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OSAMAT – post-project environmental monitoring in 2018

Final report

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National Institute of Chemical Physics and Biophysics

1. Foreword

A contract between Eesti Energia AS and National Institute of Chemical Physics and Biophysics was signed in 05.09.2018 to conduct a follow-up monitoring of pilot road sections of OSAMAT-program in 2018.

Purpose of the contract was to evaluate and analyze environmental status of Narva-Mustajõe and Simuna-Vaiatu pilot road sections constructed by using partly oil shale ash (OSA). Second objective of the work is to verify possible environmental effects of utilizing the OSA in larger scale.

The environmental follow-up program consisted of analyzing of surface water and soil samples in order to validate the release of potentially toxic trace elements and selected anions from pilot road structures to the environment. Based on the results of follow-up monitoring it is possible give scientific data for assessing the environmental impacts and evaluation of potential risks associated with construction of roads with OSA material.

The report presents the results of environmental monitoring campaigns of the pilot sections conducted in 18.09 and 04.11.2018.

2. Introduction

The preferred management option for ash flow from industrial combustion of solid fuels is utilization rather than landfilling. The production divisions of the Eesti Energia Narva power plants utilize Estonian oil shale (kukersite) to produce a total of about 9 TWh of electricity each year. At present, two different oil shale combustion processes are in use: pulverized firing (PF) and circulating fluidized-bed (CFB) combustion technologies. Due to high mineral content of kukersite (45-47 mass-%) about six million tons of oil shale ash (OSA) is produced annually [1], which is mainly deposited in ash fields near to power plants. The reasons for low-level utilization of OSA in Estonia include inconsistency in the quality of OSA, high cost of transportation and partly by the fact that according to Estonian legislation OSA is considered as a hazardous waste [2] due to highly alkaline reaction in contact with water. At the moment the OSA deposits are huge and contain high volumes of important raw materials for civil engineering purposes [3].

The strategy of utilizing combustion ash in the entire world is in constant change. On one hand, it is advantageous to make commercial use of the by-products of energy production. On the other hand, the large-scale usage of very complex wastes like OSA raises questions about environmental impact of such activities. Thus, it is essential to monitor the environmental aspects of the process where OSA is brought back into the nature, including the fate of toxic elements.

In general, for risk assessments connected with utilizing of ash in road construction, it is important to know which compounds could be released into the environment. The leaching of soluble constituents upon contact with water is regarded as a main mechanism of release, which results in a potential risk to the environment. OSA contains major matrix elements such as Ca, Si, Al, and Fe together with significant amount of minor elements, *e.g*. Mg, K, P, S and negligible amounts of trace elements [4].

The release of potentially harmful compounds, such as heavy metals from OSA is relatively low and that the OSA could be safe for use civil engineering [5]. Still, the release of toxic heavy metals is strongly pH dependent [6] at conditions prevailing in soils and the release of toxic substances could become an environmental concern. Beneficial use of the OSA in road construction requires better knowledge of leaching of soil-ash systems in order to evaluate mobilization potential of metals during soil-ash water interaction. Therefore it is essential to monitor content of hazardous elements in water and soil in areas of large-scale utilization of OSA whenever possible.

The current environmental quality criteria for OSA to be utilized in bulk quantities are rather strict in Estonia. The follow-up monitoring program evaluates the impact to surrounding environment from a road sections constructed partly with OSA material from Narva Power Plants by comparing the content of selected parameters to natural background and legal limits.

3. Materials and methods

The pilot sections were constructed on two roads in Estonia in Narva-Mustajõe and Simuna-Vaiatu road (see osamat.ee). In the road sections three types of OSA from Baltic Power Plant were used (Figures 1 and2):

- Cyclone ash from oil shale pulverized firing boiler (Cyclone PF) 5% mixed with cement 5% + aggregates (oil shale mining waste aggregate and milled asphalt concrete)
- Ash from the electrostatic precipitator of oil shale pulverized firing boiler (EF PF) 6% mixed with cement 3% + aggregates (oil shale mining waste aggregate and milled asphalt concrete)
- Ash from the 1st field of electrostatic precipitators of oil shale circulated fluidized bed boiler (EF CFB) 9% mixed only with aggregate (oil shale mining waste aggregate and milled asphalt concrete)
- Complex stabilization (traditional method) with composite cement CEM II / B-M (T-L) 42.5R.

The recipes and stabilization methods used in road sections are described in progress report no. 4 of Osamat project (2013).

3.1 Sampling

Current follow-up monitoring campaign was carried out in both pilot sections in Narva-Mustajõe and Simuna-Vaiatu road in 18.09 and 04.11.2018.

The soil-sampling was carried out by the specialist from Estonian, Latvian & Lithuanian Environment OÜ by the accredited soil sampling method ISO 10381 (Accreditation see Appendix 1). Soil samples were taken from the depth of 0.1-0.2 m. Sampling reports are presented in Appendix 2. Exact co-ordinates of sampling points were following (locations see Figures 1 and 2):

NM-1	59° 19' 45.86" N and 27° 56' 23.25" E
NM-2	59° 19' 57.46" N and 27° 57' 8.29" E
NM-3	59° 20' 7.73" N and 27° 57' 51.05" E
SV-2A	59° 01' 18.93" N and 26° 25' 21.42" E
SV-2B	59° 01' 19.31" N and 26° 25' 22.87" E
SV-3A	59° 01' 10.44" N and 26° 25' 29.79" E
SV-3B	59° 01' 10.7" N and 26° 25' 30.93" E

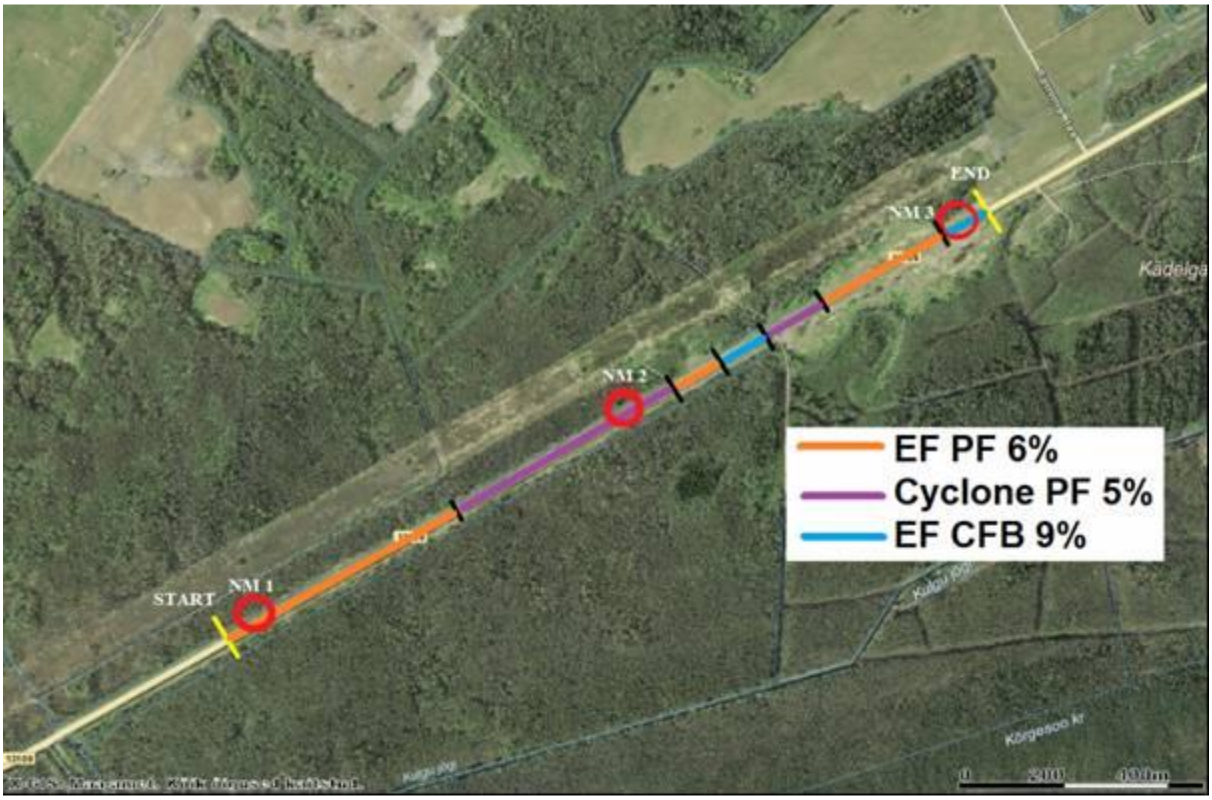


Figure 1 Locations of soil sampling points in Narva-Mustajõe pilot section.

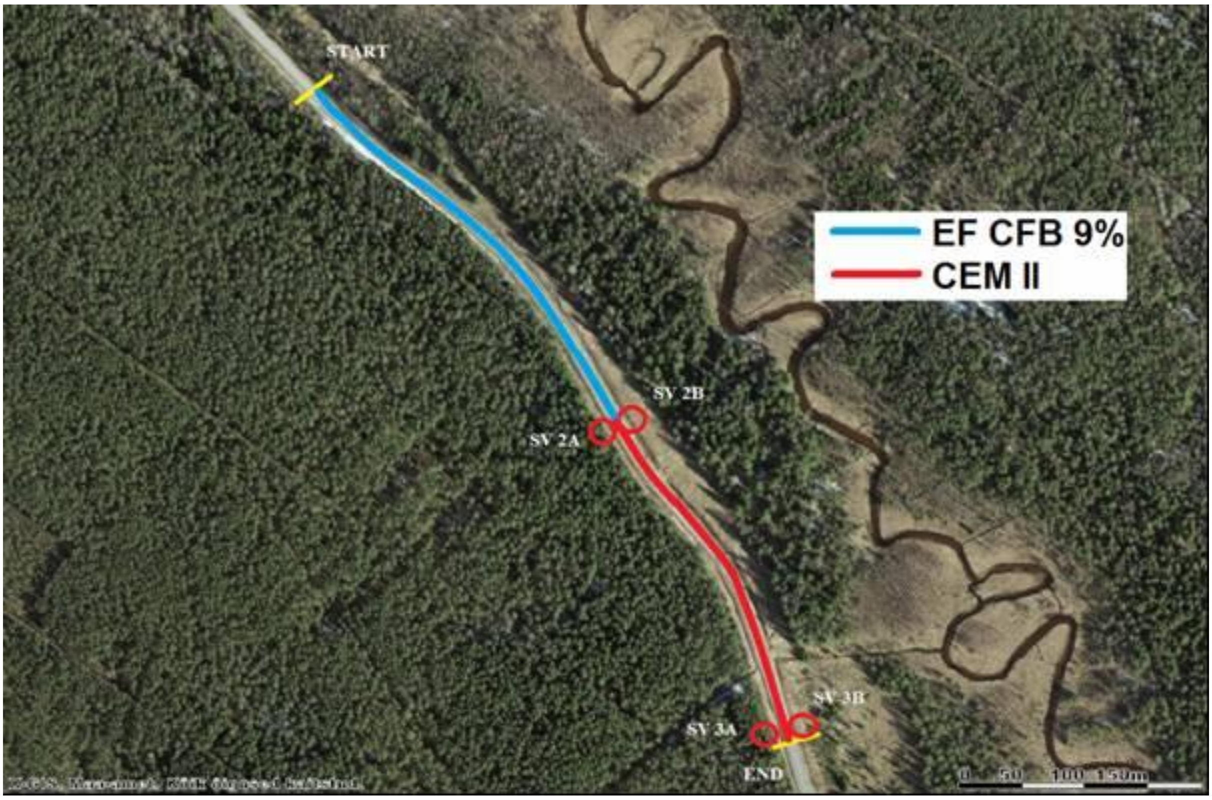


Figure 2 Locations of soil sampling points in Simuna-Vaiatu pilot section.

