracted from shungite filter samples; polyacetal (POM), polyethylene (PE) and polypropylene (PP)

Sample	MP s	MPs/g dw
Blank (water)	PE	-
Shungite: reference stored in laboratory	PE	0.02
Shungite in first row at filter	PP PE	0.55 0.41
Shungite in last row at filter	POM	0.21

6.3 Effect of filter in the Dudergofskoe-Dolgoe lake system.

Two passive filters were tested in the Dudergofskoe-Dolgoe lake system. Filters were located in Dolgoe lake below the water spillway 2 in half-submerged position, as it shown on Figure 89. Water intake for both filters was arranged in the water spillway by plastic pipes which provided water flow through the filters. Since filters were equipped by a valve to regulate water flow, the rate was set of about 3.5 liters per minute for both filters.

Figure 89 Installation of filters in the Dudergofskoe-Dolgoe lake system.

Water samples were taken from the last cameras of each filter, just before releasing water from filter, through sampling wells in lids of the filters. Samples taken from both filters were mixed and analyzed as one sample. Sampling was done simultaneously with sampling from the lake system except for one sample taken from the lakes in October 2020, before the installation of filters. Altogether 5 samples were taken from the filters in the period from December 2020 to the end of September 2021.

Table 21 Parameters included: pH, BOD5, suspended matter, nutrients, organic contaminants, and heavy metals.

Parameters	Units	07-Oct-2020		10-Dec-2020		25-Mar-2021		11-Aug-2021		08-Sep-2021		30-Sep-2021	
		Med	Max	Med	Max	Med	Max	Med	Max	Med	Max	Med	Max
Temperature	°C	11,8	11,8	0,4	0,4	1,6	1,6	20,2	20,4	13,5	13,9	8,8	9,2
pH	pH	8,1	8,1	7,9	8,1	8,0	8,1	8,4	8,5	8,5	8,5	8,1	8,1
BOD5	mgO_2/l	2,5	2,9	2,4	4,2	1,3	1,3	2,6	3,8	2,4	3,3	1,2	1,8
Susp. solids	mg/l	3,3	4,1	2,9	5,8	3,5	4,3	6,6	34,2	2,8	2,9	3,3	3,7
Total N	mg/l	5,3	5,4	6,1	8,0	6,6	7,0	3,8	3,9	4,8	4,9	6,0	6,5
Ammonia	mg/l	0,19	0,23	1,01	3,60	0,17	0,24	0,17	0,19	0,23	0,24	0,10	0,13
Total P	mg/l	0,015	0,022	0,310	1,120	0,024	0,110	0,039	0,057	0,033	0,044	0,016	0,170
Oil products	mg/l	0,010	0,012	0,017	0,035	0,012	0,031	0,028	0,040	0,007	0,010	0,011	0,018
Phenol	µg/l	n.d.	n.d.	0,90	1,00	0,61	0,66	0,58	0,63	n.d.	n.d.	n.d.	n.d.
Total iron*	mg/l	0,015	0,027	0,066	0,280	0,105	0,227	0,037	0,041	0,015	0,021	0,021	0,032
Total iron	mg/l	0,014	0,017	0,053	0,120	0,043	0,098	0,011	0,013	n.d.	n.d.	n.d.	n.d.
Aluminium*	mg/l	0,08	0,08	0,18	0,20	0,14	0,24	0,20	0,21	0,17	0,19	0,11	0,12
Aluminium	mg/l	0,06	0,08	0,17	0,18	0,14	0,19	0,11	0,11	0,16	0,17	0,11	0,12
Manganese*	mg/l	0,003	0,006	0,279	0,900	0,023	0,052	0,008	0,022	0,003	0,004	0,004	0,004
Manganese	mg/l	0,002	0,006	0,237	0,890	0,020	0,042	0,007	0,020	0,002	0,003	0,004	0,004
Copper*	mg/l	0,001	0,001	0,002	0,002	0,001	0,001	0,003	0,003	n.d.	n.d.	n.d.	n.d.
Copper	mg/l	0,001	0,001	0,002	0,002	n.d.	n.d.	0,001	0,001	n.d.	n.d.	n.d.	n.d.
Zink*	mg/l	n.d.	n.d.	0,015	0,028	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,009	0,009
Zinc	mg/l	n.d.	n.d.	0,011	0,014	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,005	0,005
Led*	mg/l	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,002	0,003	n.d.	n.d.	n.d.	n.d.
Led	mg/l	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mercury	µg/l	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*Indicates non-filtered samples

Potential hydrogen and BOD5

There was no any effect of filtering on pH observed. The parameter remained at approximately the same level in all samples, deviating from the pH in lake for a few tenths of the unite. However, BOD5 was visibly affected by filtering, as shown on Figure 90. Biological oxygen demand in samples taken from filters was twice or even thrice lower than in the lake water in all months except for March.

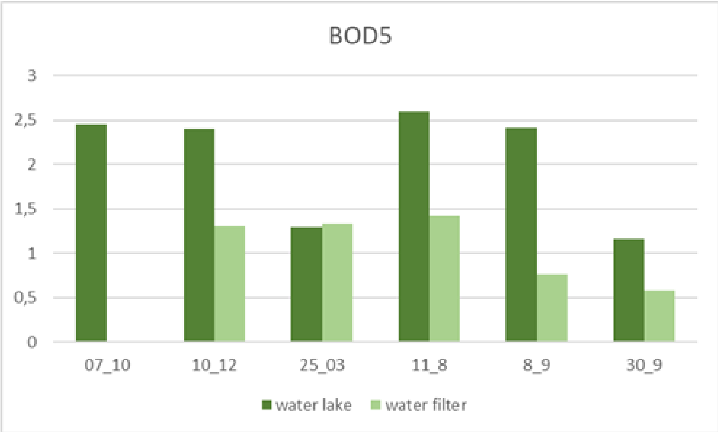


Figure 90 Effect of filtering on BOD5 in water of the Dudergofskoe-Dolgoe lake system.

Suspended solids.

Concentration of suspended solids in the lake water was relatively low, just slightly exceeding the detection limit 2 mg/l. Only the lake water sample taken in August contained more than 6 mg/l of particles. However, the effect of filter was visible in all samples taken from filter except for the one sampled in March 2021, where concentration of particles in water from filters was twice higher than from the lake (Figure 91). Concentrations of suspended solids in other samples from filters were lower than in respective samples of lake water. But since concentrations in three out of five samples taken from filter were below the detection limit, any quantification of reduction does not seem possible.

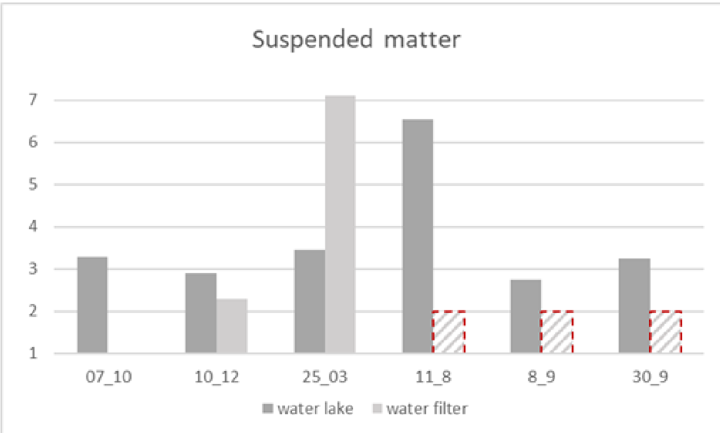


Figure 91 Effect of filtering on concentration of suspended solids in water of the Dudergofskoe-Dolgoe lake system. Striped bars indicate concentrations below the detection limit 2 mg/l.

Nutrients and organic pollutants.

In general, water in the Dudergofskoe-Dolgoe lake system is characterized by relatively low concentration of nutrients and contamination by organic pollutants. Application of combined filters had an effect on the content of phosphorus in water as shown on Figure 92. In all samples taken from filters, except for one in March, concentrations of total phosphorus were lower than in lake water. However, there was no effect on content of total nitrogen observed. The effect of filtering on content of oil products in water can be justified, but there were no concentrations of phenol above LOD (0,5 µg/l) observed in samples from filter. The latter might indicate the ability of filter to remove phenol from water, but this fact cannot be quantitively illustrated.

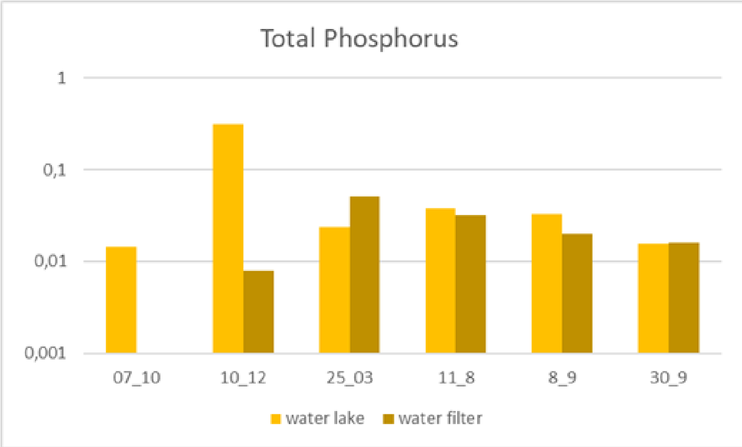


Figure 92 Effect of filtering on concentration of total phosphorus (mg/L) in water of the Dudergofskoe-Dolgoe lake system.

Heavy metals.

The effect of filter on heavy metals concentrations in lake water can be hardly unambiguously interpreted. The reason is generally their relatively low concentrations. Thus, copper and zinc were detected above detection limits only in a few samples of lake water. Since they were not detected in samples taken from filter, the effect of filtering could be qualitatively proved. Measured concentrations of iron were close to detection limit in general and, thus, in three filtered lake water samples out of 6 iron concentration were below the LOD. Thus, expectedly, non-filtered water samples from combined filters demonstrate non-detectable concentrations of iron in two cases out of five. Manganese is the only representative of the group which demonstrates reduced concentrations in almost all samples from filter. The exception is a sample taken in March 2021. Filtering water through combined filter does not affect aluminum content in water.

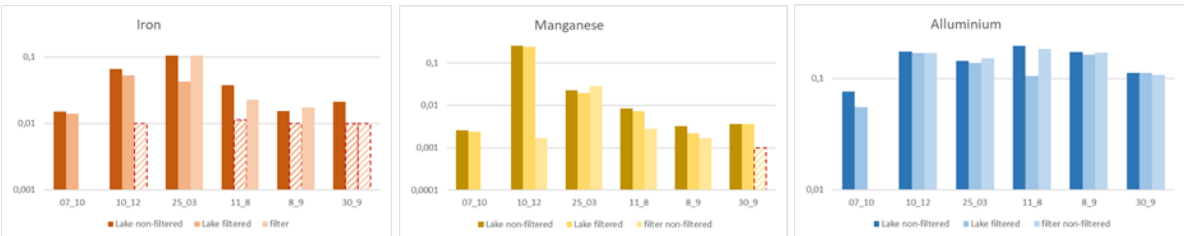


Figure 93 Effect of filtering on concentration of heavy metals in water of the Dudergofskoe-Dolgoe lake system. Striped bars indicate concentrations below the detection limit Fe=0.01 mg/l and Mn=0.001.

6.4 Effect of active filter in the pond in Pionersky park.

Active filter with productivity of about 3.5 liters per filtered water per minute was tested in the pond in Pionersky park. The filter was installed in December 2020 and operated continuously during the whole testing period until October 2021. The filter was equipped by a water pump installed in the outlet camera of the filter and providing water flow through the filter. The filter was installed in a half-submerged position in the vicinity to the water channel connecting two parts of the pond Figure 94. Energy for the pump was supplied by the battery installed under the bridge.

Figure 94 *Installation of filter in the pond in Pionirsky garden.*

Samples illustrating the effect of filter were taken from the last camera of the filter through the well in the lid of the filter. Samples were taken simultaneously with water samples from both parts of the pond after installation of the filter. Thus, altogether 5 samples of filtered water were examined, which is one sample less than from the pond, as the first samples from both parts of the pond were taken in October 2020 before the installation of filter. The same parameters as in the water of the pond were measured in the same laboratory with the accuracy given in the Table 19.

Table 22 Parameters included: pH, BOD5, suspended matter, nutrients, organic contaminants, and heavy metals.

Parameters	Units	07-Oct-2020		10-Dec-2020		25-Mar-2021		11-Aug-2021		08-Sep-2021		30-Sep-2021	
		Med	Max	Med	Max	Med	Max	Med	Max	Med	Max	Med	Max
Temperature	°C	11,8	11,8	0,4	0,4	1,6	1,6	20,2	20,4	13,5	13,9	8,8	9,2
pH	pH	8,1	8,1	7,9	8,1	8,0	8,1	8,4	8,5	8,5	8,5	8,1	8,1
BOD5	mgO_2/l	2,5	2,9	2,4	4,2	1,3	1,3	2,6	3,8	2,4	3,3	1,2	1,8
Susp. solids	mg/l	3,3	4,1	2,9	5,8	3,5	4,3	6,6	34,2	2,8	2,9	3,3	3,7
Total N	mg/l	5,3	5,4	6,1	8,0	6,6	7,0	3,8	3,9	4,8	4,9	6,0	6,5
Ammonia	mg/l	0,19	0,23	1,01	3,60	0,17	0,24	0,17	0,19	0,23	0,24	0,10	0,13
Total P	mg/l	0,015	0,022	0,310	1,120	0,024	0,110	0,039	0,057	0,033	0,044	0,016	0,170
Oil products	mg/l	0,010	0,012	0,017	0,035	0,012	0,031	0,028	0,040	0,007	0,010	0,011	0,018
Phenol	µg/l	n.d.	n.d.	0,90	1,00	0,61	0,66	0,58	0,63	n.d.	n.d.	n.d.	n.d.
Total iron*	mg/l	0,015	0,027	0,066	0,280	0,105	0,227	0,037	0,041	0,015	0,021	0,021	0,032
Total iron	mg/l	0,014	0,017	0,053	0,120	0,043	0,098	0,011	0,013	n.d.	n.d.	n.d.	n.d.
Aluminium*	mg/l	0,08	0,08	0,18	0,20	0,14	0,24	0,20	0,21	0,17	0,19	0,11	0,12
Aluminium	mg/l	0,06	0,08	0,17	0,18	0,14	0,19	0,11	0,11	0,16	0,17	0,11	0,12
Manganese*	mg/l	0,003	0,006	0,279	0,900	0,023	0,052	0,008	0,022	0,003	0,004	0,004	0,004
Manganese	mg/l	0,002	0,006	0,237	0,890	0,020	0,042	0,007	0,020	0,002	0,003	0,004	0,004
Copper*	mg/l	0,001	0,001	0,002	0,002	0,001	0,001	0,003	0,003	n.d.	n.d.	n.d.	n.d.
Copper	mg/l	0,001	0,001	0,002	0,002	n.d.	n.d.	0,001	0,001	n.d.	n.d.	n.d.	n.d.
Zink*	mg/l	n.d.	n.d.	0,015	0,028	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,009	0,009
Zinc	mg/l	n.d.	n.d.	0,011	0,014	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,005	0,005
Led*	mg/l	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,002	0,003	n.d.	n.d.	n.d.	n.d.
Led	mg/l	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mercury	µg/l	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*Indicates non-filtered samples

Potential hydrogen and BOD5

Potential hydrogen in filtered water was slightly elevated compared to the median value for the pond water Figure 95. This is typical for all months except for the first sample taken in December 2020 after the filter installation. However, pH in treated water remained at level of 8 which does not much differ from pH of water in the pond.

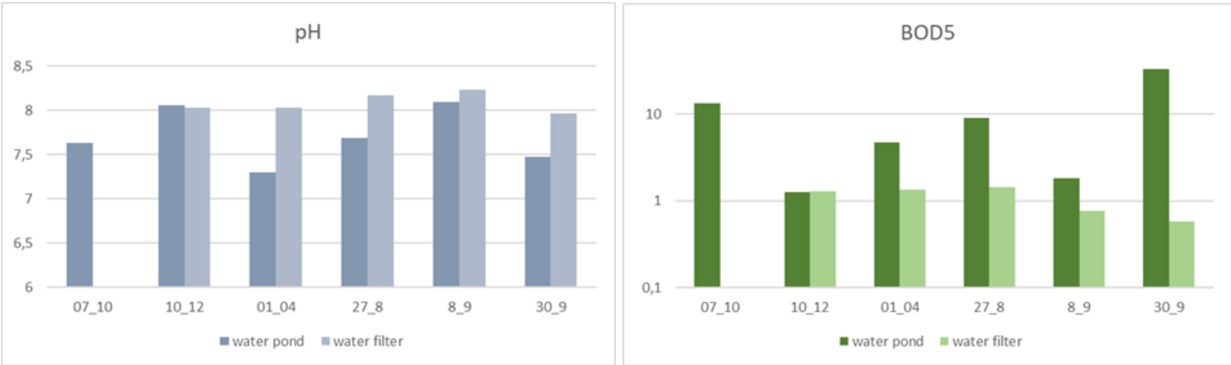


Figure 95 Effect of filtering on pH and BOD5 in the water of the pond in Pionersky park.

BOD5 measured in filtered water significantly differed from the median value for water in the pond, except for the sample take in the December (Figure 95). In general, BOD5 of all samples from filter remained at approximately the same level around 1 mgO2/l with light tendency towards decreasing in the last samples of the series. BOD5 of filtered water did not deviate together with the BOD5 of the water in the pond which was varying in the interval of more than an order of magnitude during the monitoring period. In some months BOD5 in filtered water was more than ten times lower in the pond, which demonstrated high efficiency of the filter to remove organic pollution from water.

Suspended solids.