Surface water samples were taken by the specialist from Estonian, Latvian & Lithuanian Environment OÜ by the accredited method EN 5667 (Attestation No. 1394/16, see Appendix 1). Sampling campaigns were conducted in 18.09 and 04.11.2018. Locations of surface water sampling points in Narva-Mustajõe and Simuna-Vaiatu pilot sections are presented in Figure 3 and 4. It was not possible to take surface water samples in points stated in the terms of reference due to lack of water. Sampling reports are presented in Appendix 2. Exact co-ordinates of sampling points were following (locations see Figures 3 and 4):

NM-1	59° 19' 44.09" N and 27° 56' 19.09" E
NM-2	59° 19' 53.77" N and 27° 56' 58.22" E
NM-3	59° 19' 56.27" N and 27° 57' 8.11" E
SV-1	59° 1' 24.16" N and 26° 25' 15.32" E
SV-2	59° 1' 20.79" N and 26° 25' 19.76" E
SV-3	59° 1' 13.09" N and 26° 25' 29.78" E

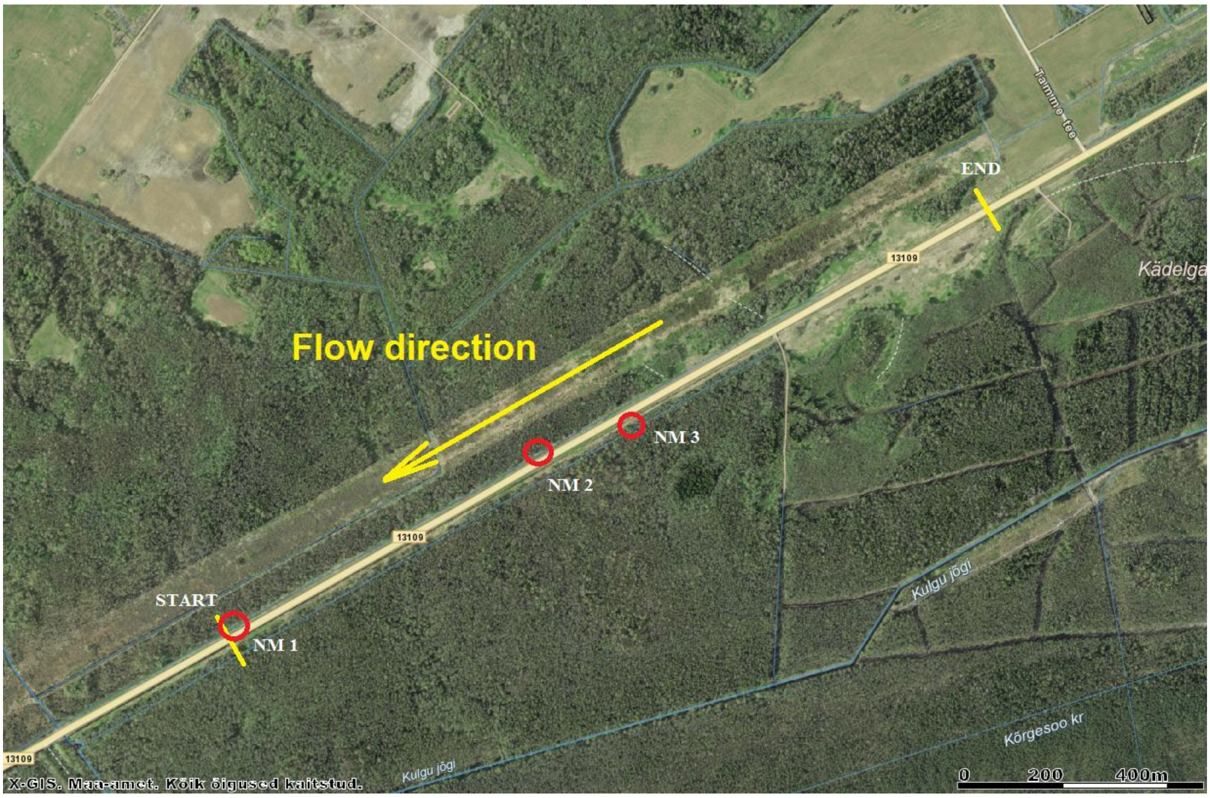


Figure 3 Locations of surface water sampling points in Narva-Mustajõe pilot section.

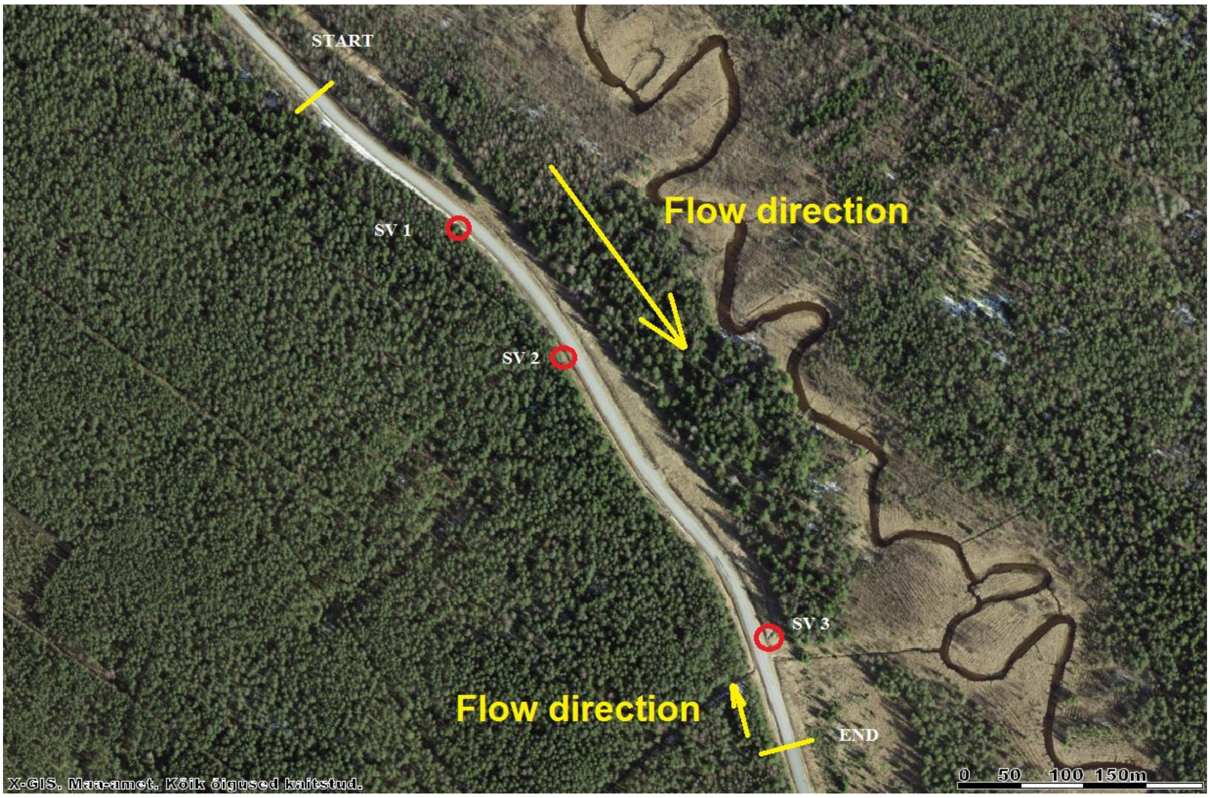


Figure 4 Locations of surface water sampling points in Simuna-Vaiatu pilot section.

3.2 Meteorological data

Data for daily precipitation and average daily temperature in September and October 2018 is obtained from the following closest meteorological stations to the pilot sections (Estonian Weather Service web page: www.ilmateenistus.ee):

For Narva-Mustajõe pilot section - Narva station N 59°23´22´´ E 28°06´33´´, distance ca 10 km,
For Simuna-Vaiatu pilot section – Väike-Maarja N 59°08´29´´ E 26°13´51´´, distance ca 10 km.

The stations are equipped with automatic precipitation sensors and the observation data is presented graphically in Figure 5.

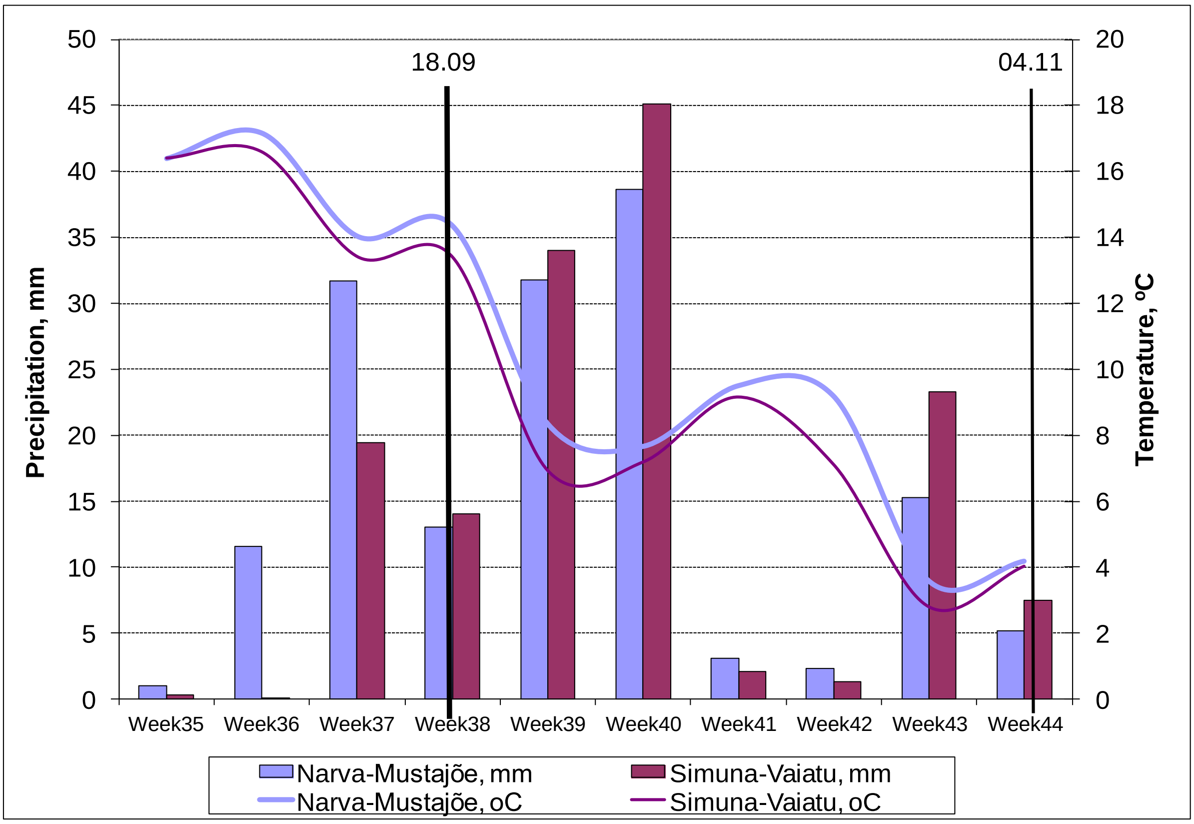


Figure 5. Weekly precipitation and average weekly temperaturesin pilot road section areas prior to during sampling period in 2018 as well as sampling dates.
(http://www.ilmateenistus.ee/ilm/ilmavaatlused/vaatlusandmed/oopaevaandmed)

As can be seen from Figure 5 the surface water samples were taken after the periods of relatively low precipitation that leaded to almost empty ditches around the pilot sections.