One of the parameters which was supposed to be affected by filtering was suspended solids. Testing campaign demonstrated the decrease general decrease of suspended solids concentration in filter water but not in all samples (Figure 96). There was almost know decrease of suspended matter observed in December when the filter was installed. December was also characterized by the lowest content of suspended matter in pond water, at the level close to the detection limit (2 mg/l). Also, a minor reduction of suspended solids in filtered water was observed in April 2021. Suspended solids were not detected in samples of filtered water taken in the following three months, which is demonstrated at the Figure 96 by striped bars. It indicates that concentrations in filtered water in those months were more than times lower than in the pond.

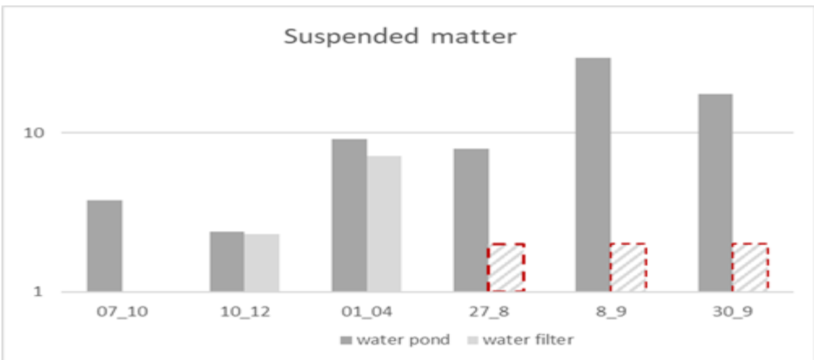


Figure 96 Effect of filtering on concentration of suspended solids in the water of the pond in Pionersky park. Striped bars indicate concentrations below the detection limit 2 mg/l.

Nutrients.

Water of the pond in Pionersky park in general is characterized by a high level of nitrogen and phosphorus content. Measurements of total nitrogen in filtered water did not reveal any effect. The same concerns ammonium which in some samples of water from the pond constituted almost 50% of the total nitrogen. However, the examination of water samples from filter demonstrated significant effect of filtering on phosphorus concentration Figure 97. Concentration of total phosphorus in all samples of filtered water except for the first one taken in December 2020 was persistently lower than in water from pond. And samples of filtered water demonstrated a continuous decrease of TP content in all samples starting from April 2021, despite the content of TP in water samples from the pond demonstrated the opposite tendency. Concentration of TP in samples taken from filtered water in the beginning and the end of September 2021, the last months of the sampling campaign, were at the level of 0.001-0.002 mg/l. That was almost hundred times lower than concentrations in the water of pond taken at the same time.

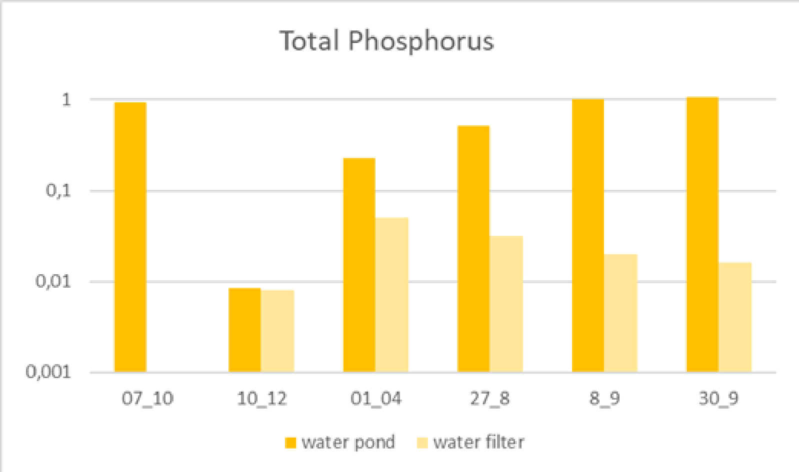


Figure 97 Effect of filtering on concentration of total phosphorus (TP) in the water of the pond in Pionersky park.

Organic pollutants.

The pond in Pionerky park was characterized by elevated concentrations of such organic contaminants as oil products and phenol. Examination of samples from filtered water illustrated the effect of combined filter on concentration of these pollutants in water. All samples except for the first one taken from filter demonstrate significant reduction of oil products content (Figure 98). In all four samples taken from filter in the period from April to the end of September 2021 concentrations of oil products were approximately three times lower than in water from the pond. Variations of oil products content in filtered water correspond to variations in the water from the pond. Phenol was detected in three samples of water from the pond – April, May, and 30 September - varying from 0,5 to 0,8 µg/l. But there was no concertation of phenol above detection limit (0,5 µg/l) observed in samples from filter, which indicates the effect of filtering on the content of this pollutant in water but does not allow to quantify this effect.

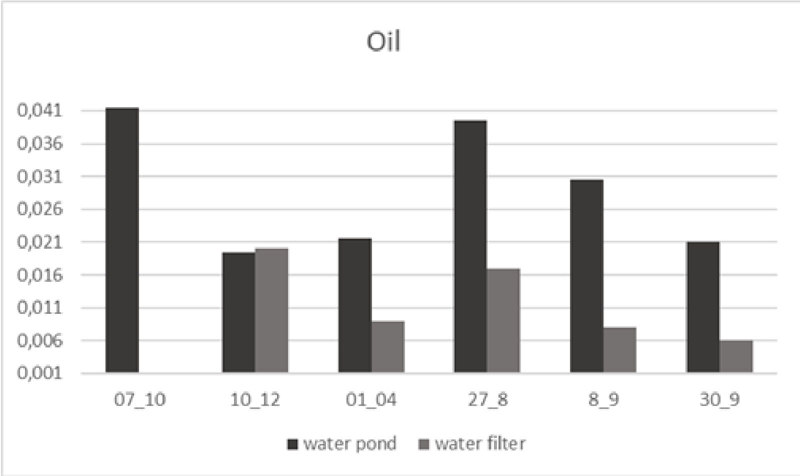


Figure 98 Effect of filtering on concentration of oil products in the water of the pond in Pionersky park.

Heavy metals.

As described in the monitoring section of this report, water in the pond in Pionersky park is characterized by elevated concentrations of heavy metals, though concentrations vary in a wide range of two orders of magnitude in different months. Filtering of ponds' water through the combined filter had different effects on analyzed heavy metals. The results of testing are illustrated by Figure 99, which demonstrates concentrations of three heavy metals in non-filtered and filtered samples from pond and non-filtered samples from filter. Significant reduction of iron and manganese concentrations were observed in the samples taken from filter in all months except for December 2020, when the filter was installed. December was characterized by the lowest concentrations of iron and manganese in water of the pond, however slight reduction of Mn concentration was observed even in December. Samples taken in the following months demonstrate a steadily increasing effect of filtering. Despite the steady growth of Fe and Mn concentrations in pond water samples taken from April to September 2021, concentrations of these metals in filtered water were steadily decreasing. Samples taken from filter in the beginning and at the end of September 2021 demonstrate reduction of iron content in filtered water more than two and manganese more than three orders of magnitude. In late September, concentrations of iron and manganese in samples from filter were below detection limits 0.01 and 0.001 mg/l respectively. The concentrations below the detection limits are reflected in Figure 99 as striped bars equal to the LOD.

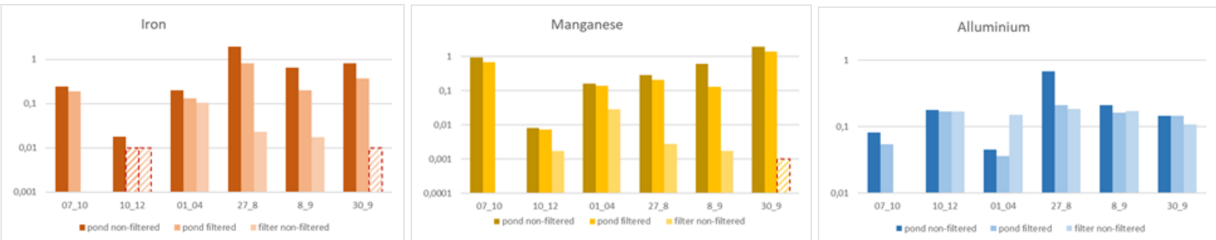


Figure 99 Effect of filtering on concentration of heavy metals in the water of the pond in Pionersky park. Striped bars indicate concentrations below the detection limit Fe=0.01 mg/l and Mn=0.001.

Concentrations of copper and zinc in samples from filter were all below detection limits (0,01 and 0,05 mg/l respectively), which indicates the reduction but does not allow any quantification and illustration of the effect. However, there was no any effect of filtering on aluminum concentration observed. In all months, except for April, concentrations of aluminum in non-filtered samples of water from filter were approximately at the level of ones measured in filtered samples of water in the pond.

6.5 Effect of active filter in storm water retention pond of the West High-Speed Diameter of St. Petersburg.

The third site where combined EM-shungite filter was tested is a retention pond of the road stormwater management system. The whole system is described in chapter 5.2. The system does not have any natural hydrological regime as it is designed to collect and treat water from Western Speed Diameter of Saint-Petersburg. The run-off from the motorway is the only water supply to the pond where the filter was tested.

The filter was installed at the exit from the pond where water from the pond enters outlet ditch to be released to the aquatic environment as shown on Figure 100. Water from the pond naturally inflowed to the filter due to the water level difference in the pond and in the ditch. Water flow through filter was set as about 3.5 liters per minute. Unfortunately, water flow in the filter was not stable strongly depending on water level in the pond. As a result, in certain dry periods the water level in the pond was not sufficient to provide flow in the filter at all.

It is obvious that contamination of water in the retention pond depends on pollutants washed out from the road. Thus, no seasonal variation of contaminants can be expected. On the other hand, contamination of the road run-off widely variates even during one rainfall. The first flush from the road surface when rain starts is always higher contaminated than the following run-off. This adds uncertainty to the study due to high variation of pollutants concentration in inlet, though, contamination of water in the pond is relatively averaged due to mixing. These notions justify that analysis based on averaging of data on pollutants concentrations throughout the whole observation period is more appropriate in this case than comparison of concentrations in individual samples. Six samples were simultaneously taken from the inlet, pond, outlet ditch and filter, all together 24 samples, as described in Table 23. The effect of the retention pond to reduce contamination of stormwater as well as the effect of the combined EM-shungite filter is described in the sections below.

Figure 100 Installation of filter in the stormwater retention pond.

Table 23 Data on stormwater quality parameters and the effect of filtering.

Parameter	Unit	inlet		pond		outlet		filter	
		Avg	Max	Avg	Max	Avg	Max	Avg	Max
pH	pH	7.2	7.4	7.2	7.4	7.0	7.3	3.6	5.6
BOD5	mgO_2/l	7.4	11.5	5.1	11.3	4.6	10.7	4.4	7.6
SM	mg/l	11.4	30.8	3.5	8.4	2.7	5.8	8.9	26.0
TN	mg/l	1.6	2.5	1.1	1.7	0.9	1.4	0.6	1.1
TP	mg/l	0.09	0.12	0.07	0.12	0.07	0.08	0.05	0.05
Oil	mg/l	0.12	0.28	0.04	0.09	0.03	0.06	0.02	0.03
Phenol	mg/l	1.48	4.72	0.76	1.00	0.72	0.90	0.61	0.61
Fe*	µg/l	2.22	6.24	0.95	1.98	0.84	1.26	6.47	13.83
Fe	mg/l	1.38	4.46	0.59	1.42	0.59	1.03	5.60	12.14
Al*	mg/l	1.48	6.39	0.27	0.54	0.20	0.34	6.48	12.87
Al	mg/l	1.30	6.39	0.17	0.36	0.14	0.26	5.37	12.14
Mn*	mg/l	0.18	0.30	0.34	1.17	0.21	0.67	0.35	0.54
Mn	mg/l	0.11	0.23	0.23	0.83	0.13	0.43	0.28	0.34
Cu*	mg/l	0.11	0.64	0.01	0.01	0.01	0.01	0.75	1.24
Cu	mg/l	0.11	0.64	0.00	0.01	0.004	0.01	0.68	1.20
Zn*	mg/l	0.31	1.04	0.18	0.55	0.05	0.08	0.93	1.25
Zn	mg/l	0.24	1.00	0.11	0.31	0.04	0.05	0.85	1.18

*Indicates non-filtered samples

Potential hydrogen, BOD5 and suspended solids.

Run-off water from the road sampled in the inlet drain in general characterized by low pH variations slightly exceeding 7 Figure 101. Potential hydrogen remains at the same level in the pond and in the outlet ditch. However, this parameter significantly differed in samples taken from the filter. pH values of water in these samples were much lower than in the pond or in the outlet ditch varying between 3 and 5,5 with average value close to 3,5. This demonstrates significant acidification of water in the filter. As expected BOD5 in the road run-off varied in wide range of values from 1 to 11 mgO2/l with average of about 8 mgO2/l (Fig. XX). Approximately the same variations of this parameter were observed in the pond and outlet ditch, but averages were twice lower than in in the inlet. Samples from filter demonstrated lower variations and slightly lower BOD5 than in the pond and in the outlet ditch.

Figure 101 Changing of pH, BOD5 and suspended solids in the water from inlet drain, retention pond, outlet ditch and filter.

Concentrations of suspended solids also widely varied in individual samples taken from inlet drain (Fig XX). Despite of average level of about 11 mg/l the highest observed concentration was as high as 30 mg/l. Average content of suspended particles in water as well as variations of the observed values was gradually reduced in the retention pond and outlet ditch demonstrating more than three times average reduction.

However, this parameter in samples taken from filter significantly exceeds concentrations observed in both the pond and the outlet ditch.

Nutrients.

Eutrophication caused by oversupply of the aquatic environment by nutrients is one of the key environmental problems of modernity. Thus, prevention of nutrients input from stormwater is one of the key environmental aspects of storm water management. In general, the road run-off at the test site was characterized by moderate concentration of nitrogen and relatively low concentration of phosphorus (Figure 102). Average total nitrogen concentration in inlet drain was about 1,5 mg/l with individual samples demonstrating concentrations up to 2,5 mg/l. The retention pond significantly reduces total nitrogen concentration in water collected from the road. Average concentration in the pond was twice as low as in the inlet drain with a narrow range of variations. Further reduction was observed in the outlet ditch. Samples from the combined filter demonstrate average concentration of total nitrogen as low as 0,6 mg/l, which was almost twice lower than average concentration in the pond. Thus, the test demonstrates that total nitrogen concentration in storm water was reduced three times after storm water treatment in the retention pond and application of the combined filter.

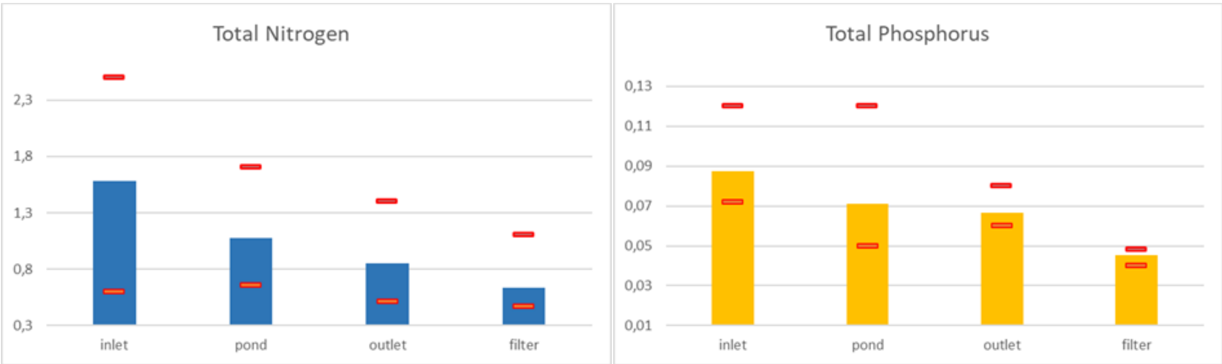


Figure 102 Changing of nutrients concentrations in the water from inlet drain, retention pond, outlet ditch and filter.

A certain effect of storm water treatment in the pond and in the combined filter on total phosphorus concentration was also observed. But this effect is not that prominent as for nitrogen, since PTOT content in the road run-off is relatively low. Average concentration of total phosphorus observed in inlet drain was slightly below 0,1 mg/l with variations in relatively narrow interval from 0,07 to 0,12 mg/l. Slight reduction of average P (up to 0,07 mg/l) content was observed in the retention pond and outlet ditch. The highest reduction of P content was observed in samples taken from the filter with an average value about 0,04 mg/l and rather low variation of concentrations in samples. So, in general the reduction of total phosphorus concentration for about 2,5 times was observed after storm water treatment in the retention pond and the combined filter.

Organic pollutants.

Run-off water from the road network is characterized by high contamination by oil products and phenolic substances. Samples from inlet drain demonstrated average concentrations of oil products and phenol 0,11 mg/l and 1,5 µg/l respectively. The highest concentrations measured in individual samples were as high as 0,3 mg/l for oil products and almost 5 µg/l for phenol. However, visible reduction of contamination by organic pollutants was achieved already in the retention pond equipped by special boom to absorb these contaminants. Average concentrations of oil products in samples from the pond and outlet ditch were three times lower than in the inlet at the level of about 0,04 mg/l. Average concentrations of phenol in the pond and outlet were twice lower than in the inlet (about 0,75 µg/l).