3.3 Analysis of soil samples

Soil samples were analyzed in the laboratory of GBA Gesellschaft für Bioanalytik mbH (Pinneberg, Germany) by accredited methods (see Table 1 and Appendix 1). Dry weight was determined by ISO 11465 with limit of quantification 0.40 wt%. Soil samples were digested according to EN 13657 and the determination of trace elements was carried out in diluted acid extracts of the samples according to following accredited methods (see Appendix 1):

Table 1 Selected trace elements in soil samples analyzed in the laboratory of GBA.

Element	Unit	Limit of quantification	Uncertainty (%)	Method
Mercury, Hg	mg/kg_{DW}	0.10	3.00	EN ISO 16171
Cadmium, Cd	mg/kg_{DW}	0.10	7.60	EN ISO 16171
Lead, Pb	mg/kg_{DW}	1.0	7.20	EN ISO 16171
Nickel, Ni	mg/kg_{DW}	1.0	7.60	EN ISO 16171
Antimony, Sb	mg/kg_{DW}	1.0	5.00	EN ISO 16171
Arsenic, As	mg/kg_{DW}	1.0	7.20	EN ISO 16171
Barium, Ba	mg/kg_{DW}	1.0	5.80	EN ISO 16171
Chromium, Cr total	mg/kg_{DW}	1.0	8.70	EN ISO 16171
Copper, Cu	mg/kg_{DW}	1.0	nd	EN ISO 16171
Molybdenum, Mo	mg/kg_{DW}	1.0	4.40	EN ISO 16171
Vanadium, V	mg/kg_{DW}	1.0	nd	EN ISO 16171
Zinc, Zn	mg/kg_{DW}	1.0	2.60	EN ISO 16171
Selenium, Se	mg/kg_{DW}	2.0	8.60	EN ISO 16171

nd – no data.

3.4 Analysis of surface water samples

Following parameters were measured *in-situ* by accredited methods during the sampling episodes (see Table 2, Appendix 1):

Table 2 Indicative parameters of surface water samples determined *in situ.*

Parameter	Unit	Uncertainty, *k=2*
pH		0.2
Electric conductivity, EC	µS/cm	0.5%
Temperature	^{o}C	0.2

YSI Professional Plus Multi-Parameter Water Quality Meter was used.

Following anions were analyzed in the laboratory of GBA Gesellschaft für Bioanalytik mbH (Pinneberg, Germany) accredited methods (see Table 3, Appendix 1)

Table 3 Anions quantified in surface water samples in the laboratory of GBA.

Anion	Unit	Limit of quantification	Method
Chloride	mg/L	0.6	ISO 10304-1:
Sulfate	mg/L	0.5	ISO 10304-1:
Fluoride	mg/L	0.15	ISO 10304-1:

Trace elements in filtrated water samples (0.45 µm) were analyzed in the laboratory of GBA Gesellschaft für Bioanalytik mbH (Pinneberg, Germany) by following accredited methods (see Table 4, Appendix 1).

Table 4 Selected trace elements analyzed in surface water samples in the laboratory of GBA.

Element	Unit	Limit of quantification	Uncertainty (%)	Method
Mercury, Hg	mg/L	0.00020	4.8	EN ISO 17294
Cadmium, Cd	mg/L	0.00030	5.3	EN ISO 17294
Lead, Pb	mg/L	0.0010	4.8	EN ISO 17294
Nickel, Ni	mg/L	0.0010	6.5	EN ISO 17294
Antimony, Sb	mg/L	0.0010	nd	EN ISO 17294
Arsenic, As	mg/L	0.00050	5.3	EN ISO 17294
Barium, Ba	mg/L	0.00050	nd	EN ISO 17294
Chromium, Cr total	mg/L	0.0010	7.2	EN ISO 17294
Copper, Cu	mg/L	0.0010	6.9	EN ISO 17294
Molybdenum, Mo	mg/L	0.0010	nd	EN ISO 17294
Vanadium, V	mg/L	0.0010	nd	EN ISO 17294
Zinc, Zn	mg/L	0.0050	8.4	EN ISO 17294

nd – no data.

3.5 Legal limits

Results of the analysis were compared against environmental quality standards. Among measured parameters there are no limit value for the temperature, electric conductivity, content of chloride and sulfate as well as content of following trace elements such as vanadium (V), antimony (Sb) and molybdenum (Mo) in surface water according to Estonian legal regulations. For these parameters the limit values for drinking and groundwater were used as indicative values (except V and Sb).

Selected trace elements in soil samples: (Table 5):
Regulation No 38 of the Estonian Ministry of Environment (adopted in 11.08.2010), Ohtlike ainete sisalduse piirväärtused pinnases (*Concentration limits of hazardous substances in the soil*), Riigi Teataja, I 2010, 57, 373 (in Estonian).

Table 5 Target and permitted values of selected trace elements in soil.

Element	Unit	Target value*	Permitted value** in residential area	Permitted value** in industrial area
As	mg/kg	20	30	50
Pb	mg/kg	50	300	600
Cd	mg/kg	1	5	20
Cr sum	mg/kg	100	300	800
Cu	mg/kg	100	150	500
Ni	mg/kg	50	150	500
Hg	mg/kg	0.5	2	10
Zn	mg/kg	200	500	1000
Sb	mg/kg	10	20	100
Ba	mg/kg	500	750	2000
Mo	mg/kg	10	20	200
V	mg/kg	50	300	1000

* target value shows the content below which the soil status is considered good.
** permitted value shows the content above which the soil is considered contaminated.

Electric conductivity, chloride and sulfate content in surface water are not regulated. Therefore the regulation on drinking water quality was used for indicative purposes (Table 6):
Regulation No 82 of the Ministry of Social Affairs (adopted 31.07.2001), Joogivee kvaliteedi- ja kontrollinõuded ning analüüsimeetodid (*Quality and control requirements for drinking water and methods of analysis*), Riigi Teataja I, 27.09.2017, 2 (in Estonian).

Table 6 Indication of limit values in drinking water.

Parameter	Unit	Limit value
Electric conductivity	µS/cm	2500
Temperature	^{o}C	-
Chloride	mg/L/	250
Sulfate	mg/L	250

pH in surface water has to be in a range of 6-9 in order to consider the status of the water body to be good:
Regulation No 44 of the Estonian Ministry of Environment (adopted in 28.07.2009), Pinnaveekogumite moodustamise kord ja nende pinnaveekogumite nimestik, mille seisundiklass tuleb määrata, pinnaveekogumite seisundiklassid ja seisundiklassidele vastavad kvaliteedinäitajate väärtused ning seisundiklasside määramise kord (*The procedure for the formation of surface water bodies and the list of these surface water bodies, which class status shall be determined, the status of surface water bodies and the quality indicators for the status of the corresponding water bodies and the procedure for determining the status*), Riigi Teataja I, 22.11.2010, 15 (in Estonian)

Content of priority substances in surface water samples (Table 7):
Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy..

Table 7 Environmental quality standards of priority hazardous metals in surface water.

Name of substance	Unit	AA-EQS*	MAC-EQS**
Hg	mg/L		0.00007
Cd**	mg/L	0.00015	0.0009
Pb	mg/L	0.0012****	0.014
Ni	mg/L	0.004****	0.034

* annual average value of the environmental quality standard;
** maximum allowable concentration of the environmental quality standard;
*** For Cd the EQS values vary depending on the hardness of the water. Hardness of the water was considered 100 to < 200 mg $CaCO_3$/L – class 4 [7];
**** bioavailable concentration.

Content of selected hazardous substances in surface water samples (Table 8)**:**
Regulation No 77 of the Estonian Ministry of Environment (adopted in 30.12.2015), Prioriteetsete ainete ja prioriteetsete ohtlike ainete nimistu, prioriteetsete ainete, prioriteetsete ohtlike ainete ja teatavate muude saasteainete keskkonna kvaliteedi piirväärtused ning nende kohaldamise meetodid, vesikonnaspetsiifiliste saasteainete keskkonna kvaliteedi piirväärtused, ainete jälgimisnimekiri (*List of priority substances and priority hazardous substances, environmental quality limit values for priority substances, priority hazardous substances and certain other pollutants, methods of their application, environmental quality limit values for the water body specific pollutants, tracking list of substances*), Riigi Teataja I, 08.01.2016, 10 (in Estonian).

Table 8 Environmental quality standards of hazardous substances in surface water.

Name of substance	Unit	MAC-EQS
Fluoride	mg/L	1.5
As	mg/L	0.01
Ba	mg/L	0.1
Cr total	mg/L	0.005
Cu	mg/L	0.015

Content of molybdenum in surface water samples was indicatively compared to limit value in groundwater :0.07 mg/L.
Regulation No 39 of the Estonian Ministry of Environment (adopted in 11.08.2010), Ohtlike ainete põhjavee kvaliteedi piirväärtused (*The environmental quality limit values of the hazardous substances in groundwater*)

3.6 Previous monitoring

Whenever possible the results of previous monitoring programs were used to obtain natural background concentrations and to analyze the trends in contents of selected parameters in soil and surface water samples.

The results of contents of selected elements in soil samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections published in monitoring program carried out in 2012 [8] and 2014-2015 [9] are presented in Appendix 3. The results on 2012 sampling can be considered as a natural background content of selected elements in the soil of pilot sections.

Surface water sampling has been previously carried out in Narva-Mustajõe and Simuna-Vaiatu pilot sections since 2011 (Figure 7). The results of previous sampling episodes are presented in Appendix 3 [8]. The results from year 2011 can be considered as a natural background of surface water in an area.