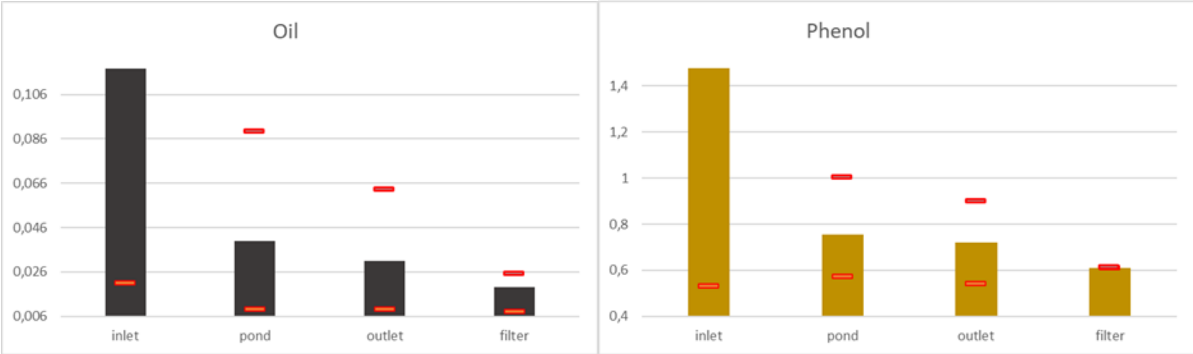


Figure 103 Changing of organic pollutants concentrations in the water from inlet drain, retention pond, outlet ditch and filter.

Samples taken from the combined filter revealed a further significant decrease of organic pollutants content in the water. Average concentration of oil products in these samples was at the level of 0,02 mg/l with variation between 0,01 and 0,025 mg/l. Observed concentrations of phenols in the filter were mainly below the detection limit (0,05 µg/l) but not higher than 0,07 µg/l. Overall, observed reductions of organic contaminants in the rad run-off after the retention pond and combined filter were almost 6 times for oil products and about three times for phenol.

Heavy metals.

Storm water from the road network at the test site demonstrated in general elevated concentrations of measured heavy metals except for lead and mercury (Figure 104). Concentrations of the two latter were below detection limits. Average concentrations of iron and aluminum in non-filtered samples from input drain were 2,2 mg/l and 1,5 mg/l respectively. Copper, manganese, and zinc were 0,2, 0,1 and 0,3 mg/l. In the retention pond and outlet ditch concentrations of these metals were visibly lower except for manganese. Average concentrations of aluminum and copper in the pond and ditch were almost an order of magnitude lower than in the inlet. Also, concentrations of iron and zinc dropped twice after treatment in the retention pond. However, concentrations of heavy metals in samples from the filter for iron, aluminum, copper, and zinc were extremely high, even higher than in the run-off water from the road.

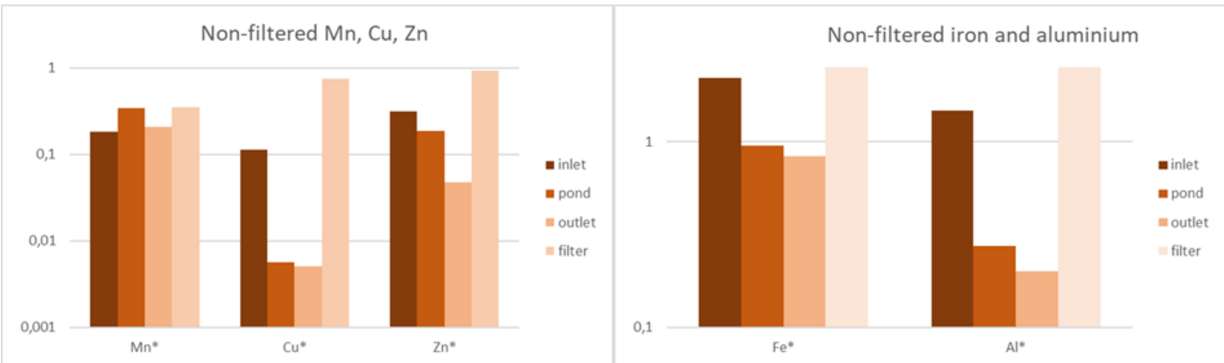


Figure 104 Change of heavy metals concentrations in the water from inlet drain, retention pond, outlet ditch and filter.

Average content of iron and aluminum in non-filtered samples was at the level of 6,5 mg/l and copper and zinc almost reached 1 mg/l. Only manganese did not demonstrate any changes. Comparison of concentration in non-filtered and filtered samples taken from the filter showed almost no difference between them for all metals (Figure 104).

7. Socio-Economic Assessment

Summary of indicators in Socio-Economical assessment consisting of feasibility studies

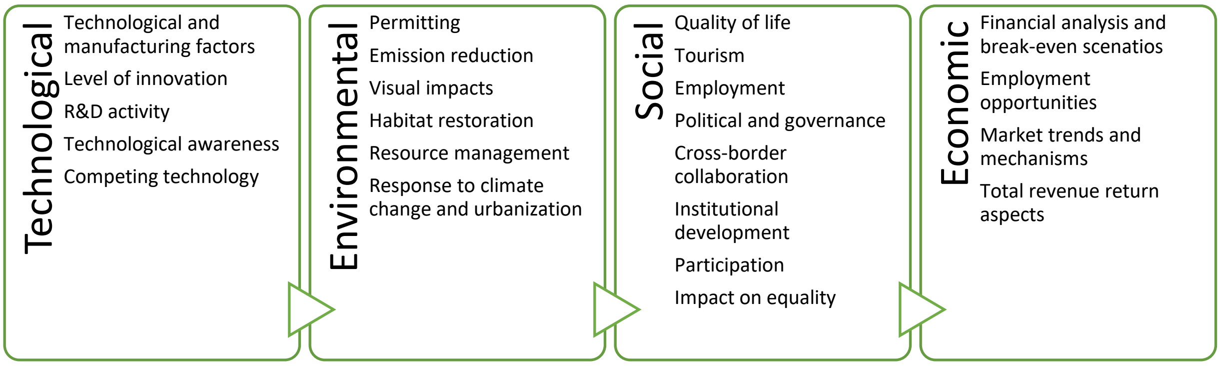


Figure 105 Summary of indicators in Socio-Economical assessment considered in the feasibility studies

7.1 Technological feasibility

As technology, the proposed purification technology is novel, and on technical readiness level after SHEM-WP project is TRL level 5-7. It was tested in a relevant environment, but commercial applications and the general concept need to be developed further. The basic concept includes mechanical filtering, natural based chemical emission reduction unit, and biological unit. The system does not require advanced level technology in applications, but development requires understanding of phenomena and role of each unit. The aim is to adapt the purification system as part of the existing drainage or wetland system, which would extend usability, but also set requirements for flexibility of solutions.

As material shungite has been applied in Russia for tens of years, and there are increasing number of industrial/commercial application developed. It is known of the health effects and applied in drinking water, and in small scale water filters. However, runoff water purification system requires technical features and capacity of system must be high. EM technology has been applied in restoration of water bodies: lakes, rivers, fishponds, etc. There are no comparable water purification concepts implemented. The presented system will benefit from a settlement pond or basin with vegetation. The aim is that the EM population would grow in its own unit and spread to recipients where the effect on natural nutrient removal cycle is seen. Seasonal variation has to be taken into account.

The system will require maintenance that can be included in the concept to ensure proper handling. The purification and re-usage of filter media are essential steps. Renewal of EM population will require fermentation period.

Biochar and activated coal filters for water purification are accepted and increasing in treatment of urban rainwater. Shungite is a coal mineral, and it has special beneficial features compared to biochar: technical durability, density, adjustable particle size, chemical sorption abilities, etc. Biochar research and applications in runoff water purification are on higher TRL level than the shungite applications. However, these biochar applications are not designed for similar runoff water filtering systems.

Annex 3 presents various concepts for purification processes applying SHEM-WP system proposed. Table 24 discuss aspects considered in technological feasibility. As technology still has room for development for more sophisticated technical solutions. One can also apply the SHEMP-WP concept as it is with minor scale-up and modifications. The system does not need huge investments, and it can adapt components from existing water purification systems.

Table 24 Technological feasibility: aspects considered in the assessment

Indicator accessed	Benefits	Costs/risks/issues
Technological and manufacturing factors	Low production costs. Feasible of LSMEs, even SMEs can adapt the technology Structure and materials can be partially adapted from existing solutions.	Commercial products will require R&D Requires understanding the special features of filtering materials. Operating requires annual maintenance and renewal of filter material.
Level of innovation	Breakthrough innovation Technical Readiness Level (TRL) 5-7, validated in relevant environment	Breakthrough innovation TRL 5-7 still requires more before the system is completed
R&D activity	Public R&D material available, namely SMEs supported during SHEM-WP project R&D on natural based solution is on focus in national and international level: collaboration and funding opportunities available Research groups specialized in shungite is available in Russia.	Requires R&D in design of the process. Combining competence and expertise in several fields is required. Technical issues in integration into a variety of runoff water purification systems. Research groups specialized in EM are globally spread, and only a few scientific studies in Nordic climate are available.
Technological awareness	Shungite has been applied in Russia for long time in various water purification. EM products are commercially available for gardening and composting in Finland. Global and national interest in natural based solutions is increasing.	EM technology is still relatively unknown and natural water related applications in cold climate are rare but increasing. Shungite as material is less studied outside Russia but increasing and available.
Competing technology	Hybrid technology combining biological units are still rare. The solution proposed is unique. Shungite mineral based solution has several benefits compared to biochar: technical durability, floating, ability to address urban contaminants via oxidation, and other sorption mechanisms.	Biochar and activated coal filters for water purification are accepted and increasing in treatment of urban rainwater. Biochar has strong research ongoing, and it can be applied as growth media for plants. Activated carbon solutions for specific purposes exist (often apply biochar and products are not technically feasible as an alternative).

7.2 Environmental feasibility

Table 25 summarizes benefits and costs/issues of environmental feasibility factors considered.

Shungite is a heterogeneous mineral that has several metals. Many of the metals, such as Fe, Al, Zn, Mg, also affect and often, namely improve the purification efficiency of filter. However, the leaching of the metals is restricted by regulations or Government Decree on Landfills (331/2013). If leaching exceeds the limits, an environmental permission is required in Finland. According to SHEM-WP study, leaching test for metals should be done for new grades entering the market. Shungite products for water purification are not commercially available in Finland. In Russia there are commercial products for water filters. There exist shungite grades that would be environmentally feasible and efficient for the purpose.

EM products are commercial products and EM cultivation/production is located inside EU and Finland. It is a global product. Main purpose is for gardening, but products are sold for improving the aquatic environment as well. No environmental permitting required in Finland. In Russia, EM is not commercially available, but it can be applied without further permitting procedures. The SHEM-WP purification system combines mechanical, sorption and biological mechanisms. The solid material floating in runoff water is removed as first step. The second step is removal of fine particles with foam and shungite layers. The fine particles contain a large fraction of urban and natural pollutants. The chemical and physical reactions continue in the purification process in shungite layer, where dissolved compounds are removed or oxidized to other less toxic compounds. Shungite layer has an effect on potentially toxic inorganic and organic compounds, which might be harmful, toxic, or volatile (odor). Organic compounds known to decrease include aromatic compounds, furans, and oils.

Variation in runoff water flow is high, and during heavy rains or snow melting, the water flushes several impermeable and permeable surfaces. As result the concentrations of solid matter and dissolved pollutants increase. The concentrations might seem low due to dilution, but due to high volume of flow, the real load to environment is seen only via masses. Figure 106 visualizes pollution reduction as mass, gram/campaign, with the hydride purification system installed in SHEM-WP. Examples are computed from Finnish field tests since the flow estimates through the field tests in St. Petersburg were not available. In Lappeenranta the whole water flows were led through filters in both sites at 2020-21 tests, and samples taken represent these flows or small settlement ponds before and after purification. Cumulative sums starting from the beginning of the sampling campaign are computed assuming volume of sampling day to represent average flow volume and concentration of average concentration on each week. Comparison is done presenting 1) cumulative mass **in influent water** flow to filters in field tests, 2) cumulative mass **in effluent after purification**, 3) mass in similar amount of lake water (**clean reference site** at Lake Saimaa, Ilkonselkä: c(N) = 0.5 mg/L, c(P) = 6 µg/L, c(Cu) = 4 µg/L, and c(Zn) = 2 µg/L (SVSY, 2021).

- In Sammonlahti CW the influent is cleaner than in Highway 6 ramp drainage flow, and in Sammonlahti field test filters the amounts of metals decreased to even lower level than in Ilkonselkä reference site. The influent load to Sammonlahti was 70 g of Zn. The filter system removed total 23 g leading to 47 g emission load during the 3 months. When compared to Ilkonselkä clean site, the similar amount of water would contain 56 g of zinc. It can be concluded that filtered runoff water contains 16 % less zinc than the clean lake water. Original untreated influent to CW contained 25 % more zinc than the reference lake site.
- Copper load in Sammonlahti was similarly decreased. The original influent and reference site water both contained about 56 g of copper. The filtering system removed 12 g of copper, and the purified water contained 21 % less copper than the reference site.
- Zn and Cu amounts were higher in Highway 6 ramp CW, and removal raters were lower, but the pollution reduction was estimated to be significant. Zink removal was estimated to decrease from 454 g to 306 g. The target based on the reference site would have been 192 g. Still 148 g removal equals to removal of 56 % of the target amount. The removal could be improved by increasing

amount of shungite in the filter, or by adding second filter unit into the pipe. However, the snowmelt is the major cause of this pollution load, and an alternative technical solution for high hydrological flow season in May might be the most efficient solution.
- Highway6 ramp CW the Cu removal was 163 g (492 g – 329 g), which is 54 % of the target. The decrease in runoff water is significant and could be improved similar way to zinc.
- Nutrient removal in both example cases was also significant. Total 2 740 g of P and 17 820 g N were removed. Still the emission load to Saimaa was 188 g of P, and 21 360 g of N.
- The nutrient removal could still be improved namely in Sammonlahti. The unpurified water contained 462 g of P, and 27 kg of N. The amounts were decreased to 295 g and 15 kg, which were 46 % and 60 % of the target. Again, the main pollution load occurred in May in time of the snow melting.
- In Highway 6 ramp the P has been removed on the same level to the clean reference site. The influent contained 28 kg of P and purified effluent 290 g, which is similar to the clean lake water reference site. Removal rate was 99 %.

The catchment aquatic system near the city has higher amounts than the reference site applied. The major environmental load appeared in May or during the heavy rains, and it could not be fully compensated with these pilot filters.

Nitrate removal occurred mainly in the settlement basin after the filter system. The removal rate of dissolved nitrate in Sammonlahti was found to increase from 20 % to 35 % when compared years 2019 and 2021, which might indicate effect of EM in the recipient aquatic system. In Sammonlahti nitrogen represented 85-90 % of total nitrogen. Nitrite-N was less than 1 %. Ammonium content varied typically 3-10 %, and removal of ammonium in the shungite filter was detected. It is also likely that some organic compounds were affected in the sorption and cultivation units and improved the natural removal cycle. Removal of organic matter in mechanical separation had a positive effect that is not evaluated here.

Significant improvement in other minor and trace metals (e.g., Al, Ni, Cd, Pb) could be detected. These concentrations were on low level in the runoff water and their removal might be detected in single case studies. Also, Fe, Mn and Mg removal occurred case dependently. Fe and Al showed correlation to P concentration, and it can be assumed these metals have formed phosphate compounds. The factors and phenomenon affecting are complex, and thus uncertainty of the results was high, and general conclusions on removal rates could not be made. Organic compounds (BOD5), solid particles, aromatic compounds (phenol) and oil compounds were found to decrease in the shungite filters. Microplastic particles were found to retain in the filters. All results were supported by the laboratory experiments. More studies on shungite sorption capacity and effect of mechanical separation of particles is required to optimize the purification system.

No or very minor effect on chloride and sulphate concentrations, or pH (conductivity) in field tests were detected. In these test sites oil or phenol compounds were not found.

Table 25 Environmental feasibility

Indicator accessed	Benefits	Costs
Permitting	EM does not require permitting in Finland.	Applying shungite in Finland would require actions, but the procedure is established, and cost is estimated 600 € per imported lot.
Emission reduction	Decrease in pollutants discharged via urban run-off water: metals, organic compounds (oils, furan), fine solid material, phosphate, odors EM improves nutrient intake by plants from the water and decreases indirectly the nutrient load to recipient. EM inhibits growth of harmful bacteria through competitive exclusion (e.g., cyanobacteria) and increases diversity of phytoplankton population. EM application initiated positive changes in the ecosystem by means of excessive organic matter decomposition (sediment)	Shungite and filter disposal after 5-10 years lifespan Shungite leaching metals have to be evaluated EM is functional only in warm water where the natural intake of nutrients occurs. Main EM effects are seen as long-term improvement, and verification would require long-term complicated monitoring of aquatic systems. Removal of sedimented nutrients and organic waste from the system (filter and bond) is required to complete the cycle.
Visual impact	Enables compact solutions that improve visual appearance of urban water elements (ponds, parks)	Requires planning.
Habitat restoration	Improved influent water quality of urban catchment areas (water bodies) Health and biodiversity in aquatic systems of bonds and other water bodies improves	New filter implementation may require land construction
Resource management	Shungite available in Karelia EM produced in Finland Landscape, land-use, spatial planning: space saving	Shungite is non-renewable and mined from a quarry EM cultivation and fermenting takes 1-2 weeks
Response to climate change and urbanization	Address “the increase of rain and storm due to climate change” issue Address the urbanization due to low space demand in spatial planning Distributed purification system is feasible to implement in existing urban and sub-urban systems (purification improvement as distributed *at-site* solution) Functional for several urban origin emission pollutants Feasible for handling of high flow and variation, if required.	Flood, melting and stormwater issues might benefit additional constructions or unit operations.

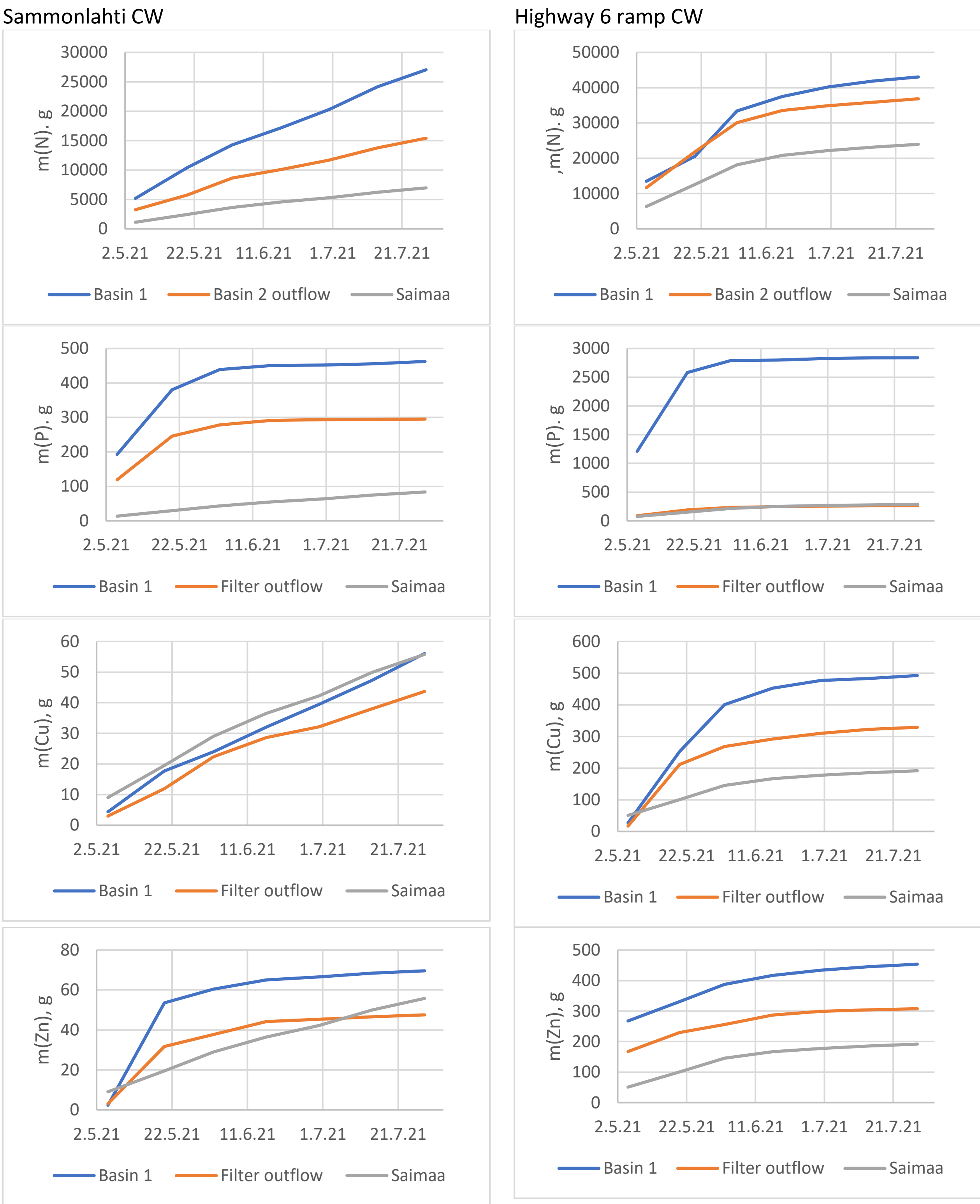


Figure 106 Comparison of masses computed via concentrations and volume flows: 1) cumulative mass in influent water flow to field filters in field tests, 2) cumulative mass after purification, 3) mass in similar amount of lake water (clean reference site at Lake Saimaa, Ilkonselkä: c(N) = 0.5 mg/L, c(P) = 6 µg/L, c(Cu) = 4 µg/L, and c(Zn) = 2 µg/L (SVSY, 2021) (Kraft, 2019).

7.3 Social feasibility

Table 26 introduces social indicators accessed. Improving quality of life would be gained via a healthier environment. The proposed purification system can be considered as a nature-based solution that can provide a multitude of services of great social, economic, and environmental values. Implementing the filter into historical constructions and other parks attracting tourists would benefit the regional economy due to increased activity. Cross-border collaboration and economy will accelerate regional development, increase business opportunities, and institutional collaboration. These changes occur at scales extending well beyond the local scale of an individual application.

In chapter “Policy relevance” the governmental and policy accelerators were addressed: UN Sustainable Development Goals 2030 , EU Marine Strategy Framework Directive, the European Green Deal, EU Biodiversity for 2030 Strategy, and EU Adaption to Climate Change Strategy were discussed. Protection of the Baltic Sea Marine environment is the ultimate goal of the Helsinki Convention (HELCOM). The main regional policy agreement – the Baltic Sea Action Plan identify measures which are to be jointly undertaken by the Baltic Sea countries to prevent contamination of the marine environment.

Basic principles of the aquatic environment protection are established by the Federal Law of Russian Federation on Environment Protection and Federal Water Code, which includes documents prohibiting discharge of untreated wastewaters in the environment and establishing regulations for storm water management.

The EU Floods Directive (2007/60/EC) and the Finland’s national legislation for its implementation include preliminary flood risk assessment, flood mapping and flood risk management planning. The municipalities are responsible for the flood risk management related to pluvial floods. Due to the legislation the handling of runoff water and pluvial flooding in urban areas have more focus in all Finnish municipalities. In addition to flood act and degrees, EU Water Framework Directive (2000/60/EC) and EU Urban Wastewater Directive (91/271/EEC) define Finnish Acts (parliament) on land use, water resource management, maintenance and cleaning of public areas, environmental protection, and nature conservation. Government and Ministries Decrees complete and define actions regulated in the Acts.

The social factors are strong motivators behind the presented methodology.

Table 26 Social feasibility indicators addressed with SHEM-WP water purification process

Indicator accessed	Benefits	Costs
Quality of life	Improved urban and sub-urban environment Improved health of citizens Allows decorative implementation and improvements in parks at residential areas.	Solutions and implementation must take into account the urban environment. The system has to be protected against vandalism and other external factors.
Tourism	Requires relatively small space and can be implemented in existing systems allows installation into historical constructions Allows implementation into parks and other relevant outlets to improve the environment Sustainable tourism values increase	Requires visually attractive or acceptable design
Employment	Low start-up costs SME-friendly business Can be an additional business opportunity to any size company	Less activity in winter months
Political and governance	See chapter “1.2 Policy relevance”	Environmental permitting might be required for land use, and environmental acceptance.
Cross-border collaboration	Russian expertise and production are most valuable in Finland for entrepreneurs, authorities, and academic bodies. EM production and increased expertise in Finland will be beneficial for Russian bodies.	Different rainwater and runoff water treatment policies and systems may cause challenges. St. Petersburg is a metropole and has special features when compared to Finnish cities.
Institutional development	Combines expertise knowledge from both countries and would benefit academic society via collaboration. Environmental and water resource management related authorities, and municipality bodies benefit from increased international and regional collaboration.	Environmental institutions and bodies have to ground their work on their own Decrees and national recommendations which might prevent international join development
Participation	Public audience will visually see impacts on cleaner aquatic bodies Urban runoff water pollution load and emission mitigation are missions every citizen can affect. Increased awareness allows indirect participation. Purification system could be available and feasible for even small houses	National restrictions and availability can narrow household applications
Impact on equity	The technology has no limitations related to gender	none

7.4 Economic feasibility

Table 27 introduces economic factors assessed in feasibility evaluation.

An economic feasibility report on SHEM-WP filter system was written by LCA consulting (Appendix 6). In the report it was concluded that based on background information it can be stated that the need for runoff water purification treatment will be increased due to increased amount of runoff water in future. Therefore, the need for the SHEM-WP business exists as well as customer base exists.

The costs analysis showed that the main benefits of the SHEM-WP process are targeted into the reduction of land use and savings for land use work. Additionally, the cost analysis shows that maintenance costs of SHEM-WP process is low, approximately 13 % of both passive filter types from overall costs. For active filters, the energy demand of pump should be added. The main costs were manufacturing of the system (3000-4000 €), and annual cost for treatment of purification liquids (as hazard waste). Total annual maintenance and implementation costs were estimated 400-500 €/filter, which includes the materials, renewal, purification, cultivation, and work costs. The shungite life span can be assumed to be at least five years with proper cleaning, and activation. According to the laboratory tests, the capacity still increased after 10 renewal cycle. The effect of high water flow could not be estimated in laboratory conditions. In field tests the results seem to support the assumption that as minimum the shungite can be applied for 5 years in filter, before it is thermally treated in high temperature (combusted in 900 ºC). The final end-use of shungite could be as highly active adsorbent. High mass-loss is expected in this final thermal step (80-90 %).

Shungite and EM could be replaced with other materials. The obvious replacement for shungite would be activated biochar. Due to high water volumes the particle size has to be preferably 1-5 mm to ensure penetration and mechanical filtering effect. Biochar physical properties are not optimal: density and durability are lower. It can be assumed that the high flow pressure will cause grinding and loss of fine particles leaching out. Re-usability of biochar in filters is questionable and would lead to increased material and waste management costs. Biochar has to be cleaned before end-use. Biochar is also lacking many sorption abilities shungite has. Thus, they are not comparable materials.

Based on the study results, it can be stated that due to low direct revenue from resale of shungite the financial risk is high. Therefore SHEM-WP business would be profitable when SHEM-WP filter system is sold as a service to municipalities. SHEM-WP process is beneficial for municipalities from land use reduction and land use work point of view as well as low maintenance costs of SHEM-WP process. Overall, due to the increased need for wetlands in the future, SHWM-WP process forms an exceptional and cost-efficient possibility for municipalities to control the runoff water formed in the urban area. In addition to saving land-use there are several socio-economic aspects that support utilization. There is a global focus on climate change. In the research region it estimated 25 % increase in precipitation. The flood risk management plans for urban and sub-urban areas will accelerate novel solutions, and the proposed shungite-EM system can be seen as cost efficient natural based solution for handling pluvial flooding waters in urban areas. The system itself is a purification system, but applicable for handling many urban pollutants in flooding water.

Table 27 Economic feasibility

Indicator accessed	Benefits	Costs
Financial analysis and break-even scenarios	Manufacturing and implementation of filters is low cost (3000-5000 €) Annual maintenance cost estimated max 500 € End-use of shungite with thermal treatment will produce highly active carbonous material	Maintenance costs mainly arise from disposal treatment costs and working hours. Total field benefits depend on indirect revenue return via saved land usage, improved environment, health, and social aspects that motivate municipalities in adapting the technology.
Employment opportunities	Global market, allow flexible business models	Might require distributed locations and travelling
Market trends and mechanisms	Global focus on handling storm water and run-off water has increased and new green/non-chemical/natural based solutions are developed. Distributed rainwater purification systems in spatial city planning are increasing globally.	Prosperity depends on the willingness-to-pay of the public sector. Requires marketing the new product for environmental authorities, city planners, and other potential customers.
Total revenue return aspects	Governmental and municipal strategy counts spatial saving and green values. Healthier and more attractive environment	Requires considering the land space savings and green values in decision making Not profitable without willingness to pay of municipalities or other customers.

8. Discussion and conclusions

1. The main goal of the project was the assessment of effectiveness of innovative natural material (shungite) in combination with effective micro-organisms (EM) for removal of pollutants from urban runoff water. For the assessment: fieldwork to collect shungite rock was arrange; a number of laboratory tests have been performed in Finland and in Russia as well as extensive field campaign to test shungite-EM filters was arranged at different natural water objects and stormwater management sites in both countries.
    a. Shungite is heterogenous material containing various functional groups, bacteria, and impurities. Four varieties of shungite rock were collected for testing and only one was considered the most applicable. Laboratory tests were used to investigate sorption capacity of these shungite species and to prove the environmental feasibility of its application as natural sorbent with leaching tests.
    b. Specific laboratory study was focused on the investigation of possible chemical and thermal treatment procedures to increase sorption capacity of shungite. In addition, this laboratory study pursued the aim to develop technological procedures for cleaning shungite rock already used for filtering with its subsequent reuse.
    c. Combining shungite material and EM in filters required specific investigation of the most suitable substrate for the EM growth. EM method involved growth of micro-organisms in filter and spread in the aquatic body from the filter. Ceramic inert material was recommended to be used as substrate for EM growth. Other alternatives could be porous lava rocks or sterilized shungite. Combined EM-shungite filters were designed in Finland and in Russia for testing at the selected test sites in both countries.

d. All together eight different sites were selected for testing combined shungite-EM filters – four sites in Finland and four in Russia. Selection of sites provided testing filters at the sites with different hydrology and chemical composition of water. Selected sites included run off water from residential and small industrial areas to Sammonlahti constructed wetlands (Lappeenranta); run off from road network next to Lappeenranta and Saint-Petersburg; water in natural lake system Dolgoe-Dudergoffskoe (Russia) and a closed pond in urban environment of St. Petersburg. Selection of these sites provided demonstration of the effectiveness of filters for purification of water with contamination originating from various human activities and characterized by various concentrations of nutrients, organic contaminants, suspended solids, and heavy metals.

2. Laboratory tests proved that shungite has the ability for selective sorption of various water contaminants. Sorption capacity of shungite depends on many parameters such as content and composition of carbon and minerals in the rock, rock structure and physicochemical properties, physical and chemical properties of filtered water, including concentrations of chemicals to be adsorbed from this water. The effectiveness of shungite-based filters also depends on the water flow regime and pre-treatment of shungite rocks. It is important to note that the capacity of shungite rocks to adsorb ions is limited and the rock starts releasing adsorbed ions when the saturation level is exceeded. Filters can also release adsorbed ions in case of changing of chemical and physical parameters of filtered water. The effectiveness of shungite rock to sorb chemicals dissolved or suspended in water can be increased through specific chemical or physical treatment of the rock. In addition, since certain bacterial communities naturally develop on shungite samples, it interferes with effective microorganisms (EM) in some cases demonstrating synergetic effects.
   a. Activation of shungite by thermal and/or chemical treatment was found essential to increase its adsorption capacity. Chemical activation applying alkali treatment of shungite material was considered to be the most economically feasible procedures to increase the capacity of anion and cation adsorption. Thermal treatment at 400-500oC was found applicable for sterilization and cleaning of shungite. The thermal treatment was recommended as a step before final alkali (NaOH) activation for the reuse of shungite filters.
   b. In addition, since certain bacterial communities naturally develop on shungite samples, it interferes with the effective microorganisms (EM) in some cases demonstrating synergetic effects. Verification was carried out with nutrient removal tests and microscopic studies (optical and scanning electron microscope). It was concluded that if EM is directly added to shungite, it boosts the growth of its own bacterial community. The bio population of shungite is heterogenous which might be beneficial for purification of urban runoff water. However, in case the bio population of shungite rock is not known, it is safer to sterilize it with thermal activation or use a separate growth chamber for EM population.
3. Combined filters integrating shungite and effective microorganisms (EM) were designed in Finland and in Russia. Though the design of filters slightly differed they all were based on a common principle providing that water flows through consequent chambers containing EM and shungite. Most of the filters used natural water flow. But one active filter equipped by electric pump was tested. All filters had mesh installed before the filtering material to remove large particles.
4. Field testing campaigns of EM-shungite combined filters were arranged slightly differently in Finland and Russia which allowed to investigate different aspects of the filter's application. In Finland testing campaigns were arranged primarily in warm season from May till September, since the field test sites were frozen in winter months until the beginning of May. Some campaigns lasted only for two months with weekly sampling. The filters technical durability over the winter was monitored. In Russia, the sampling campaigns at all test sites continued a one-year period from October 2019 to October 2020. Sixth sets of samples were almost simultaneously taken at all testing sites. Tests in both countries included sampling of water in the testing site before and after filtering.

Almost similar sets of parameters were measured at the testing sites. These parameters included pH, nutrients, organic contaminants, and heavy metals. But there were some differences between analytical methods applied in Finland and in Russia. Only filtered samples were analyzed in Finland while in Russia nutrients and organic contaminants were identified in non-filtered samples while heavy metals in both filtered and non-filtered samples. In general, the following conclusions on the application of the combined EM-shungite filters for stormwaters originating from different urban areas and natural water sites can be derived from the testing campaign.

5. Eutrophication caused by leaching of nutrients to the aquatic environment is one of the key environmental issues of the Baltic Sea and its catchment area. Diffuse sources, which stormwater belongs to, are considered as a dominating source of nutrients, especially phosphorus. In general, combined filters demonstrated high efficiency to remove phosphorus. Laboratory tests demonstrated moderate ability of shungite to absorb phosphate anions. But since shungite also sorbs organic contaminants it is highly likely that shungite based filters also remove phosphorus from organic compounds. In some cases, concentration of phosphorus in filtered water was decreased more than an order of magnitude which might be a result of chemical reaction between phosphate and iron ions leaching from sulphides contained by shungite with subsequent precipitation of iron phosphate compounds in the filter. High ability to remove phosphorus was demonstrated at the test sites with elevated P concentrations such as the pond in Pionerski garden (St. Petersburg) and Highway 6 ramp filter (Lappeenranta) or stormwater retention pond (St. Petersburg).

   On the other hand, shungite based filters did not demonstrate high efficiency for nitrogen removal. Both laboratory tests and field observations demonstrated that shungite does not absorb nitrates but absorbs ammonia cations. Slight reduction of total nitrogen concentration in filtered water might also be explained by removal of nitrogen containing organic contaminants. Particularly, this effect was observed in storm water retention pond (St. Petersburg) where average total nitrogen concentration in water from filter was almost twice lower than in outflow from the pond. Field tests In Finland demonstrated the increase of nitrogen removal in the secondary basin after the filter. Compared to reference years 2019 or 2020, the removal of nitrogen was clearly improved, which suggests EM functioning in the recipient aquatic system. The natural removal of nutrients is found to decrease when temperature decreases (in September or early October). It can be assumed the EM being active in aquatic environment when temperature is higher than +10 ºC (+6 ºC).