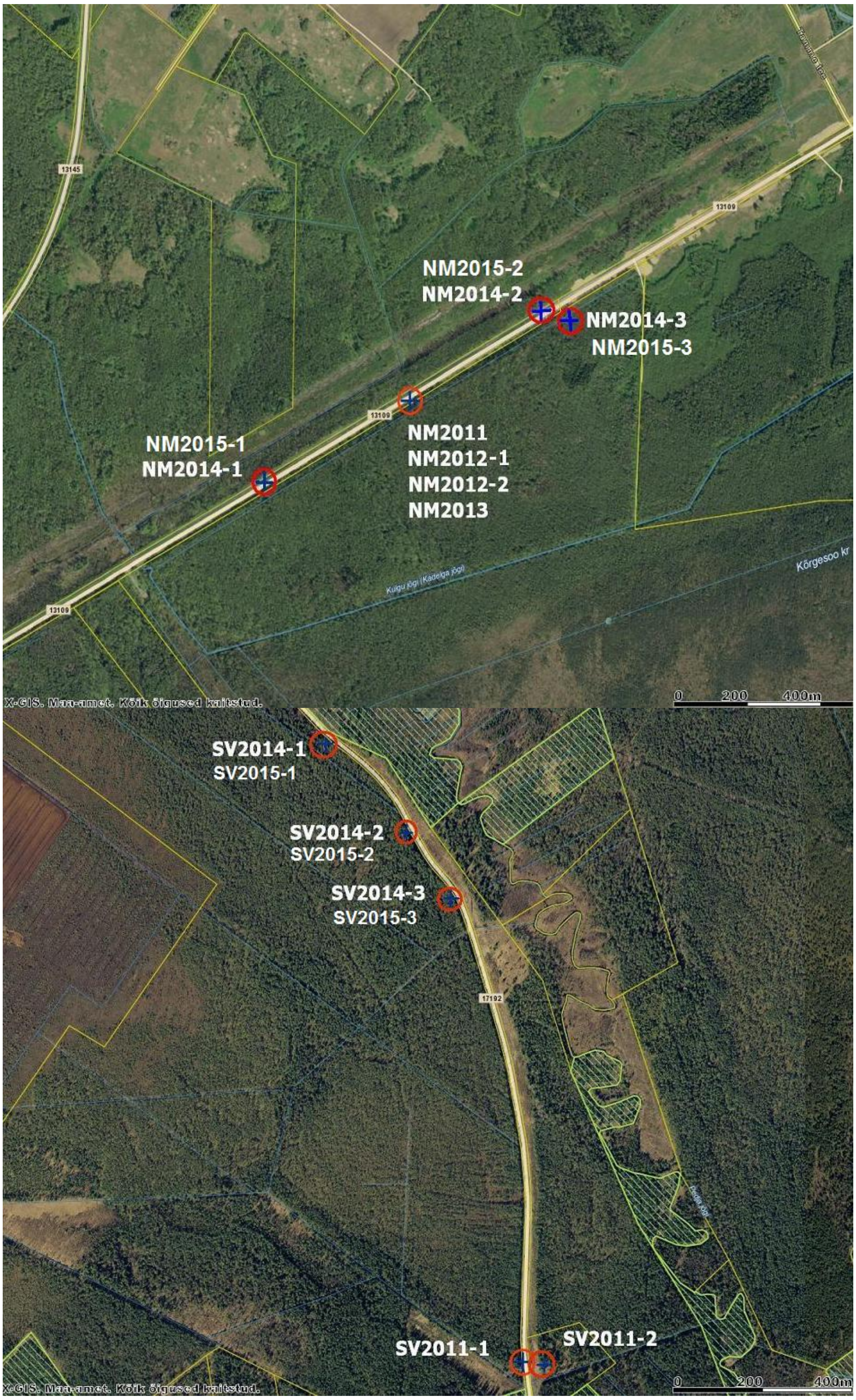


Figure 7. Surface water sampling points in previous sampling campaigns in Narva-Mustajõe (above) and Simuna-Vaiatu pilot sections (below),

4. Results of 2018 sampling campaigns

4.1 Soil

During 2018 monitoring program soil samples were taken in 18.09. and 04.11.2018.

- Locations see Figures 1 and 2,
- Results see Table 9 and 10.
- Sampling Plan see Appendix 2 (Proovivõtukava, *in Estonian*)
- Sampling protocols see Appendix 2,
- Chains of Custody see Appendix 2
- Laboratory Test Reports No.: 2018P518265 / 1 and 2018P522214 / 1 see Appendix 2.

Table 9. Contents of selected elements in Narva-Mustajõe soil samples collected in 2018

Date			18.09.2018			04.11.2018		
Sample name			NM-1	NM-2	NM-3	NM-1	NM-2	NM-3
Parameter	Unit							
Sampling depth	m		0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2
Dry weight	mass-%	-	86.5	82.3	88.3	85.4	81.3	89.6
Element		TV*						
Arsenic, As	mg/kg	20	1.9	3.8	1.2	1.4	4.7	1.5
Lead, Pb	mg/kg	50	10	13	4.0	7.5	9.6	9.0
Cadmium, Cd	mg/kg	1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chrome, Cr sum	mg/kg	100	5.7	6.0	4.1	9.0	12	3.9
Copper, Cu	mg/kg	100	13	18	12	5.1	15	7.6
Nickel, Ni	mg/kg	50	4.5	6.4	3.0	<1.0	7.9	2.6
Mercury, Hg	mg/kg	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zinc, Zn	mg/kg	200	17	24	11	30	34	20
Antimony, Sb	mg/kg	10	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Barium, Ba	mg/kg	500	26	121	13	35	70	15
Molybdenum, Mo	mg/kg	10	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Vanadium, V	mg/kg	50	8.3	11	5.8	16	15	8.4
Selenium, Se	mg/kg	1	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0

Table 10. Contents of selected elements in Simuna-Vaiatu soil samples collected in 2018

Date			18.09.2018				04.11.2018			
Sample name			SV-2A	SV-2B	SV-3A	SV-3B	SV-2A	SV-2B	SV-3A	SV-3B
Parameter	Unit									
Sampling depth	m		0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2	0.1-0.2
Dry weight	mass-%	-	91.0	93.1	95.1	89.0	63.0	83.4	89.6	57.4
Element		TV*								
Arsenic, As	mg/kg	20	1.5	1.9	1.9	1.7	2.8	1.0	2.0	1.4
Lead, Pb	mg/kg	50	3.9	2.5	2.7	4.4	5.2	2.6	5.7	7.5
Cadmium, Cd	mg/kg	1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chrome, Cr sum	mg/kg	100	3.8	4.9	3.8	5.0	3.0	<1.0	3.4	1.1
Copper, Cu	mg/kg	100	13	12	10	12	6.7	6.3	6.9	5.1
Nickel, Ni	mg/kg	50	3.1	3.4	2.9	3.9	1.3	<1.0	2.3	<1.0
Mercury, Hg	mg/kg	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zinc, Zn	mg/kg	200	15	12	10	13	12	10	15	10
Antimony, Sb	mg/kg	10	<1.0	<1.0	<0.1	<1.0	1.1	<1.0	<1.0	<1.0
Barium, Ba	mg/kg	500	11	16	12	18	17	7.0	15	13
Molybdenum, Mo	mg/kg	10	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Vanadium, V	mg/kg	50	5.8	7.0	6.6	7.1	5.8	4.0	7.1	4.8
Selenium, Se	mg/kg	1	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0

4.2 Surface water

During 2018 monitoring program the surface water samples were taken in 18.09 and 04.11.2018.
Locations see Figures 3 and 4. It was not possible to take water samples as planned because of lack of water in ditches in both sampling campaigns. Also the water level was extremely low in most of the sampling points during sampling campaigns (for example Picture 1). Latter gives some uncertainty to the results of collected surface water samples.

- Results are surface water analysis are presented in Tables 11-13.
- Sampling protocols see Appendix 2,
- Laboratory Test Reports No.: 2018P518603 / 1 and 2018P522448 / 1 see Appendix 2.

Picture 1. Low water level in sampling point SV-1 in 4.11.2018.

Table 11 Indicative parameters of surface water samples from Narva-Mustajõe and Simuna-Vaiatu pilot sections in 2018, comparison with indicators and natural background level.

Narva-Mustajõe sample name				NM2018-1		NM2018-2		NM2018-3	
Date			27.07.11	18.09	04.11	18.09	04.11	18.09	04.11
Parameter	Unit	Indicative value	Natural background						
pH		range 6-9	7.41	6.96	6.3	7.43	7.13	7.50	7.63
Electric conductivity	µS/cm	max 2500	1034	1588	1040	690	753	577	651
Chloride	mg/L/	max 250	44	14	14	50	26	59	88
Sulfate	mg/L	max 250	<5	883	335	305	282	93	32
Fluoride	mg/L	max 1.5	nd	0.4	<0.3	0.21	<0.3	0.23	<0.3

Simuna-Vaiatu sample name				SV2018-1		SV2018-2		SV2018-3	
Date			27.07.11	18.09	04.11	18.09	04.11	18.09	04.11
Parameter	Unit	Indicative value	Natural background						
pH		range 6-9	7.58	7.49	5.7	7.37	7.43	7.85	7.55
Electric conductivity	µS/cm	max 2500	435	710	469	904	406	549	226
Chloride	mg/L/	max 250	5.3	49	5	53	5.6	24	2.4
Sulfate	mg/L	max 250	<5	137	66	177	42	58	13
Fluoride	mg/L	max 1.5	nd	0.33	<0.3	0.33	<0.2	0.22	<0.15

nd – no data

Table 12. Trace elements in filtrated (0.45 µm) surface water samples from Narva-Mustajõe pilot section in 2018 and comparison with EQS and available background level.

Sample name				NM2018-1		NM2018-2		NM2018-3	
Date			27.07.11	18.09	04.11	18.09	04.11	18.09	04.11
Element	Unit	MAC-EQS*	Natural back-ground**						
Hg	mg/L	0.00007	nd	<0.00020	<0.00020	<0.00020	<0.00020	<0.00020	<0.00020
Cd	mg/L	0.0009	nd	<0.00030	<0.00030	<0.00030	<0.00030	<0.00030	<0.00030
Pb	mg/L	0.014	0.0077	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Ni	mg/L	0.034	nd	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
As	mg/L	0.01	0.0081	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Ba	mg/L	0.1	**0.36*** **	**0.12**	**0.12**	**0.29**	**0.20**	0.092	**0.21**
Cr sum	mg/L	0.005	0.78	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Cu	mg/L	0.015	nd	<0.001	<0.001	0.0017	0.0016	<0.0010	<0.001
Zn	mg/L	0.01	nd	**0.015**	**0.047**	<0.0050	**0.057**	<0.0050	**0.033**
Mo	mg/L		0.00066	0.0011	0.0014	0.0013	0.0024	<0.0010	<0.0010
Sb	mg/L		nd	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
V	mg/L		0.0013	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010

nd – no data

* MAC-EQS for priority substances Directive 2013/39/EU, other hazardous substances Regulation No 49 of the Estonian Ministry of Environment;

**2011 sampling episode (non-filtrated sample);

*** Sample NM-0 taken in 21.07.2015 for natural background level outside the pilot section area

Table 13 Trace elements in filtrated (0.45 µm) surface water samples from Simuna-Vaiatu pilot section in 2018 and comparison with EQS and available background level.

Sample name				SV2018-1		SV2018-2		SV2018-3	
Date			27.07.11	18.09	04.11	18.09	04.11	18.09	04.11
Element	Unit	MAC-EQS*	Natural back-ground**						
Hg	mg/L	0.00007	nd	<0.00020	<0.00020	<0.00020	<0.00020	<0.00020	<0.00020
Cd	mg/L	0.0009	nd	<0.00030	<0.00030	<0.00030	<0.00030	<0.00030	<0.00030
Pb	mg/L	0.014	0.0056	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Ni	mg/L	0.034	nd	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
As	mg/L	0.01	0.0009	0.001	0.0012	0.00086	0.00087	<0.0005	0.00062
Ba	mg/L	0.1	nd	0.060	0.054	0.087	0.042	**0.16**	0.02
Cr sum	mg/L	0.005	<0.0005	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
Cu	mg/L	0.015	nd	<0.0010	0.0011	<0.0010	<0.0010	<0.0010	0.0011
Zn	mg/L	0.01	nd	<0.0050	**0.035**	<0.0050	**0.064**	<0.0050	**0.049**
Mo	mg/L		0.00014	0.0085	0.0029	0.0059	0.0031	0.0030	<0.0010
Sb	mg/L		nd	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010
V	mg/L		0.0011	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010

nd – no data

* MAC-EQS for priority substances Directive 2013/39/EU, other hazardous substances Regulation No 49 of the Estonian Ministry of Environment;

**2011 sampling episode (non-filtrated sample);

*

5. Summary of the results and trends

During the course of the environmental monitoring in September and November 2018 following samples were collected and analyzed in the pilot sections of Narva-Mustajõe and Simuna-Vaiatu roads:

14 soil samples and 12 surface water samples (locations see Paragraph 3.1). Sampling reports as well as the results of analysis are presented in Paragraph 4 and Appendix 2.