   Various organic contaminants are typical for runoff from urban areas. It results in high biological oxygen demand as well as in contamination of aquatic environment by oil products and aromatic organic compounds such as phenol. Combined EM-shungite filters demonstrated high efficiency for removal organic contaminants from water. In almost all field tests BOD5 in water from filters was significantly lower than in the water. In some test sites characterized by high level of organic contamination such as pond in Pionerski park (St. Petersburg) BOD5 in water from filter was more than an order of magnitude lower than in the pond.

   Ability of shungite filters to adsorb oil products was demonstrated by both lab and field tests. But it largely depends on concentrations of oil products in water. Filters demonstrated high efficiency to remove oil products at relatively elevated concentrations. The removal mechanisms do not include only chemical sorption but also physical ones, and in filters the removal of oil compounds could be improved by applying commercial foam layers specific for oil capture. In the field tests filters revealed the ability to reduce oil concentration in water up to five times (pond in Pionerski park), but at the level of oil products concentrations below 0,01 mg/l almost no reduction was observed. Shungite filters also remove phenols, but the effect is hardly quantifiable due to general low concentrations of this contaminant in the water of field test sites.

Laboratory tests revealed that shungite has high ability of selective absorption of heavy metal cations. Various tests demonstrated high absorption of copper and zinc. On the other hand, lab tests did not show absorption of iron, but on the contrary, leaching of this metal from shungite rock. However, field tests demonstrated that concentrations of iron and manganese in water samples taken after filtering were lower than in the influential water. It might be partly explained by filtering particles. But a comparison of filtered and non-filtered samples showed that iron and manganese present in surrounding water primarily in dissolved form while removal rate was in some cases more than an order of magnitude. Removal of iron might be explained by reaction between iron and phosphate in filter due to slight lowering of pH resulting from oxidation of sulfides in 117hungite, with subsequent filtration of iron phosphate particles. But this hypothesis is to be proved by further studies due to the complex factors affecting natural material and urban water flow. When iron concentration was higher than aluminum concentration in Sammonlahti CW, a positive correlation was found between phosphorus and iron ions. However, as aluminum concentrations increased this correlation diminished and it was assumed phosphorus to form phosphates with Al instead of Fe. It was also found that in seasons with very low or no inflow- the algae started to grow inside filters, and after one week the filter started leaching phosphates and Al or Fe, that supports forming of $AlPO_4$ and oxidation of iron compounds. The amount of leaching out was obviously small due to low flow rate.

Field tests fully proved efficiency of shungite filters to remove copper and zinc from water. Unfortunately, quantification of the removal rate was not possible due to low concentrations of this metals in water in Russian samples. As a result, concentrations of copper and zinc were below detection limit in almost all samples from filters in St. Petersburg field tests. However, Finnish laboratory verified the removal of Zn and Cu, applying analytical method (ICP) with lower detection limits. Even though the concentrations in runoff water are low, they were found to be higher than in the reference lake water site. The filter could remove these metals in Sammonlahti to the same level as in the reference site. In Highway 6 site the concentrations in runoff water were higher and the goal – reference concentration – was not reached, though, the observed improvement of water quality demonstrated the removal of Cu and Zn. At the same time, field tests did not reveal any effect of EM-shungite filter on the aluminum concentrations, which were relatively low.

Nickel adsorption in filter was observed only when its concentration is relatively high. Due to the adsorption mechanism of Ni, it competes with Cu and Zn. In higher ionic presence of these three elements, the adsorption of Cu > Zn >> Ni. According to preliminary lab studies, in case of relatively high ion concentrations of Cu and Zn, they prevent Ni adsorption on the surface and start replacing Ni ions bound to shungite surface via ion exchange. This might also cause leaching of Ni from shungite.

6. Several specific physical and chemical processes were observed during field testing campaigns. Effectiveness of combined EM-shungite filters changing with time. Field observations demonstrated an increase of the capacity of filters to remove phosphorus, heavy metals and reduce BOD during the year of observation. In many cases, the highest effectiveness was observed after almost a year of exploitation, when the removal rate of these contaminants increases by an order of magnitude (e.g., the pond in Pionerski park).

   Another observed effect was significant reduction of hydrogen index in filtered water with simultaneous growth of heavy metals concentrations at one of test sites. These processes were observed in one filter established in the water retention pond of the North West High-Speed Diameter of St. Petersburg. Almost all water samples taken from filter demonstrated pH twice as low as pH of water from the pond. At the same time concentrations of copper, zinc, iron, and aluminum were almost ten times higher than in the pond. This phenomenon might be explained by decomposition of sulfides with subsequent release of sulphur containing anions and metal cations to water. This hypothesis can be proven by the fact that concentration of manganese in samples from filter which is almost not present in sulfide minerals remained unchanged. Increased concentrations of aluminum could be explained by its losses from aluminum silicates contained by shungite rock. The fact that this oxidation process was observed only at one test site is explained by water flow regime. Since water level in the storm water management system strongly depends on precipitation, in dry periods water level in filter was such low that it did not cover shungite rocks and they contacted with atmospheric oxygen which resulted in oxidation of sulfides and leaching of heavy metals and sulphate ions. Soil oxidation, known in areas comprised of rocks with high content of sulfides, exemplifies the same process. Unfortunately, sulphur concentration was not monitored at this test site.

7. Despite the facts which prove efficiency of combined application of EM and shungite for the removal of contaminants from water the subject requires further investigation to fill in a number of knowledge gaps.
    a. One of the key aspects of the efficient use of shungite as filtering material is its composition. Additional studies, including geological, mineralogical, and geochemical investigation of the rocks are needed to identify varieties which are the most suitable for application in filters.
    b. Sorption effect of combined filters visibly depends on conditions where the filter was used. It includes water flow, temperature, and pH parameters as well as operational time. Field tests proved that sorption capacity of shungite material is limited, it should be regularly cleaned with thermal treatment and NaOH for further reuse. All that effect physical and chemical properties of the material and consequently its sorption capacity.
    c. Design of filters requires further investigation to develop constructions which would be the most technologically suitable and economically feasible for application in different conditions. The main challenges are defined are the high flow rate, variation in flow rate, and prefiltering of solid material flooding in the flow.
    d. Further study of the sorption properties of shungite rocks is needed. Only a limited number of priority contaminants were investigated. Ability of shungite rock to absorb legacy organic contaminants such as TBT or emerging pollutants such as PFAS, pharmaceuticals and microplastics require further investigation.
    e. EM chambers could be developed further to ensure the growth of EM inside the chamber (filter) for the warm season. The recipient aquatic system plays a major role in nitrogen removal, and to ensure EM efficiency in it, the design of this secondary and settlement basin should be taken into account.
    f. Technological aspects of application of filters based on EM and shungite rocks are to be further developed. It includes the development of technical guidelines for the cleaning and reactivating of shungite material, recommendations on water flow, temperature, and other technical parameters.

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APPENDICES

Appendix 1 Analytical instruments applied

Short description of main analytical methods and samples preparation procedures in LUT

	Analytical method	Instrument	Analytes	Sample preparation
1	Ion-selective electrode (glass probe)	Knick Kondukto-meter 702	pH Conductivity	Mixing the sample before the analysis, measured in 60 min from sample arrival to laboratory. SFS 3021:1979 SFS-EN 27888:1994
2	Ion chromatography	Thermo Scientific Dionex ICS-1100	Cl^-, NO_3^-, SO_4^{2-} (cation: NH_4^+). PO_4^{2-} concentrations were under detection limit	SFS-EN ISO 10304, Modified ISO 7150-1:1984 Filtered, 45 µm
3	Ion-selective electrode	Consort multi parameter analyzer C3040	NH_4^+ (NO_3^-)	Direct measurement (non-filtered)
4	High-temperature-combustion	Shimadzu Total Organic Carbon Analyzer TOC-L series	Total dissolved nitrogen, TDN. TOC	Total concentrations, filtered 45 µm
5	Gas chromatography (with solvent extraction)	Various instruments	Hydrocarbon oil index	ISO 9377-2:2000, SFS-EN 14039 *SFS*-EN *ISO 9377*-2:2001
6	inductively coupled plasma mass spectrometry, ICP-MS	Agilent Technologies 7900	Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Te, Au, Hg, Pb, Bi, U, P	SFS-EN ISO 17294-2:2016, in-house method calibrated against accredited methos
7	Scanning electron microscope, SEM, images	SEM: HITACHI SU3500	image	In-house methods, drying and coating when applicable
8	energy-dispersive X-ray spectroscopy. EDS mapping	ThermoScientific UltraDry	chemical element distributions	SEM and EDS apply same samples
9	Raman spectroscope	Thermo Scientific, DXR3xi with OMNICxi software	Microplastic and mineral identification	In-house Fenton treatment for microplastics analysis Drying of shungite rock samples for mineral identification.

Short description of analytical methods and samples preparation procedures in Russian lab.

	Analytical method	Instrument	Analytes	Sample preparation
1	Direct measurement	Combined measuring instrument, Seven 2GO S model S2 with pH-electrode In Lab Expert Pro-ISM-IP67	pH	Mixing the sample before the analysis
2	Iodometric method, titration	Digital titrator (mechanical single-channel BIOHIT)	Biological oxygen demand	Mixing the sample before the analysis
3	Photometry	Spectrophotometer laboratory model DR-2400	Chemical oxygen demand	Oxidation by potassium bichromate in an acidic environment
4	Photometry	spectrophotometer KFK-3KM	NH_{4+}	Filtering through membrane filters, pore diameter 0.45 µm
5	Gravimetric	Electronic laboratory scales GH-252	Suspended matter	Mixing the sample before the analysis
6	Photometry	UVmini-1240 spectrophotometer (Shimadzu)	Total phosphorus, TP	Oxidation with potassium peroxydisulfate, the molybdenum blue method with reduction by ascorbic acid. Autoclavation for 25-30 min, T=132°, P=0,2 MPa
7	Fluorometric	Fluid analyzer Fluorate-02, modification "Fluorate-02-3M"	Oil products	Extraction of the full volume of the sample with hexane.
8	Gas Chromatography	Gas chromatograph GC-2010	Phenols	Mixing the sample before the analysis
9	Chemiluminescence	TOC-Vcpn Total organic carbon and nitrogen analyzer (Shimadzu)	Total nitrogen, TN	Method of catalytical oxidation of nitrogen in water and determined instrumentally by chemiluminescence
10	ICP-OES, plasma-optical emission	Emission spectrometer with inductively coupled plasma IRIS Intrepid II XSP RADIAL	Metals filtered	Filtering through membrane filters, pore diameter 0.45µm, preservation by concentrated HNO3 2-5 ml/dm3 (up to pH <2)
11	ICP-OES, plasma-optical emission		Metals non-filtered	Preservation by concentrated HNO3 2-5 ml/dm3 (up to pH<2)
12	Cold steam method	Mercury Analyzer	Mercury	

Appendix 2 SEM and EDS images of shungite

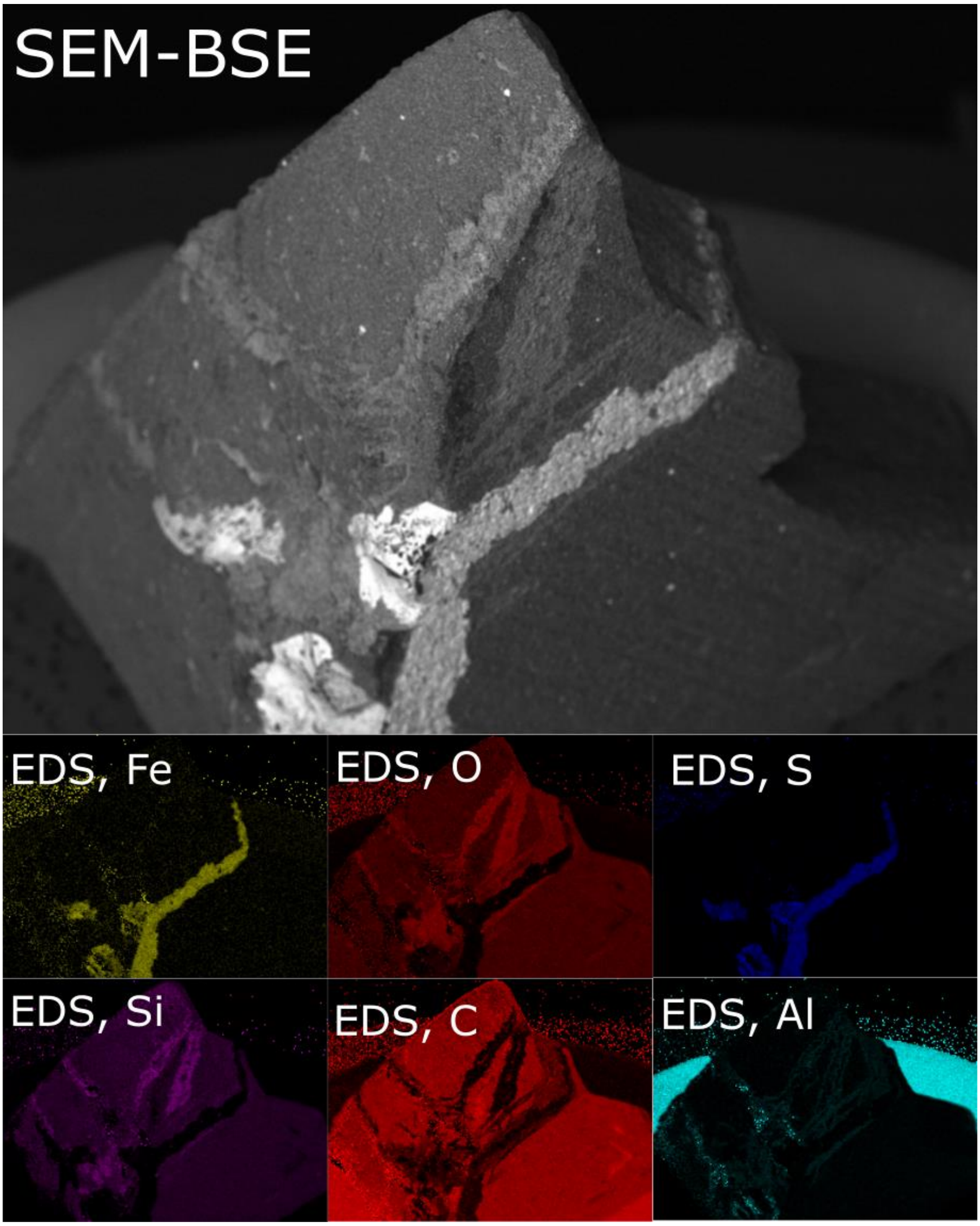

Figure 1 of Appendix 2

Example of high carbon content shungite rock SEM image and elemental EDS maps of six chemical elements on surface. Surface is covered with carbonous compounds. FeS and $FeSO_4$ regions can be visually detected as well as silica compounds. Aluminum is present as a minor element.

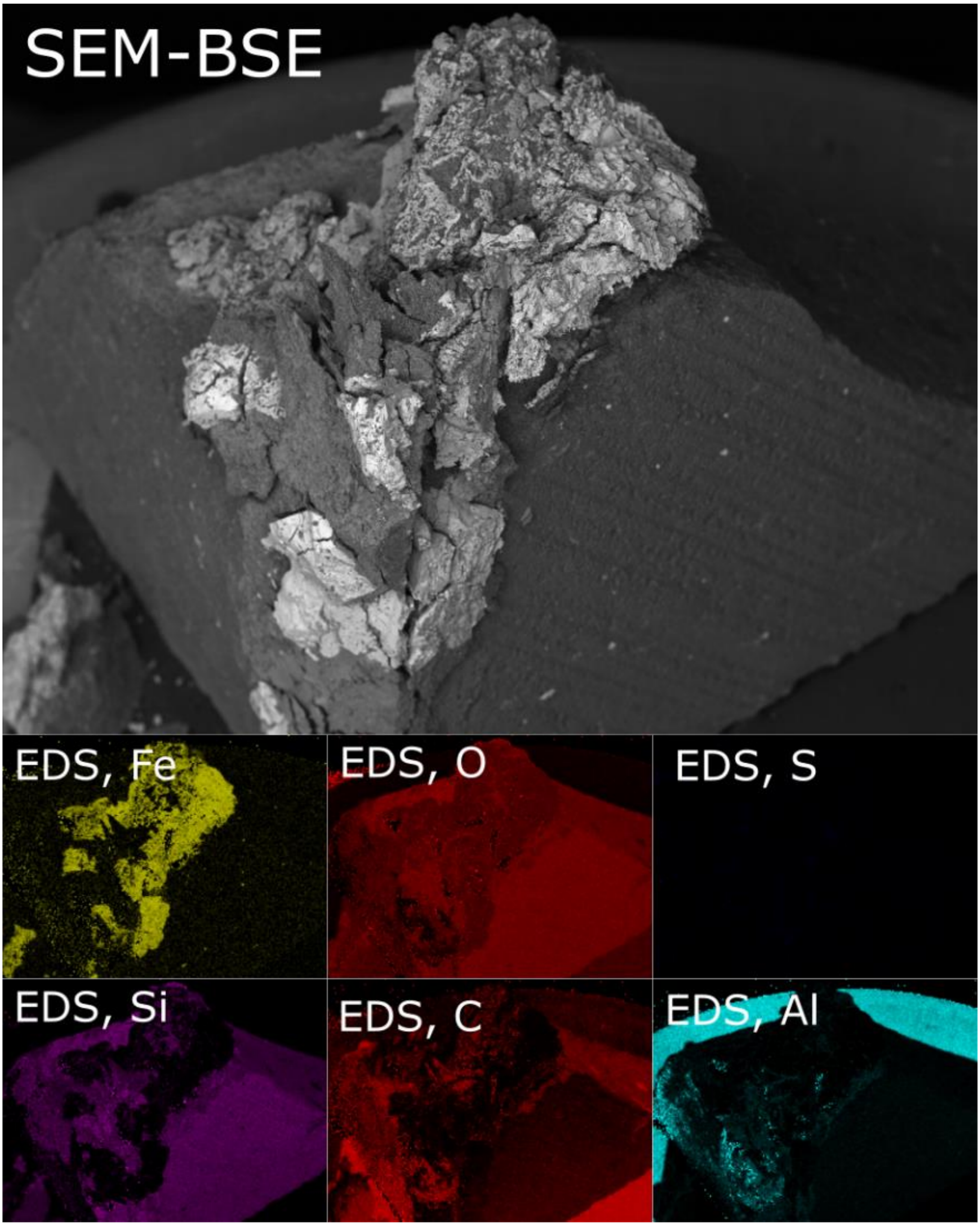

Figure 2 of Appendix 2

The structure of shungite rock were affected when treated in 900 ºC: SEM image and elemental EDS maps of six chemical elements on surface. Surface is covered with carbonous compounds. Sulphur from FeS and FeSO4 compounds disappeared.