5.1 Soil

Soil samples were taken from the banks of both pilot road sections at depth 0.1-0.2 m in 18.09 and 04.11.2018. The content of trace elements in soil samples was compared to the legal limits and natural background level. Content of all trace elements was below target values set by the national regulation[1] in all samples.

In following tables the content of trace elements in composite sample taken in 2012 and mean content of elements in the soil samples taken in 2014, 2015 and 2018 are compared (Tables 14 and 15). For the sake of clarity also the mean content of the trace elements in Estonian soil is presented.

[1] No 38 of the Estonian Ministry of Environment (adopted in 11.08.2010), Ohtlike ainete sisalduse piirväärtused pinnases (Concentration limits of hazardous substances in the soil), Riigi Teataja, I 2010, 57, 373 (In Estonian)

Table 14. Average content of selected elements (mg/kg_{dry}) in Estonian soil according to literature compared to average content in Narva-Mustajõe soil samples.

		Previous monitoring			Current monitoring	
Element	Estonian soil mean	Composite 30.05.12	Mean (n=3) 22.07.14	Mean (n=3) 22.07.15	Mean (n=3) 18.09.18	Mean (n=3) 04.11.18
As	nd.	4.6	6.0	2.9	2.3	2.5
Pb	16	13	11.3	10.0	9	8.7
Cd	0.4	<0.2	0.1	0.12	<0.1	<0.1
Cr_{sum}	42	18	15.5	7.4	5.3	8.3
Cu	11	<10	10.8	7.8	14.3	9.2
Ni	22	10	9.3	5.1	4.6	5.3
Hg	0.03	<0.1	<0.1	<0.1	<0.1	<0.2
Zn	37	40	39.7	35.7	17.3	28
Sb	nd	<0.5	<0.1	<0.1	<0.1	<1.0
Ba	383	76	86	35.8	53	40
Mo	1.3	<2	2.3	<1	<1	<1
V	44	34	22.3	12.2	8.4	13
Se	nd	<1	<2	<2	<2	<2

nd – no data.

Table 15. Average content and range of selected elements (mg/kg_{dry}) in Estonian soil compared to average content in Simuna-Vaiatu soil samples.

		Previous monitoring			Current monitoring	
Element	Estonian soil mean	Composite 30.05.12	Mean (n=2) 22.07.14	Mean (n=2) 22.07.15	Mean (n=4) 18.09.18	Mean (n=4) 04.11.18
As	nd.	3.5	2.2	4.5	1.8	1.8
Pb	16	15	5.2	10.1	3.0	5.3
Cd	0.4	0.26	<0.1	0.08	<0.1	<0.1
Cr_{sum}	42	7.3	6.3	7.1	4.2	2.5
Cu	11	<10	4.4	5.6	11.7	6.3
Ni	22	4.1	3.5	4	3.1	1.2
Hg	0.03	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	37	24	23	28	12.3	12
Sb	nd	<0.5	<0.1	<1.0	<0.1	<1.0
Ba	383	65	22	40	13	13
Mo	1.3	<2	<0.1	0.6	<0.1	<1.0
V	44	11	9.4	9.4	6.5	5.4
Se	nd	<1	<2.0	<2.0	<2.0	<1

As can be seen from the tables 14 and 15 the mean content of analyzed trace elements in samples taken in 2018 is lower or similar to natural background and when compared to values of samples taken in 2014 and 2015.

When compared the content of soil in current follow-up monitoring program to previous monitoring and to average content in Estonian soil following conclusions can be drawn:

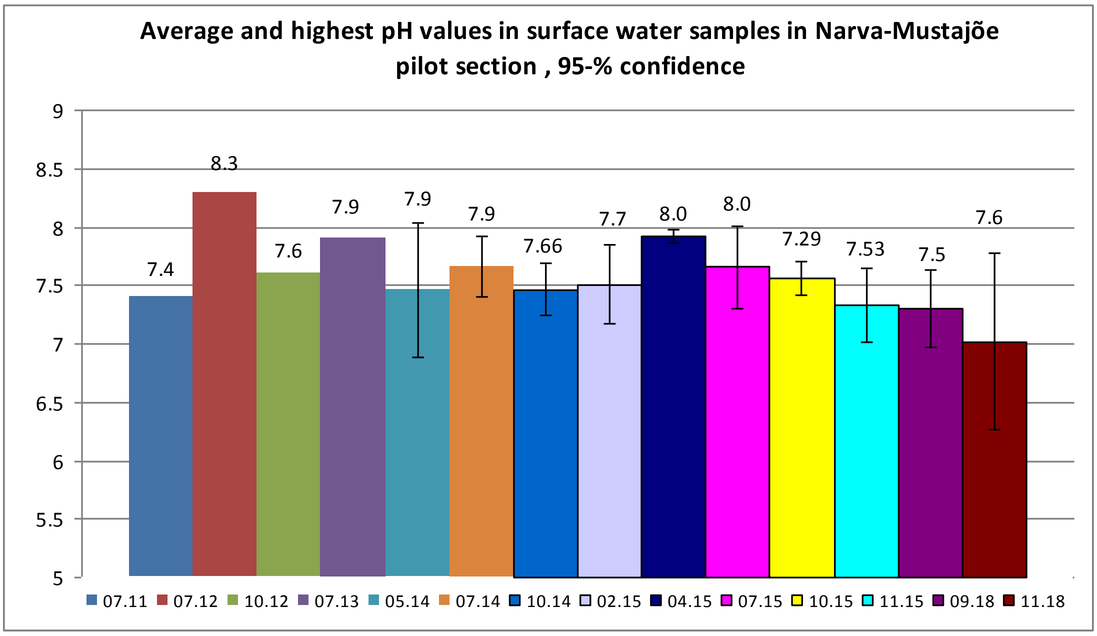
- the effect of OSA in road construction onto content of trace elements in soil is negligible.

5.2 Surface water

For following the long-term trends (2011-2015) of selected parameters in surface water in the pilot areas it is possible to use only those parameters that were measured in previous monitoring campaigns i.e. pH, EC, chloride, sulfate, As, Cr, Pb, Mo, V. Content of Cr and V in all water samples is below limits of detection therefore these metals are not included in the analysis. For the calculation of average concentrations, values below the limit of quantification were set to half of the value of the limit of quantification concerned [10].

5.2.1 Indicative parameters

Following indicative parameters are presented pH, electric conductivity, content of chlorides and sulfates (Figures 8-12). These indicative parameters were also monitored in previous environmental programs of two pilot sections.



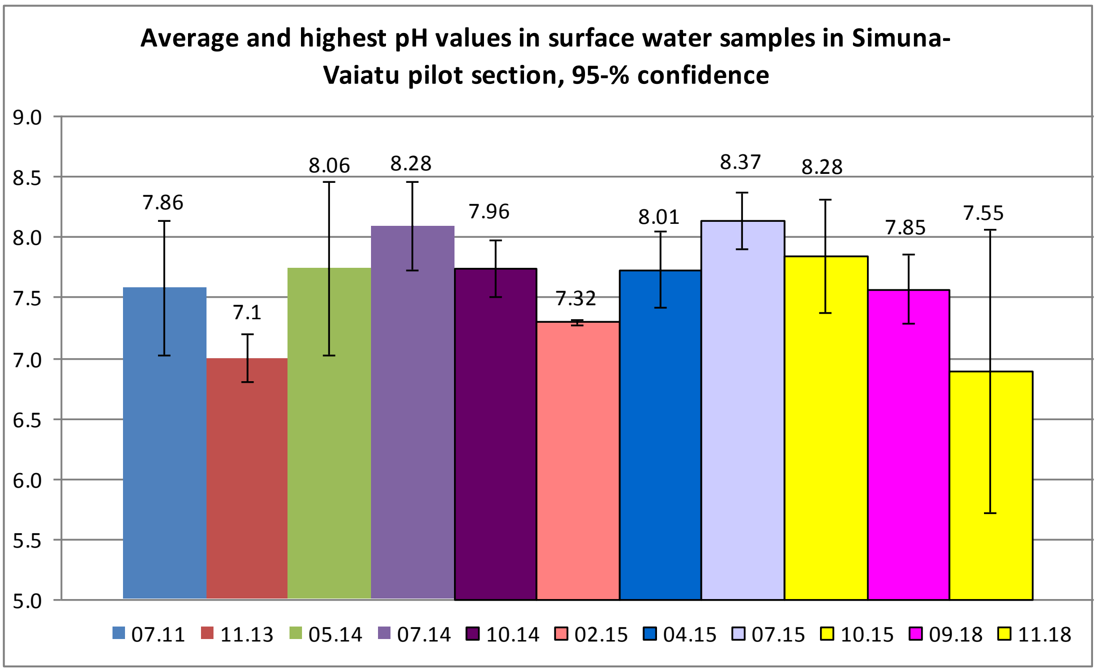
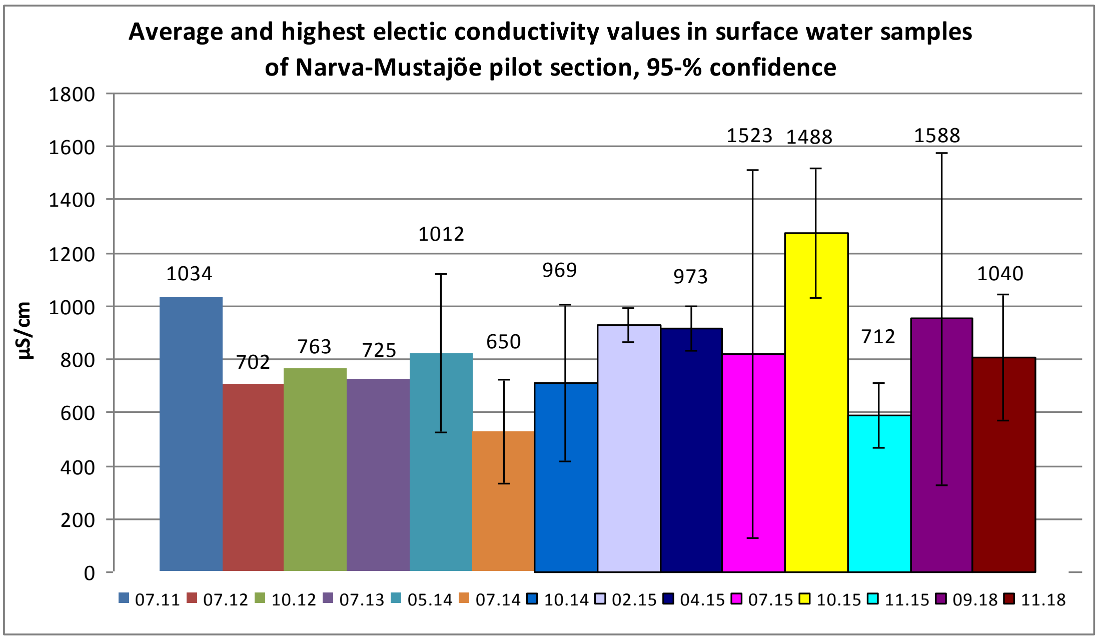


Figure 8 Observed pH values of water samples during monitoring of Narva-Mustajõe and Simuna-Vaiatu pilot sections.