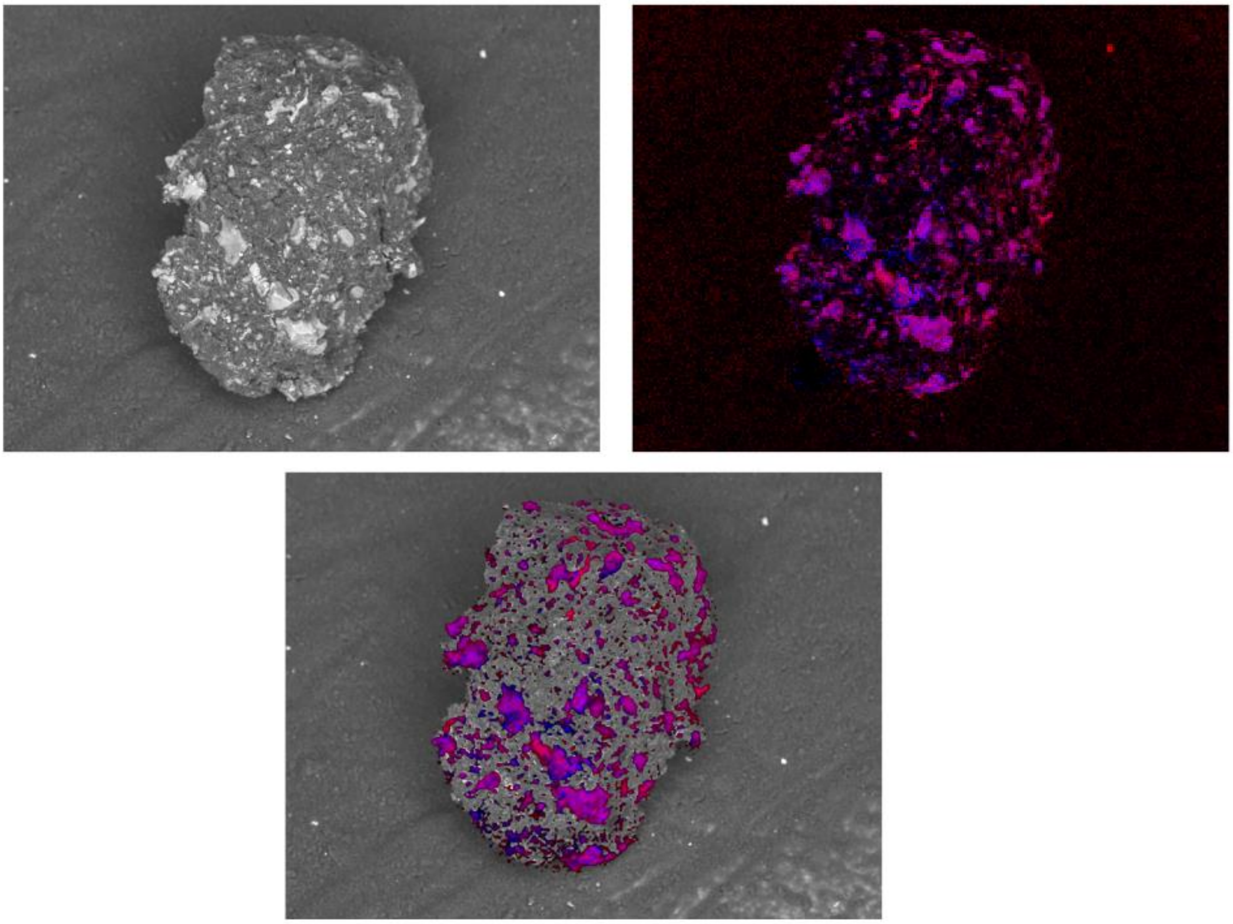

Figure 3 of Appendix 2

Low carbon content shungite example: SEM image of particle, and EDS maps of Oxygen (red), Silicon (blue), Silicon oxide (purple) projected on the particle. In SEM images the heavier element that conduct electricity well are often seen as brighter regions. Shungite contains silica compounds that have metals. However, some of the metal ions occur also as sulphides and sulphates. EDS maps of surfaces could be utilized in defining chemically active groups and sorption mechanisms.

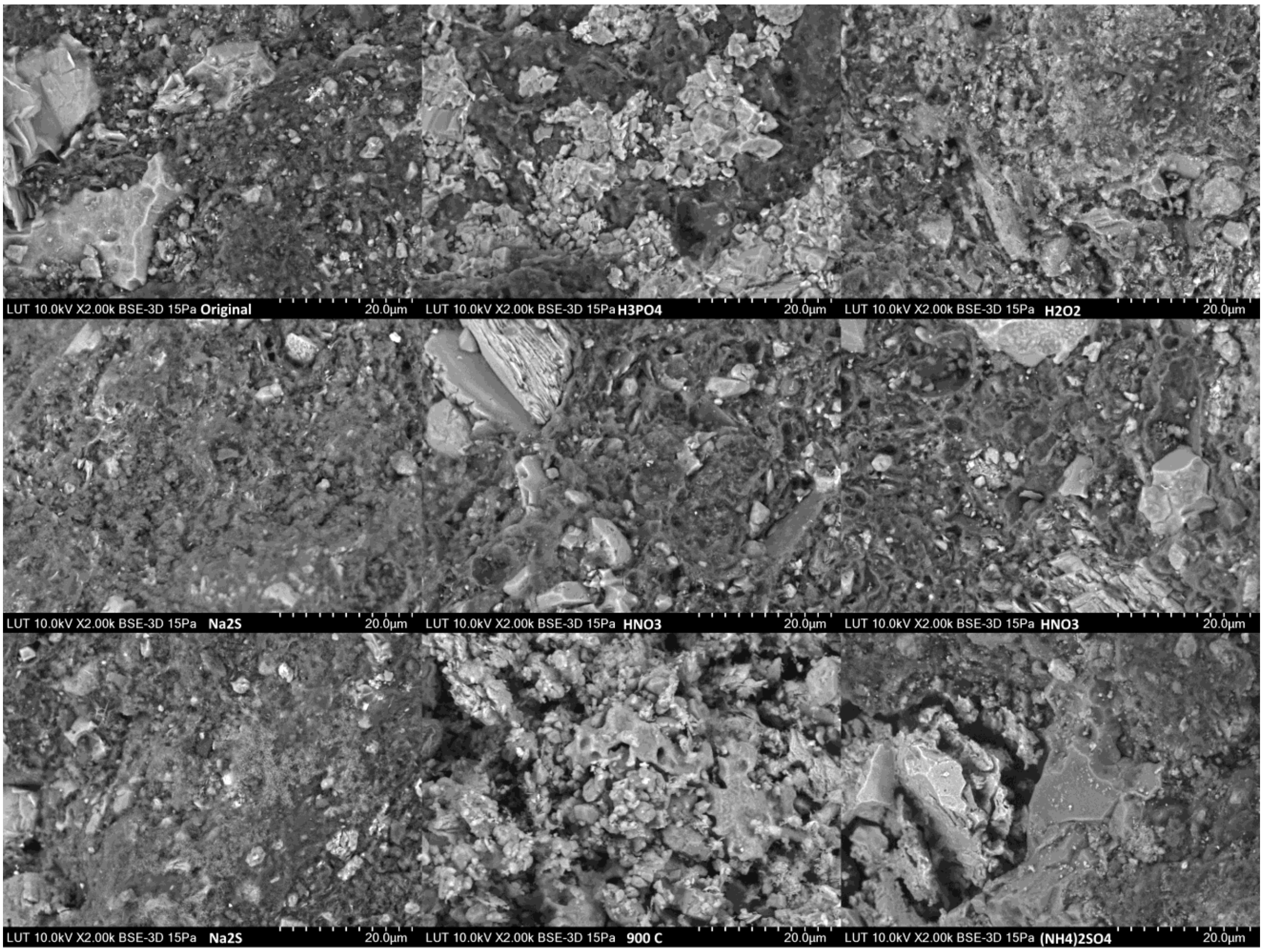

Figure 3 of Appendix 2

Examples of SEM images of shungite rock surfaces treated with various activation chemicals.

Appendix 3: Concepts of purification processes applying SHEM-WP system

Figures illustrate 6 different runoff purification processes

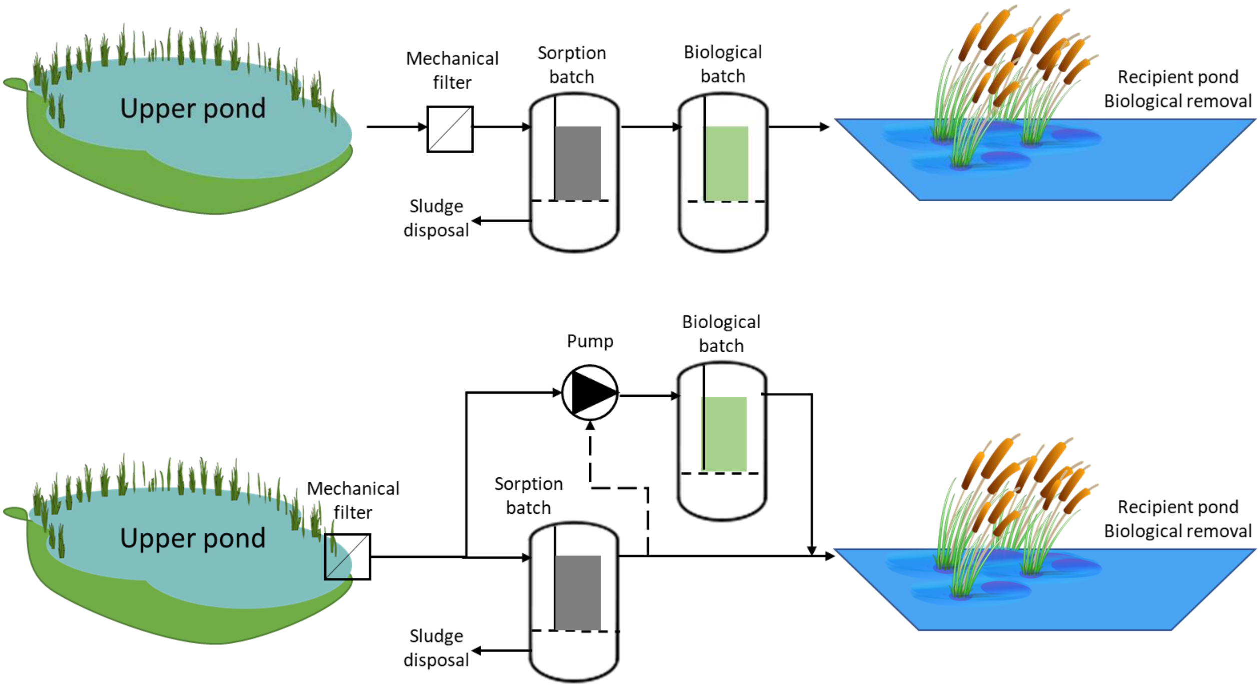

Figure Appendix 3.1

On ground purification processes contain mechanical filtering, sorption unit and biological unit. Sorption and biological units are either 1) in line without backflow option (upper) or 2) parallel (lower). Pump can take constant flow either before or after the sorption unit. Applicable for example between two ponds. Solutions are aiming to keep biological cultivation unit separate from the other units. Special attention can be paid to biological unit and the impact of microorganisms in the recipient pond. Latter design also allows optimization of EM cultivation. Option 1 is easy to implement and manage. It can be recommended, when there is low variation in inflow.

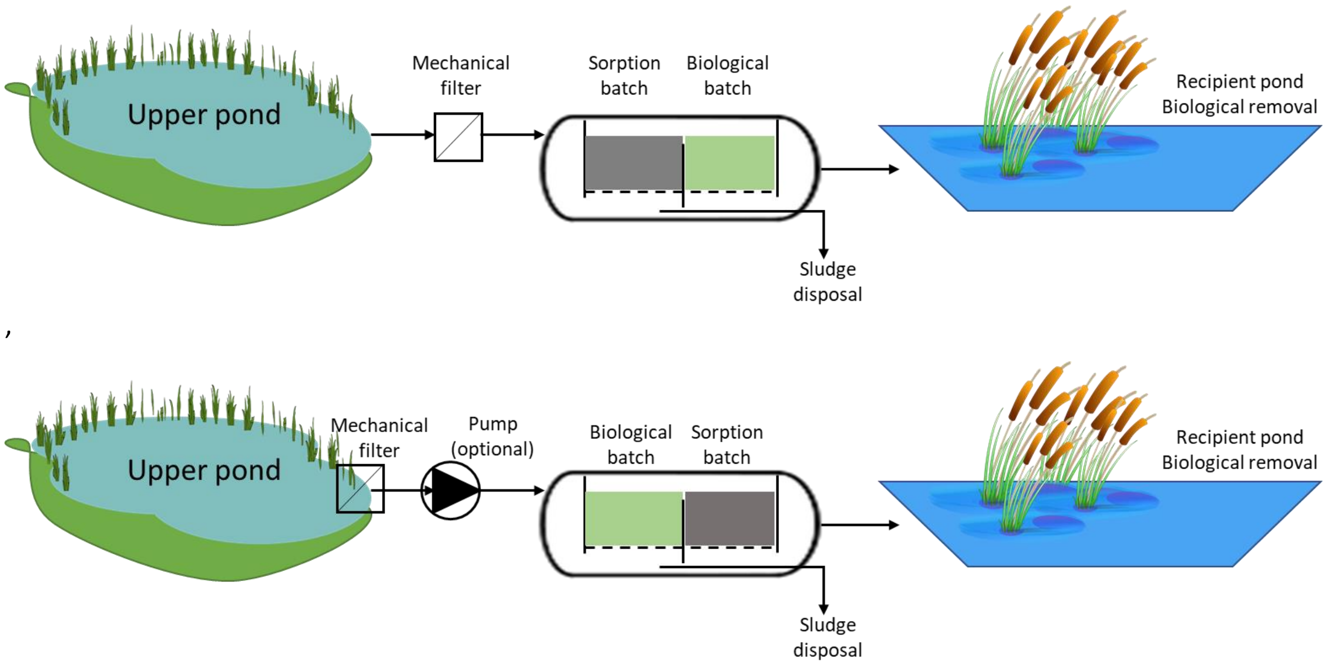

Figure Appendix 3.2

On ground or into water landscape solutions: sorption unit and biological unit are merged. Flow goes through both batches. EM microbes spread to the whole purification unit, and the whole unit serves as a cultivation chamber. EM boosts all microbial growth in shungite and foam material. The sorption unit can be applied as filter for small particles and chemical compound reduction either before (1) or after (2) the biological unit.

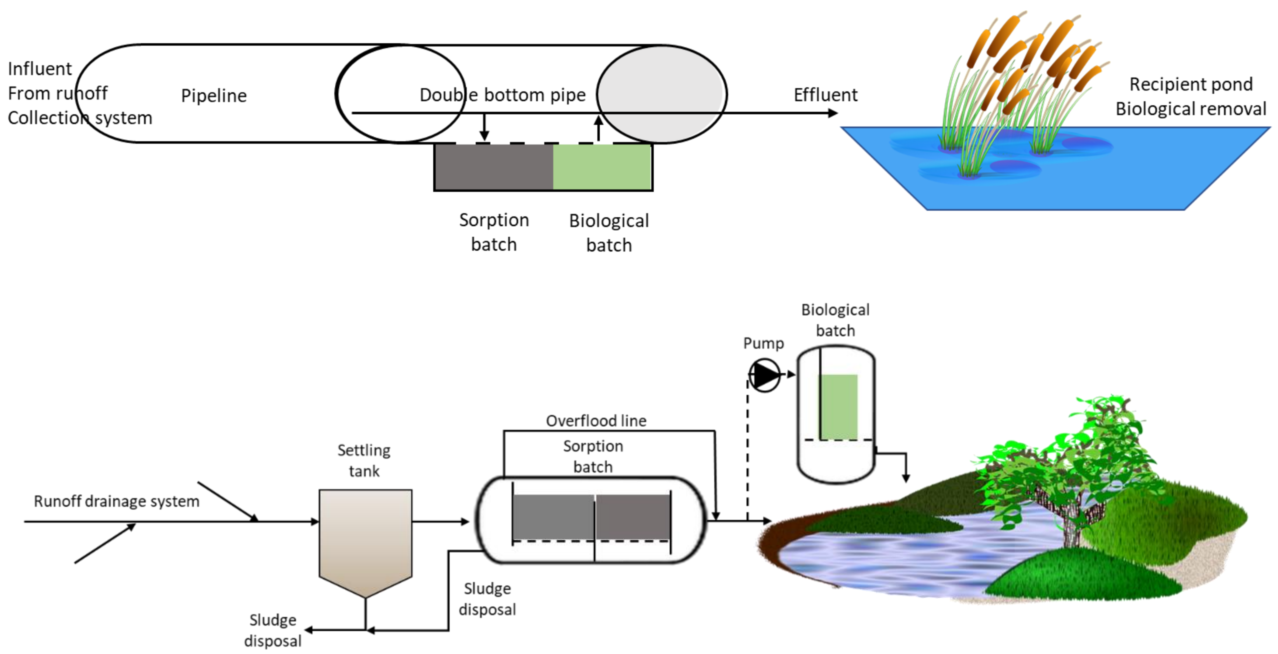

Figure Appendix 3.3 Underground or in-transportation-system solutions. 1) System implemented in pipeline, 2) sorption unit implemented into runoff drainage system and independent biological unit is applied to dose cultivated EM to recipient aquatic system or soil at shore.