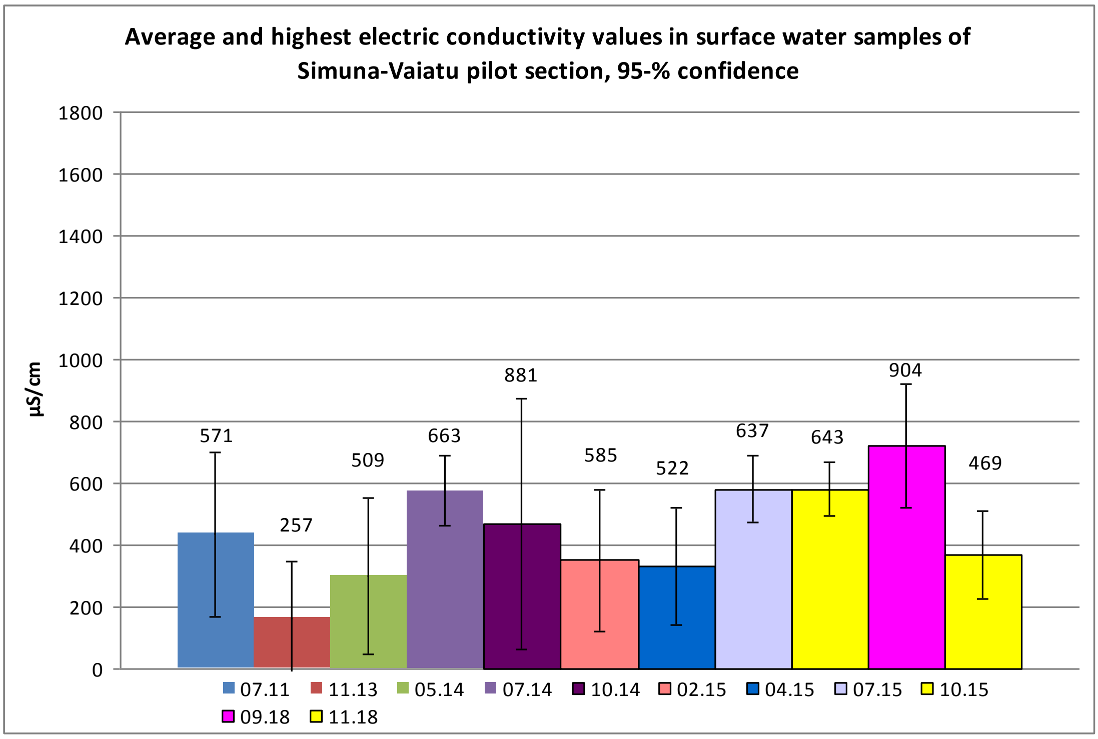
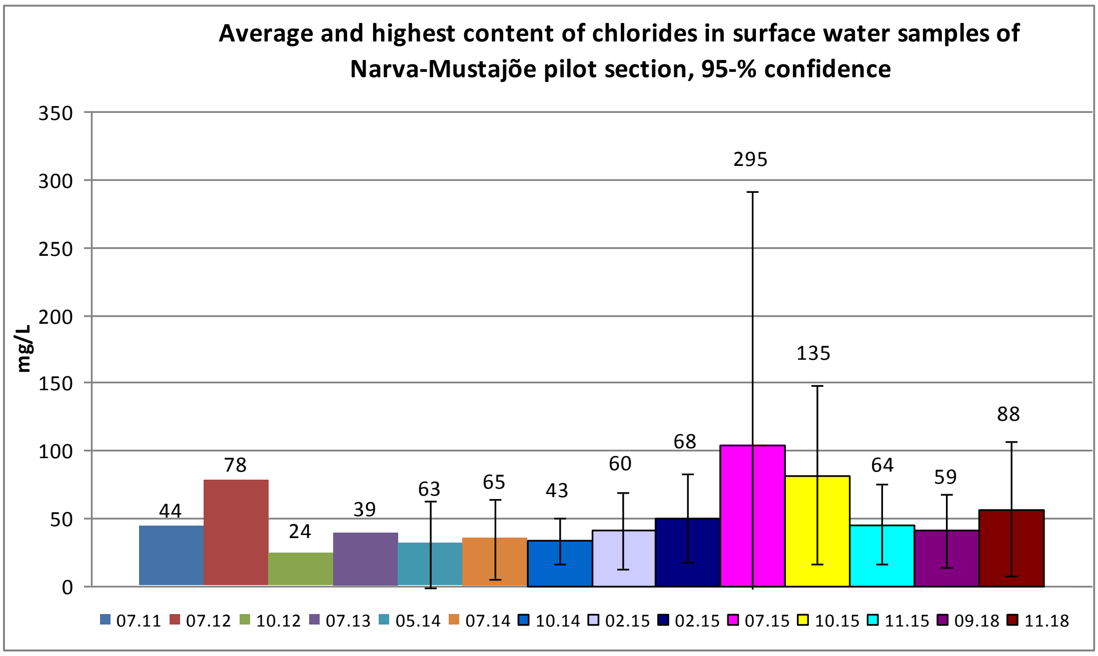


Figure 9 Observed electric conductivity values of water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections.



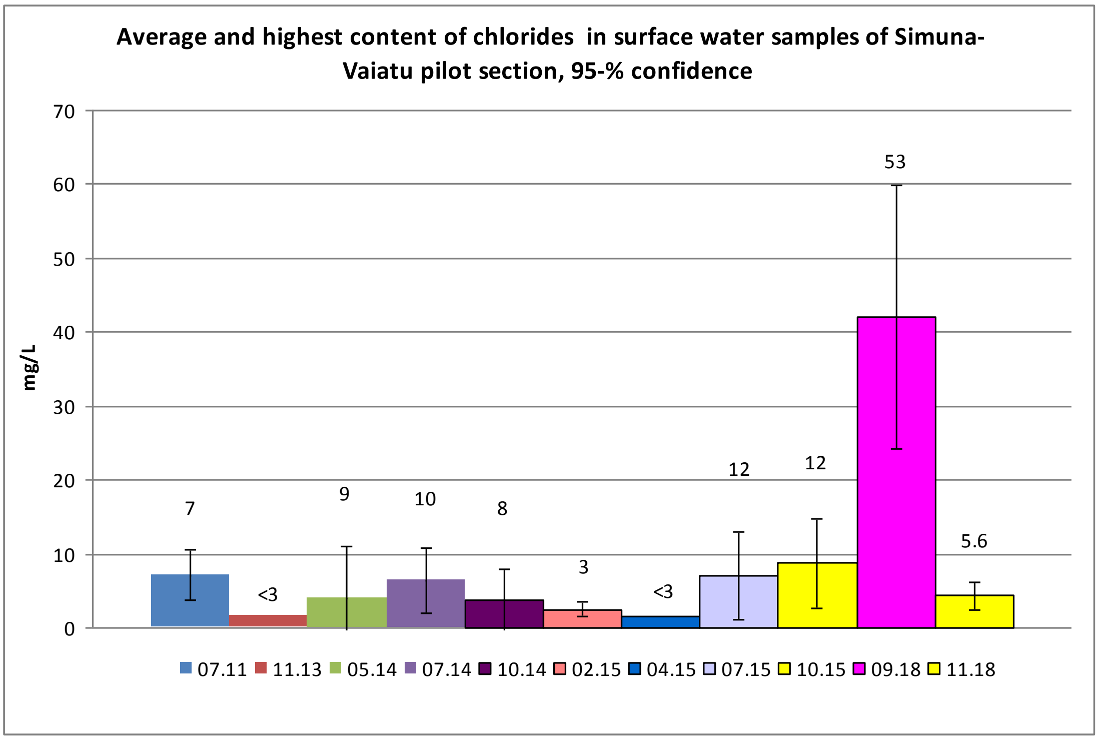
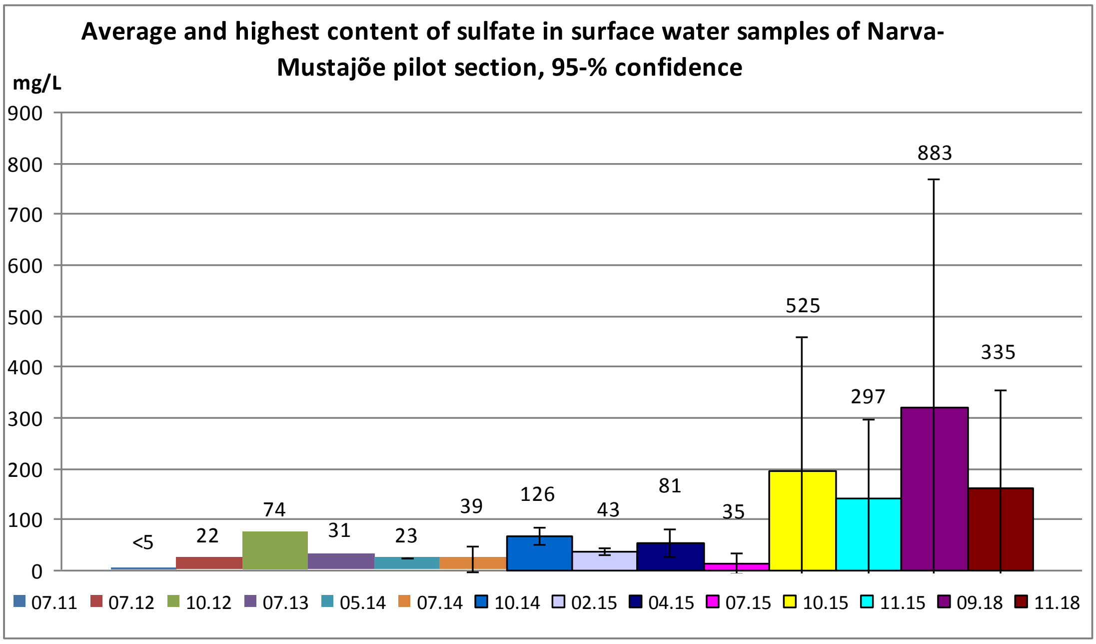


Figure 10 Observed content of chlorides in water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections. NB! Different scales.