Table Annex 3: alternative variations in units and inflow

Discussion	Field test	Influent control	Sorption unit	Biological unit	Flow mixing between units	2nd settlement pool or pond
1. <u>Independent chambers: On ground.</u> EM does not affect shungite or foam microbial growth. Mechanical and sorption units purify water entering biological units. Microorganisms live in their cultivation chamber. Flow rate depends on precipitation and surface level on the upper pond. (Fig 3.1a)	Yes	No	1st	2nd	No	Yes
2. Independent chambers: On ground Otherwise, similar to #1 <u>but influent to biological unit is controlled</u> ensuring optimal flow rate. Influent to sorption unit is natural. (Fig 3.1b)	No	**Yes**	1st	2nd	No	Yes
3. Independent chambers: On ground or into waterbody <u>Biological unit is before the sorption unit</u>. EM will affect microbial growth in sorption unit and foams (if applied). The inflow to biological unit is not purified and contaminants have an effect, but the influence also contains more nutrients and bio-populations.	No	No/Yes	**2nd**	**1st**	No	Yes
4. Through chambers flow: Into pond Inflow to system is controlled with <u>an electronic pump</u>. Flow mixing between sorption and biological is allowed. EM can apply the sorption material (shungite) as growth media. (Fig. 3.2)	Yes	Yes	1st	2nd	**Yes**	Yes
5. Through chambers flow: Into waterbody Purified effluent with EM is released to a river or large water landscape. Effect of EM might be hard to define, and cultivation chamber should be of relevant size. Otherwise, similar to #4 (Fig. 3.2)	Yes	Yes	1st	2nd	Yes	**No**
6. Through chambers flow: On ground or into waterbody The order of biological and sorption units can be changed. That would increase the surface area and delay EM growth media. (Fig. 3.2)	No	Yes	**2nd**	1st	Yes	Yes
7. Horizontal flow: **Underground/into pipelines** Implementation into pipeline or sewer system. Less sensitive to vandalism. Maintenance issues. Implementation might require construction work. (Fig 3.3a)	Yes	No	1st	2nd	Yes	Yes
8. Shugite filter: Underground/into pipelines Sorption and mechanical filtering can be applied without the biological unit. Feasible when outflow from filter is to runoff water transportation system, and growth of bio-population in it is not desired. The biological unit can be placed next to the settlement pool or pond and operated independently from shungite filter, or the unit can apply namely water purified with the shungite unit as influent. (Fig. 3.3b)	No	No/Yes	1st	**none**	No	No

Appendix 4 Economic feasibility assessment by LCA consulting

City of Lappeenranta

Heli Kumpulainen, LCA Consulting Oy
26.10.2021

Economic Feasibility Study of SHEM-WP Filtration System

City of Lappeenranta

20.12.2021

CBC 2014-2020
SOUTH-EAST FINLAND - RUSSIA

Funded by the European Union, the Russian Federation and the Republic of Finland.

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Content

1 INTRODUCTION

Many urban areas have a high portion of impervious surface of their total urban area. Urbanization as well as scarcity of land use tends to increase the share of impervious surfaces. Risks concerning pluvial flooding increases as result of intense rainfall. During heavy precipitation, water cannot infiltrate into the ground, thus storm water loads both municipal wastewater treatment as well as natural water reservoirs in a form of runoff water.

Climate Adapt has estimated, that due to climate change, intense precipitation events are more likely to become more frequent (Climate Adapt, 2021). According to estimations heavy precipitation during winter in the City of Lappeenranta and the City of Saint Petersburg urban area tends to increase when yearly estimations are formed from 1971-2000 to 2071-2100 (figure 1). Increase rate varies from 25 to 35 % from the initial situation for both cities.

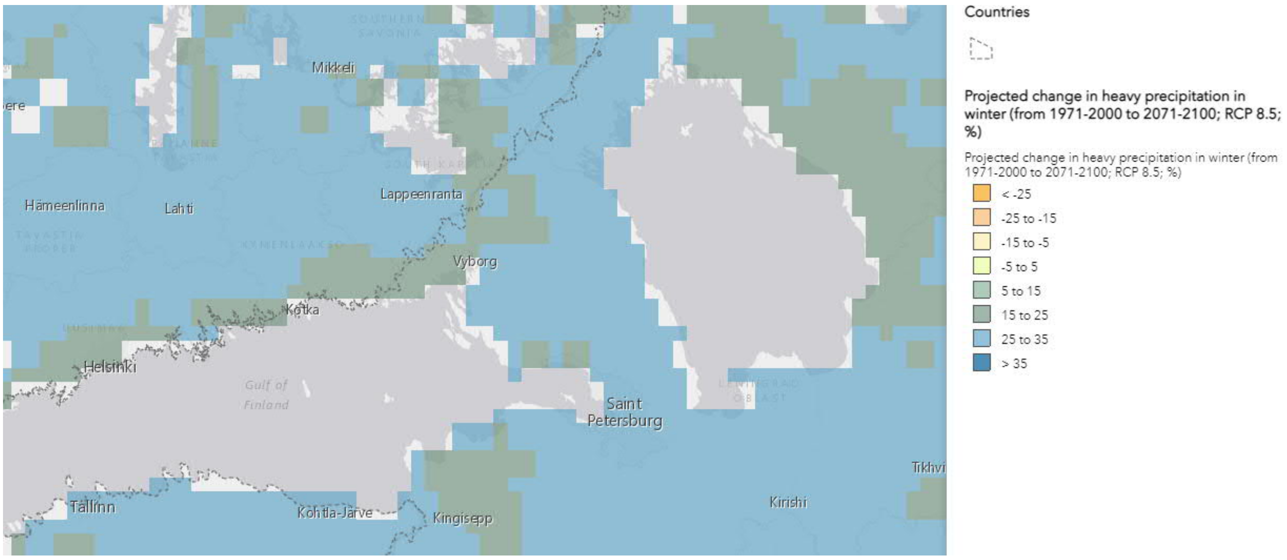


Figure 1. Projected change in heavy precipitation in winter.

Heavy precipitation in the cities varies during different seasons and yearly and may have high local peaks. In 2019, the total rainfall at the City of Lappeenranta has been 600 mm and St. Peterburg 525 mm (figure 2).

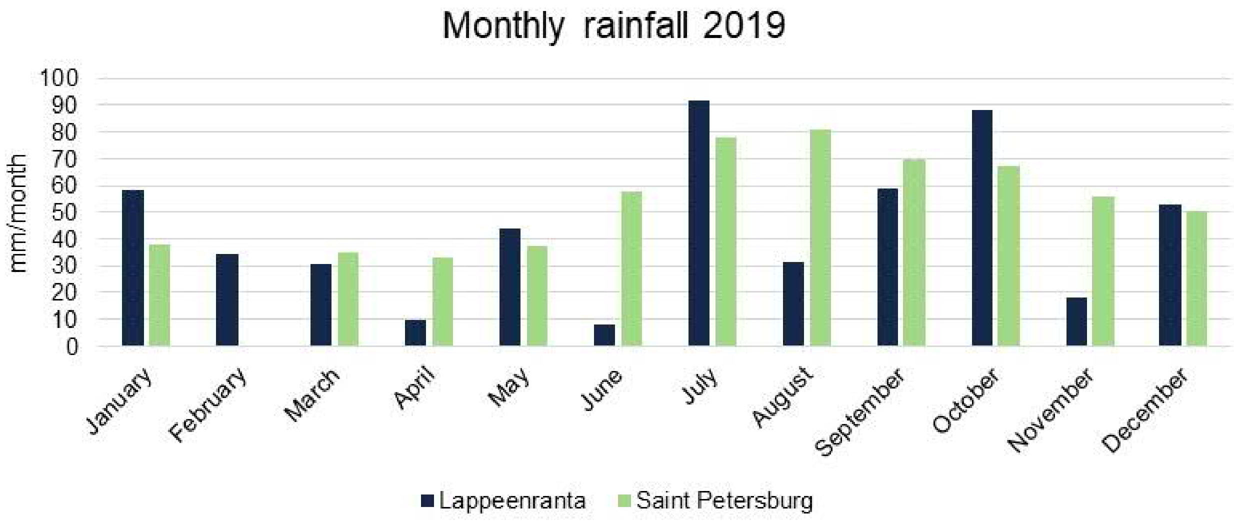


Figure 2. Example of annual (2019) precipitation at city of Lappeenranta and St. Petersburg.

As the rainfall hits on the ground, it divides into several different fractions which will burden different infrastructures based on the stream flow and the structure of surface. When the amount of impervious surface is less than 10 %, partly (40 %) rainfall will evaporate into atmosphere, partly infiltrate deeply into ground (25 %), and partly (25 %) shallow infiltrate into ground. Runoff water is formed 10% of total rainfall (figure 3).

As the impervious surface increases to be 35-60 %, then 30 % of all rainfall will evaporate into atmosphere, 20 % infiltrate deeply into ground and 15 % shallow infiltrate into group. Runoff water is formed 30 % of total rainfall. As the amount of impervious surface increases over 75 %, then 30 % of all rainfall will evaporate into atmosphere, 10 % infiltrate deeply into ground and 5 % will shallow infiltrate into ground. Runoff water is formed 65 % of total rainfall (figure 3). Formed runoff water loads municipal wastewater treatment plant and whole sewage system.

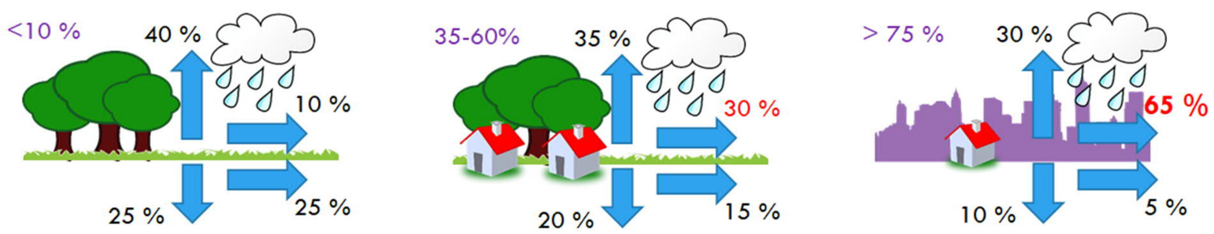


Figure 3. Relationship between impervious surface and surface runoff. In natural or sub-urban environment typically has less than 10 % impervious surface, while in the most common urban area about 35-60 % is pawed. In megapolis, such as St. Petersburg, even 75 % of surface can be impervious.

City of Lappeenranta is full of impervious surfaces. Change in impervious surfaces during three years period has been even up to 60-80 % compared into existing sealing (figure 4).

When excluding all surrounding area and concentrating only for central area at the City of Lappeenranta, it can be acknowledged that approximately 40-50 % of the central area of the City of Lappeenranta is impervious surface. Especially this area increases the risk of runoff water flooding during intense rainfalls, as the runoff water formed in this area is yearly approximately 180 mm/m^2 (180 000 m^3/km^2).

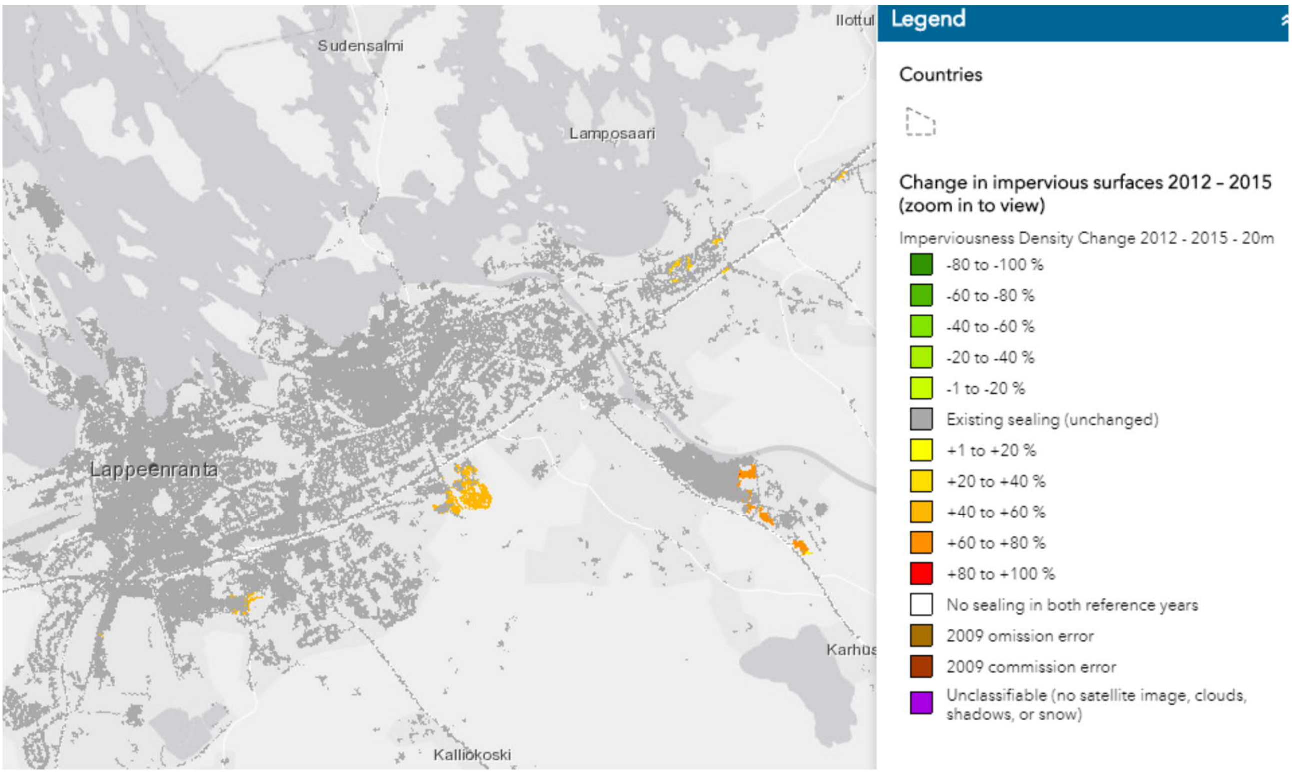


Figure 4. Change in impervious surfaces 2012-2015 in Lappeenranta region.

When combining the information from picture 3 and 4 it can be acknowledged that 30 % of total rainfall is formed as runoff water. Additionally, it has been acknowledged that wastewater treatment plant of the City of Lappeenranta treats approximately 30 % more water than is fed into the water network. The main water purification plant of Lappeenranta (Toikansuo) treats about 6 Mm^3/a, which equals to annual precipitation of 10 km^2 area in the region or run-off from 30 km^2 urban area (Lappeenrannan Energia, 2021). The zoning area of Lappeenranta city is 177 km^2, and the shallow and surface run-off waters are led to lake Saimaa via tens of constructed wetlands and other pipe pre-purification systems. (Tengbom Eriksson Arkkitehdit, 2017). Thus, the formed runoff water forms a burden to water network and surrounding environment including Lake Saimaa.

Cities may prepare themselves and reduce the risk of runoff water flooding by reducing the amount of surface water entering the sewage system. One approach is to treat the excess runoff water constructing wetlands with natural and chemical free filter systems.

2 TECHNICAL IMPLEMENTATION

The filter system applied in this feasibility assessment consists of filter system with foam, three cells of shungite, EM cell, and secondary foam layer, in this order. Principle of the structure is presented in figure 5.

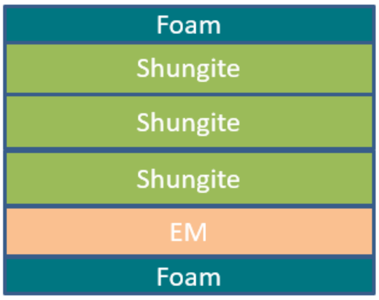
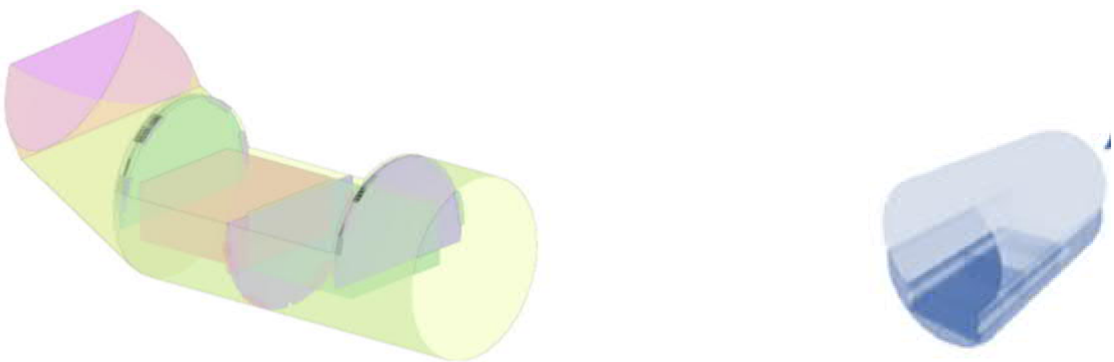


Figure 5. Principle of the filtration system.