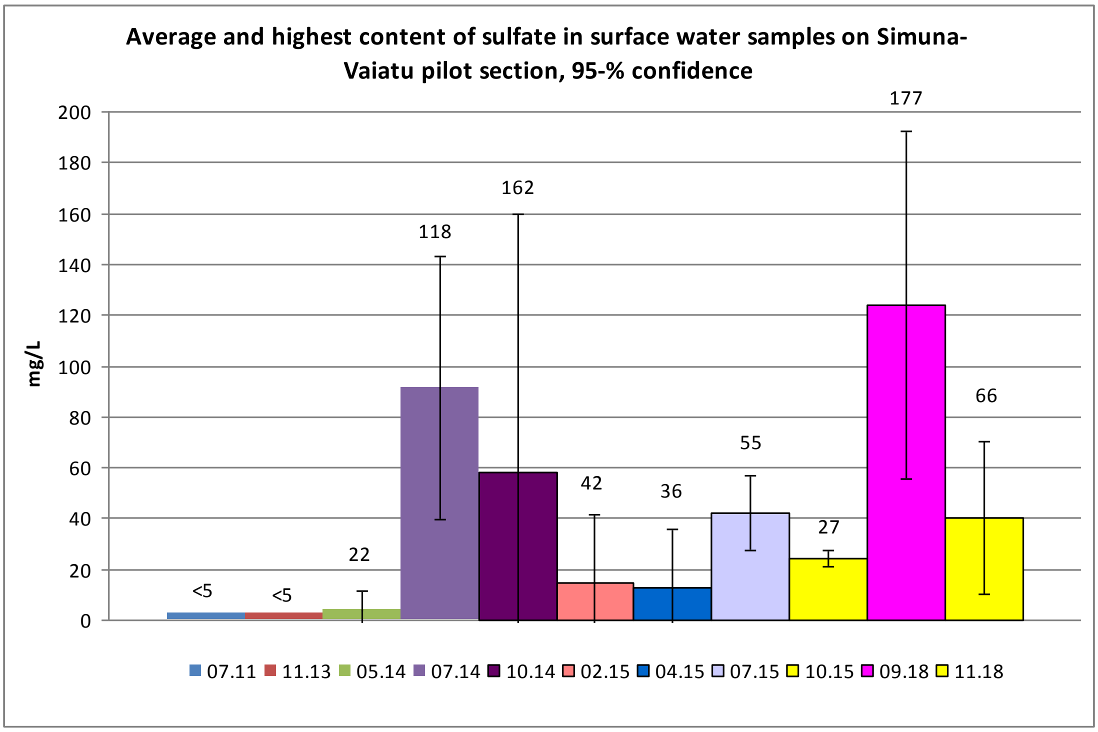
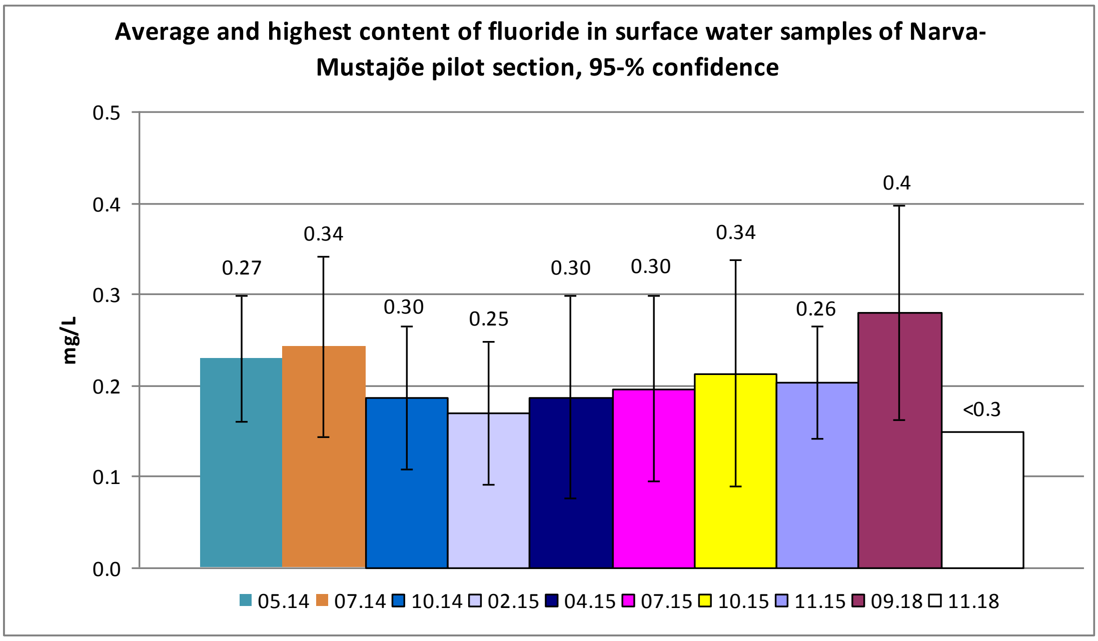


Figure 11 Observed content of sulfate in water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections. NB! Different scales.



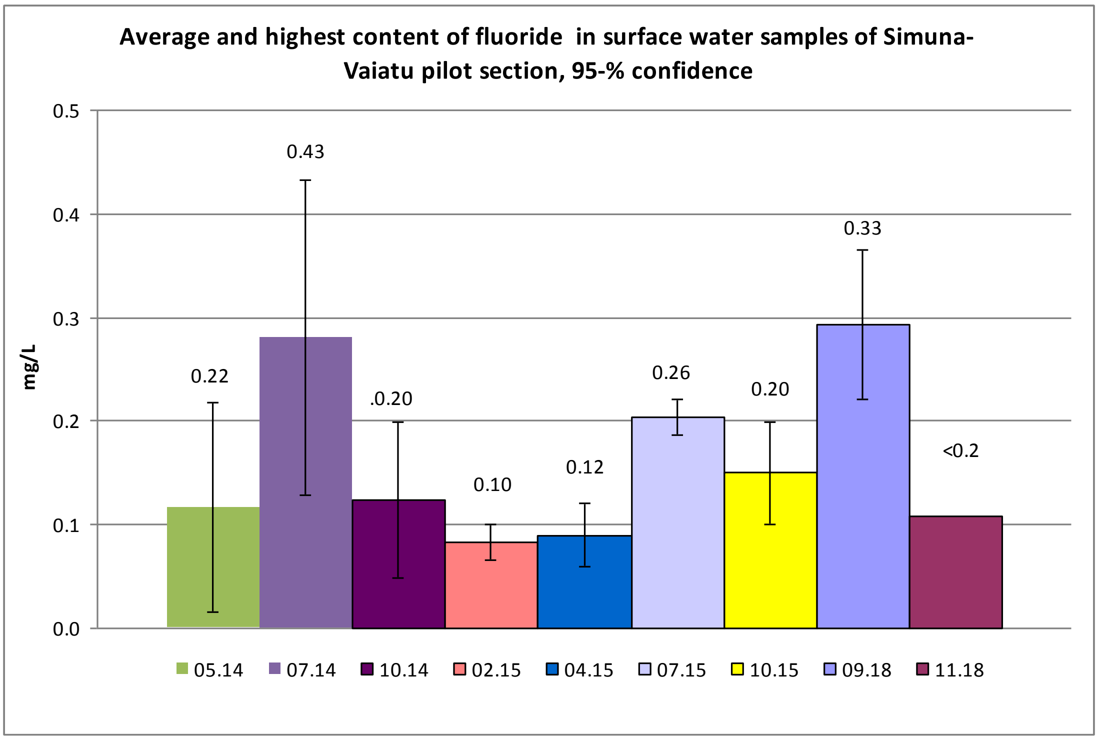


Figure12. Observed content of fluoride in water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections (Limit concentration 1.5 mg/L).

As can be seen from Figure 11 the road construction with OSA has affected the content of sulfates in surface water in both pilot sections. Concentration of sulfate and chloride ions in surface water is many times higher in Narva-Mustajõe pilot section compared to Simuna-Vaiatu section. The content of chlorides and values electric conductivity is similar to previous observations with one exception in samples taken in September 2018 in Simuna-Vaiatu section. Content of fluoride in surface water is below limit concentration in both pilot sections (max 1.5 mg/L).

5.2.3 Trace elements

Content of following trace elements is presented in following Figures 13-16 – lead, arsenic, molybdenum and barium. First three metals were monitored in previous programs and are natural constituents in the environment of two pilot sections. In must be noted that in previous monitoring programs the content of trace elements was determined from non-filtrated samples.

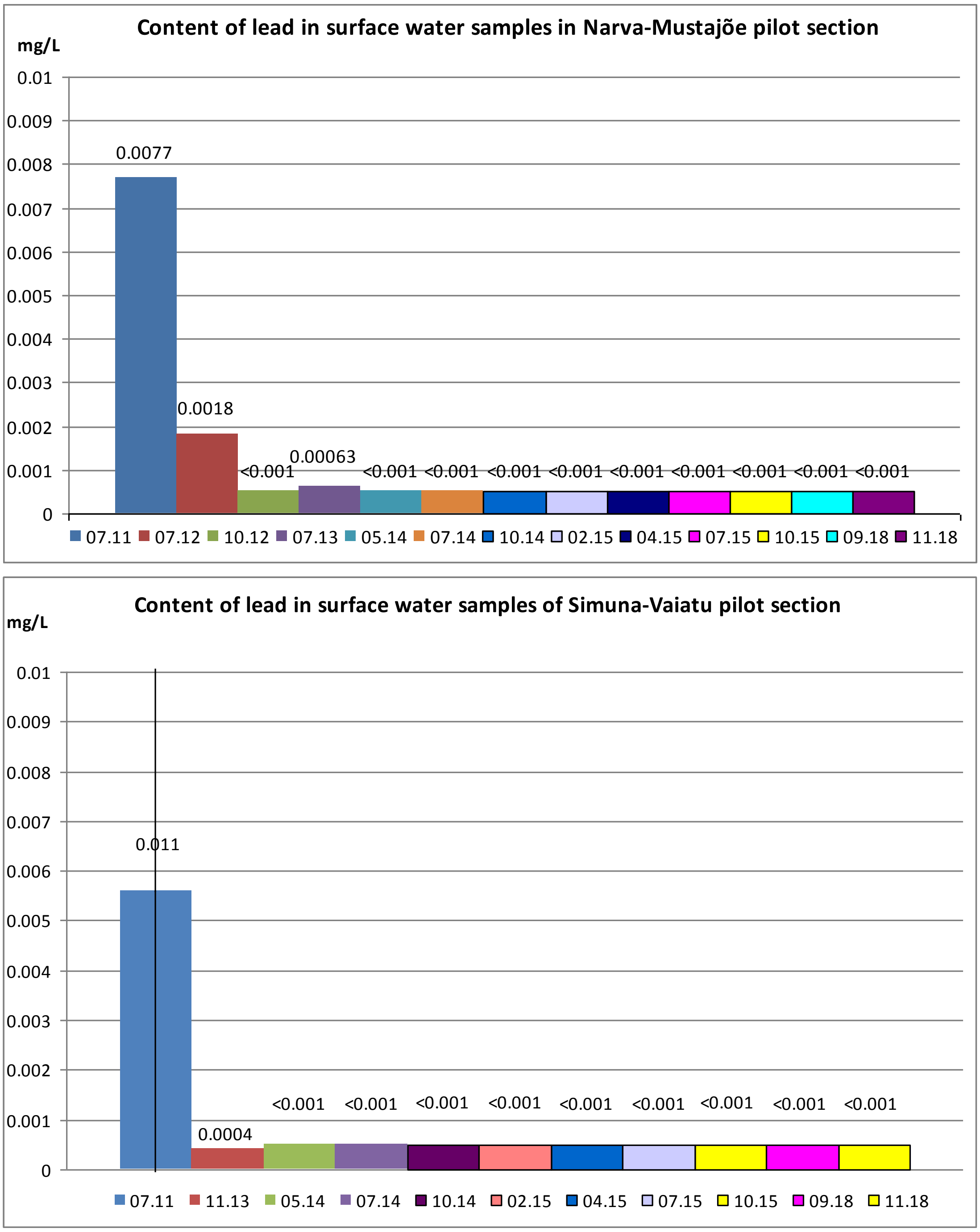
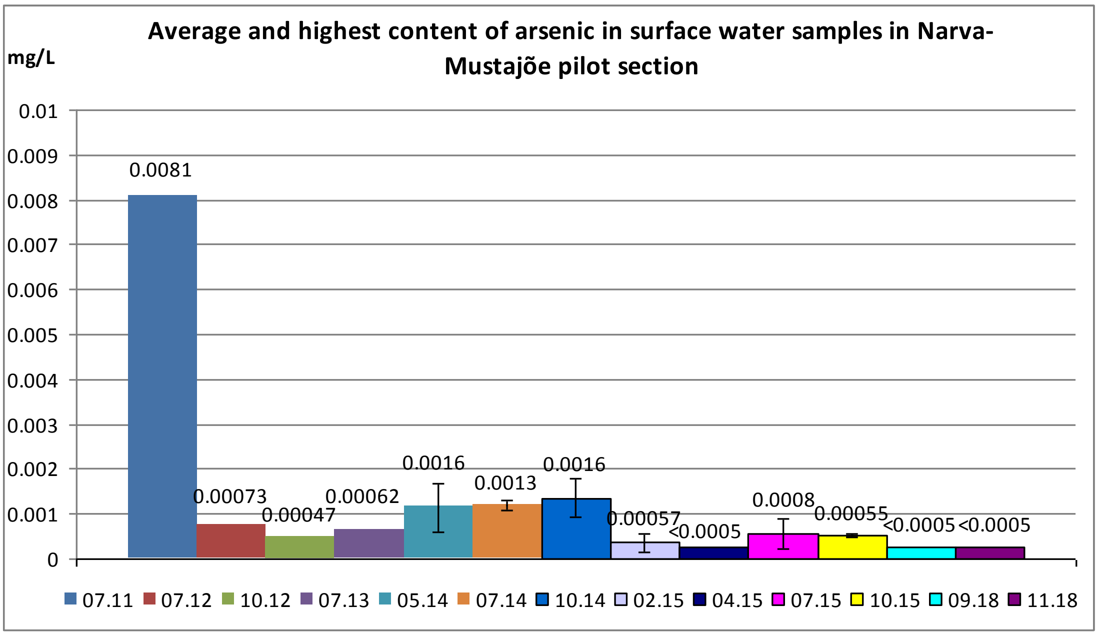


Figure 13. Observed content of lead in water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections (MAC-ECS for lead in surface water is 0.014 mg/L, 07.11 analysis from non-filtrated sample).