Two different types of filters are considered in this feasibility study: vertical and horizontal filter (figure 6). Multiple filter units can be placed in a row forming series of filter units. Additional flow barriers in vertical filter are added to enable the water flow efficiently through filter units and prevent solid matter entering into filter unit. In the horizontal filter, water is fed into the filter system through a ramp covered with fabric. Fabric prevents solid matter flowing into filter. The environmental efficiency of the filtration system and water purification results are presented in the main report of SHEM-WP.



(1) (2)

Figure 6. Technical drawings of vertical flow (1) and horizontal flow (2) filters.

SHEM-WP water filtering process is easy to set up. Firstly, SHEM-WP filter is built. Building process is presented in the main report of SHEM-WP. Secondly, filter is transported and installed to the wetland. Some amount of land construction work may be performed to finalize the filter installation. Thirdly, filter is maintained twice a year (in spring and autumn). During maintenance shungite is activated with NaOH and thermal treatment, EM-cultivate and foam is replaced. The EM-cultivate is not applied during winter, when material may be frozen or temperature drops under +6 C. However, in this study is assumed that EM-cultivate is used for during whole year.

3 ECONIMICAL STUDY

The studied system includes all costs and revenues of the SHEM-WP commercial process (figure 7):

- Foundation costs,
- Operation costs (including maintenance costs of filtrate module)
- End of use phase costs
- End of phase revenues

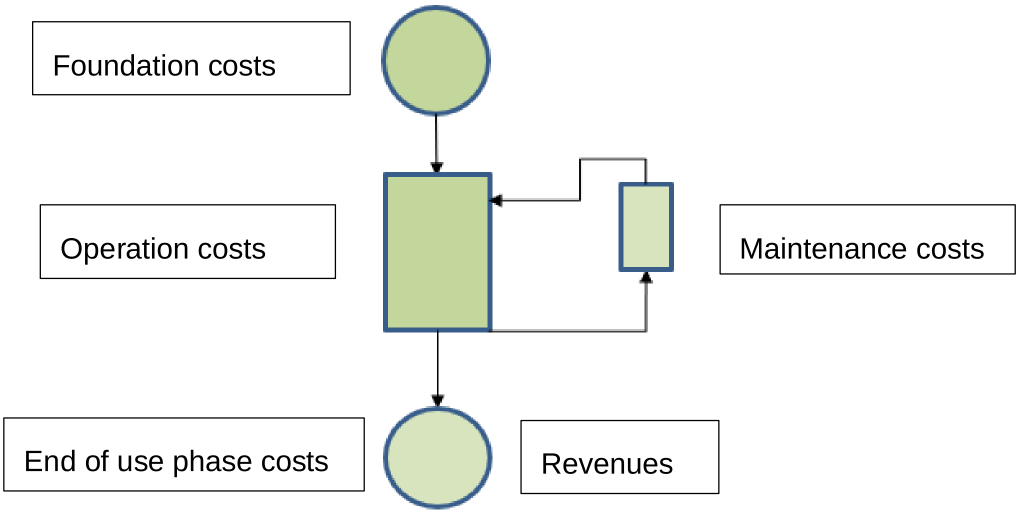


Figure 7. Principal drawing of studied system.

Foundation costs of the filtration system includes material and manufacturing costs. These costs consist of purchase cost of ready to use shungite, costs of plastic pipe od 50 cm, foam, ceramic particles, filtration frame as well as activation chemicals. Additionally, EM cultivation cost is included.

Operating costs of the system includes assembly and transportation cost of filters, and activation cost of shungite as well as maintenance cost of growth media. Activation of shungite includes thermal and chemical treatment.

End of use phase costs includes waste treatment of activation chemicals, transport costs of shungite for final thermal treatment and energy costs related into final thermal treatment of shungite.

Revenues may be formed from resale of shungite and reduction of land use and decrease in land use work. These revenues formed in the process are estimated and are included in the study.

Studied system and system boundary in detail is presented in figure 8.

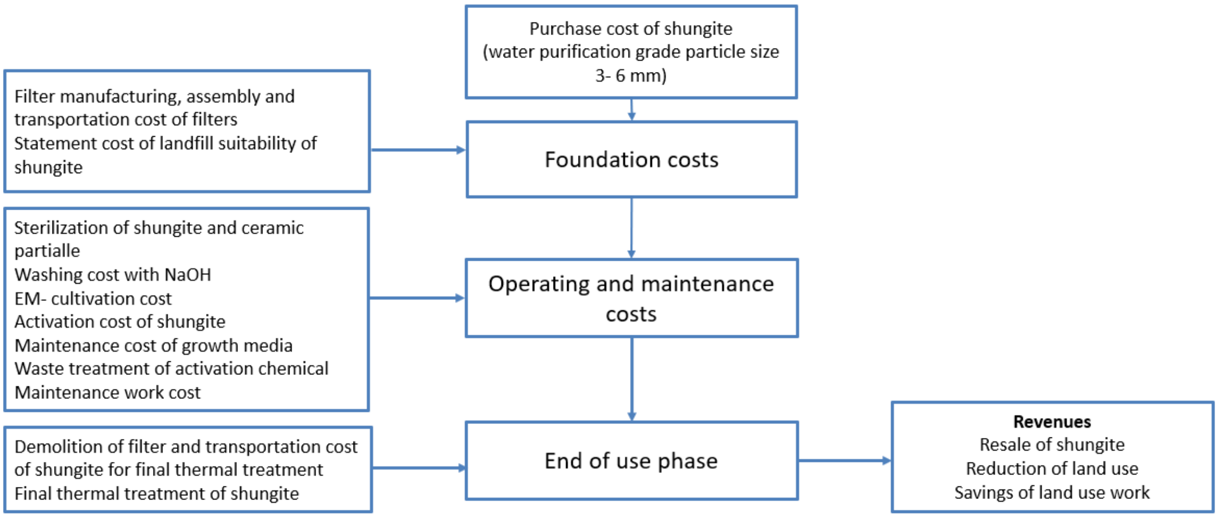


Figure 8. Studied system and system boundary.

3.1 Costs analysis

The detailed costs of each phase and assumptions behind the costs are presented in tables 1-3 below, costs are assumed to be for one year operation.

Main assumptions of foundation costs:

- Cost of shungite is 10-16 €/kg. Highest cost is assumed. The amount of shungite used in filter is assumed to be 20 kg.
- Statement cost of landfill suitability of shungite is based on Finnish authority costs and one statement is estimated to be enough for one purchased batch depending on the size of the batch.
- Assembly and transportation costs include building cost of filters, transportation of filters, and installation costs (land work and assembly).

Table 1. Foundation costs for vertical flow and horizontal flow filters.

Cost	Vertical filter flow cost, €	Horizontal filter flow cost, €
1 Purchase cost of shungite	640 €	640 €
1 Statement cost of landfill suitability of shungite	600 €	600 €
1 Assembly and transportation cost	1 900 €	2 000 €
Total	**3 140€**	**3 240 €**

Main assumptions of operating and maintenance costs:

- Thermal treatment and sterilization are assumed to be performed in stove heated with natural gas. The process steam consumption is assumed to be 1,23 MWh/1 ton of shungite input. The sterilization of shungite and ceramic particles are assumed to be performed at the same time, thus the cost of heating is halved for both. Sterilization is performed by heating the shungite and ceramic particle to 500 °C for 20 minutes.
- For activation of shungite the 5 mol NaOH is used. The relation between NaOH and amount shungite is 1:1. The activation chemical is directed into hazardous waste treatment after the use.
- EM-cultivation cost includes feeding cost of EM-cultivate.
- Amount of ceramic particles for cultivation is 10 g. Cost of ceramic particles based on secondary ceramic particles costs (re-used ceramic particles).
- Vertical filter has frame without rails and horizontal filter has frame with rails. Amount of filtration fabric used is assumed to be 1 meter for each vertical flow and horizontal flow filter. Cost for 1 meter of filtration fabric is 1 €. During maintenance filtration fabric is changed, but frame is kept the same.
- Maintenance working cost is assumed to be 50 €/h and maintenance time assumed to be 2 hours for both filter types. Maintenance is performed once during operating year.
- Activation cost for shungite includes washing shungite with 0,5 M NaOH and heating shungite to 500 °C for 20 minutes. Washing chemical is directed for hazardous waste treatment.
- Washing and activation chemical (NaOH) is hazardous waste. The cost of hazardous waste treatment is assumed to be 2-6 €/kg at waste treatment facility (LCA Consulting, Esa Nummela 2021). Highest price is assumed.
- Maintenance cost of growth media includes heating growth media to 500 °C for 20 minutes.

Table 2. Operating and maintenance costs for vertical flow and horizontal flow filters for one year of operation.

Cost	Vertical filter flow cost, €	Horizontal flow filter cost, €
2 Sterilization of shungite	1 €	1 €
2 Washing cost with 5 M NaOH	40 €	40 €
2 EM-cultivation cost	1 €	1 €
2 Ceramic particles cost and sterilization cost.	2 €	2 €
2 Frame cost, including filtration fabric.	22€	102 €
2 Activation cost of shungite 0,5 M NaOH	4 €	4 €
2 Maintenance cost of growth media	1 €	1 €
2. Hazardous waste treatment	240 €	240 €
2 Maintenance work cost	100 €	100 €
Total	**411 €**	**492 €**

Main assumptions of end of use phase cost

- Demolition time for vertical filter is assumed to be 3 hours and for horizontal filter 8 hours. Transportation time for final thermal treatment is assumed to be1 hour for both filters. Working hour cost is assumed to be 50 €/h.
- Final thermal treatment includes heating of shungite to 500 °C for 20 minutes.

Table 3. End of use phase cost for vertical flow and horizontal flow filters after filter operation.

Cost	Vertical flow filter cost, €	Horizontal flow filter cost, €
3 Demolition of filter and transportation cost of shungite for final thermal treatment	200 €	400 €
3 Final thermal treatment of shungite	2 €	2 €
Total	**202 €**	**402 €**

3.2 Total costs

Total foundation and implementation costs for vertical flow filter are 3 140 €, and for horizontal flow filter 3 240 €. Annual maintenance costs for vertical filter are 411 € and for horizontal filter 492 €.

The cost difference between filters is due to higher amount of installation, maintenance, and demolition work of horizontal filter. Additionally, horizontal filter frame has rails for easier installation and maintenance.

Foundation phase is most expensive phase for both filters, in where the transportation and assembly costs form 60 % of all foundation costs. Maintenance costs of the filter systems are only 12-13 % from the total costs excluding the end of phase costs.

After 5-10 years utilization the shungite will be renewed, and if the lifespan of the whole filter system is assumed to end the costs with renovation costs are for vertical filter 202 € and for horizontal filter 402 € excluding the optional land construction work. Optional accessories such as extra pipes might cost 500-1000 €. In table 4 and table 5 below are presented total life span costs for five-year operation period.

Table 4. Total costs for vertical flow filter for five-year operation period.

Total cost	**Year 1 Implementation**	**Year 2 Operating**	**Year 3 Operating**	**Year 4 Operating**	**Year 5 Operating**	**End of use costs**
Foundation and installation	3 140 €					
Maintenance	411 €	411 €	411 €	411 €	411 €	
End-of-use costs						202 €
Total	3 551 €	411 €	411 €	411 €	411 €	202 €
Grand for total life span						**5 397 €**

Table 5. Total costs for horizontal flow filter for five-year operation period.

Total cost	Year 1 Implementation	Year 2 Operating	Year 3 Operating	Year 4 Operating	Year 5 Operating	End of use costs
Foundation and installation	3 240 €					
Maintenance	492 €	492 €	492 €	492 €	492 €	
End-of-use costs						402 €
Total	3 732 €	492 €	492 €	492 €	492 €	402 €
Grand for total life span						**6 102 €**

3.3 Revenue analysis

After use, the shungite is resale for further use. Revenues occurs also for reduction of land use and savings for land use work. Assumptions for revenue analysis is presented below.

Main assumptions of revenues

- Revenue of resale of shungite as an activated cardon is estimated. The market price to special activated carbon is estimated as 10 €/kg. Mass loss in final thermal treatment can be up to 90 %, thus the amount of activated carbon from 20 kg of raw shungite is estimated as 2 kg.
- Reduction of land use is estimated for both minimum, average, and maximum land use. Land use savings are estimated for 10m x 10m area. Minimum savings: no land use savings occur 0 €/m^2. Average savings average square price of City of Lappeenranta is used 17 €/m^2. Maximum: average square price of City of Paris 10 000 €/m^2.
- Savings for land use work is estimated so that four wetlands can be build into of 10m x 10m area. Building cost of sedimentation tank for municipal wastewater treatment plant is assumed to be 3 000 €/m^2. Building cost for sedimentation area for natural ground is assumed to be 105 €/m^2. Cost for municipal wastewater treatment plant and natural ground includes foundation cost and building costs.

Table 5. Revenues for vertical and horizontal filters for five-year of operation.

Revenue type	**Vertical flow filter revenue €**	**Horizontal flow filter revenue, €**
Resale of shungite	20 €	20 €
Reduction of land use savings minimum	0 €	0 €
Reduction of land use savings average	1 700 €	1 700 €
Reduction of land use savings maximum	1 000 000 €	1 000 000 €
Savings of land use work when sedimentation tank is built for municipal wastewater treatment plant.	1 200 000 €	1 200 000 €
Savings of land use work when sedimentation tank is built for natural ground (natural pond).	42 000 €	42 000 €
Total, minimum with municipal settling tank **Total, minimum with natural settling pond**	**1 200 040 €** **42 040 €**	**1 200 040 €** **42 040 €**
Total, average with municipal settling tank **Total, average with natural settling pond**	**1 201 741 €** **43 741 €**	**1 201 741 €** **43 741 €**
Total, maximum with municipal settling tank **Total, maximum with natural settling pond**	**2 200 040 €** **1 042 040 €**	**2 200 040 €** **1 042 040 €**

Both, vertical and horizontal, filter have similar revenues. Minimum revenues, 42 040 €, occurs when reduction of land use saving is 0 € and savings of land use work is estimated based on natural settling pond. Maximum revenues, 2 200 040 €, occurs when reduction of land use saving is 1 000 000 € and land use work is estimated based on municipal settling tank.

If filter is placed into existing wetland to intensify the operation of wetland and if it replaces building at least one wetland or settling tank, the savings are at least building costs of one natural or municipal settling tank as well as maintenance costs.

4 RISKS DEFINITION AND ASSESSMENT

SHEM-WP process is beneficial from economical point of view due to land use reduction and land use cost. As the cities aim to be platforms and forerunners of entrepreneurships, the target is to form SHEM-WP process into business opportunity, should proper entrepreneur be available to begin the business. Proper entrepreneur could be a company which already has all need infra to perform the business. For business opportunity the risks of SHEM-WP process have been defined. First risk defined is the need for business and second risk the financial risk targeting towards business and is based on economic analysis performed in study.

Firstly, the risk of need of SHEM-WP business is assessed. It has been recognized that the climate change increases the amount of heavy precipitation and urbanization increases the amount of the impervious surfaces. Thus, municipalities will face the need for new settling tanks or natural settling ponds. Due to high construction costs of settling tanks and high land use cost, the need for SHMEP-WP industry increases and lasts in the future. Risk for SHEM-WP business is minimized especially in all urbanized areas where the scarcity of the land is high.

Secondly, the financial risk and form of business is assessed. Based on the cost analysis, the risks of SHEM-WP business are related to direct revenues of the process. Even the savings of land use and land use work occurs, the direct revenue for resale shungite is not high due to market price of activated carbon. Therefore, the direct revenue versus total cost of SHEM-WP process is not profitable when SHEM-WP process is sold as it is.

If the business is formed as a form of service for municipalities, then entrepreneur may charge all costs from municipality. Revenues are then at least total costs of vertical flow or horizontal flow filter plus the revenue of resale of shungite.

Entrepreneur may form for example five-year service contract with municipality with costs n 1 000 €/filter/year. If one city purchases service with 10 filters, the yearly revenue/city for entrepreneur would be 10 000 €. Overall, 107 cities and 2020 communities are in Finland, so customer base exists already. Due to high construction costs of settling tanks and high land costs it would be beneficial for municipalities to purchase the SHEM-WP as a service. Additionally, the maintenance cost of the SHEM-WP process is low which also beneficial for municipalities. Municipalities would form savings at least amount of minimum of natural settling tank construction cost minus the entrepreneur charge in the service type of business.

5 CONCLUSIONS

In this study the economical background of SHEM-WP process is presented and analyzed. Additionally, the risks of SHEM-WP process as business opportunity are recognized and estimated.

Based on background information it can be stated that the need of SHEM-WP process will be increased due increased amount of runoff water in future. Therefore, the need for the SHEM-WP business exists as well as customer base exists.

The costs analysis shows that the main benefits of the SHEM-WP process is targeted into the reduction of land use and savings for land use work. Additionally, the cost analysis shows that maintenance costs of SHEM-WP process is low, approximately 13 % of both filter types from overall costs.

Based on the study results, it can be stated that due to low direct revenue from resale of shungite the financial risk is high. Therefore SHEM-WP business would be profitable when SHEM-WP is sold as a service to municipalities. SHEM-WP process is beneficial for municipalities from land use reduction and land use work point of view as well as low maintenance costs of SHEM-WP process. Overall, due to the increased need for wetlands in the future, SHWM-WP process forms an exceptional and cost efficient possibility for municipalities to control the runoff water formed in the cities urban area.

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