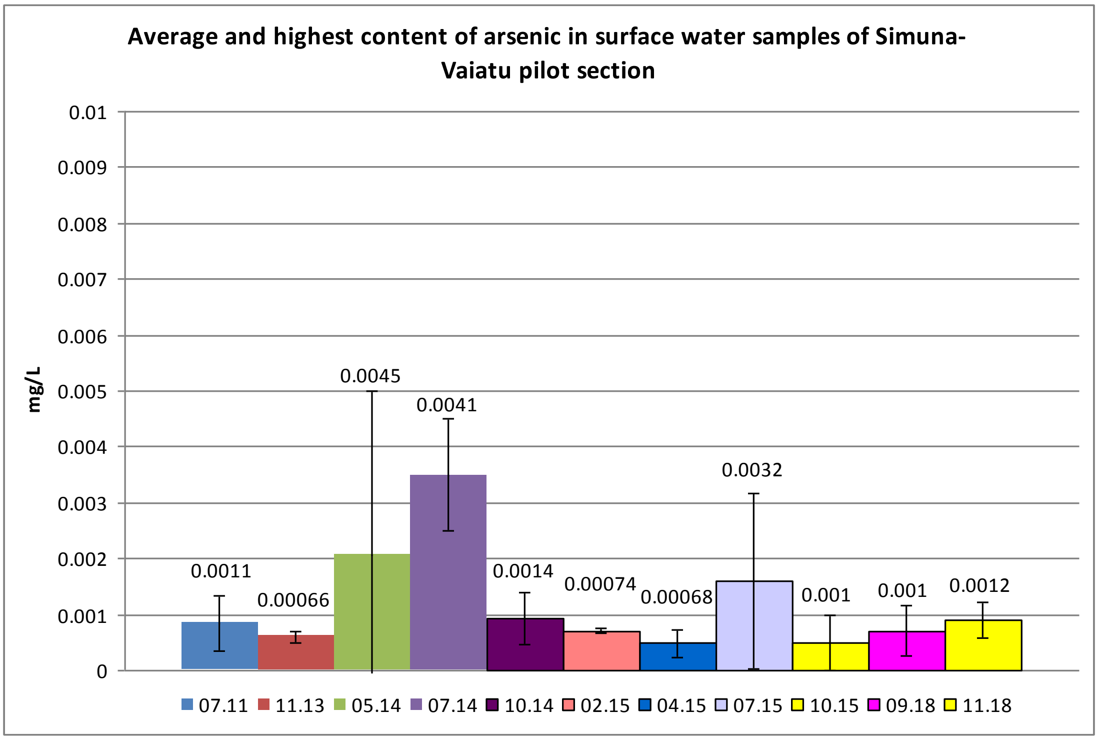
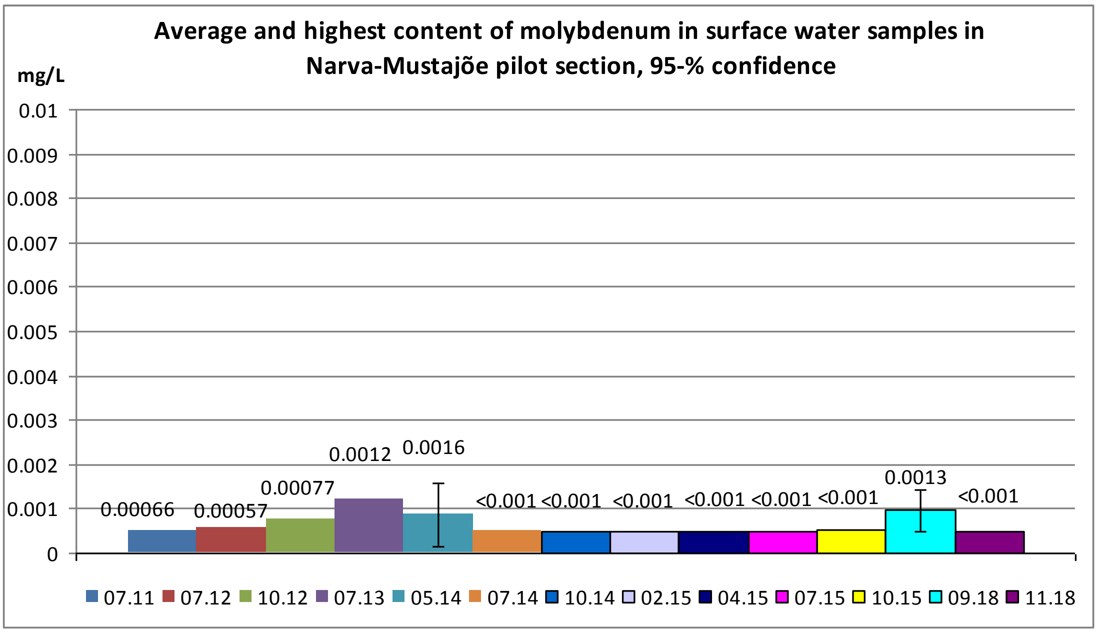


Figure 14 Observed content of arsenic in water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections (MAC-ECS for arsenic in surface water is 0.01 mg/L, 07.11 analysis from non-filtrated sample).



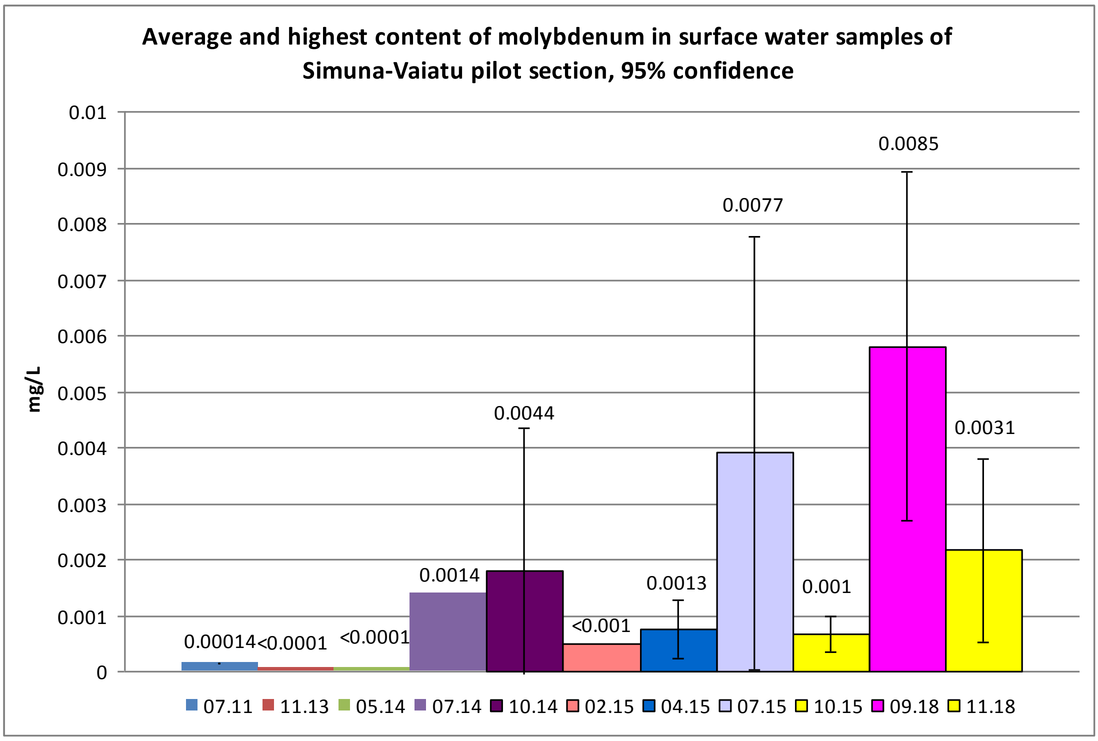
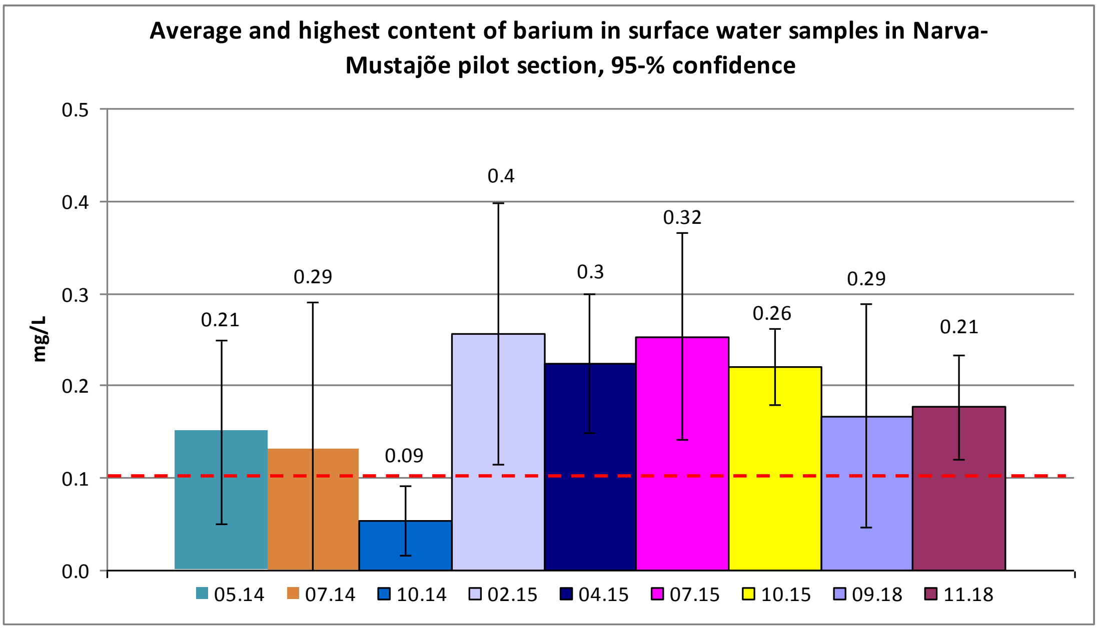


Figure 15 Observed content of molybdenum in water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections (Limit value in groundwater: 0.07 mg/L).



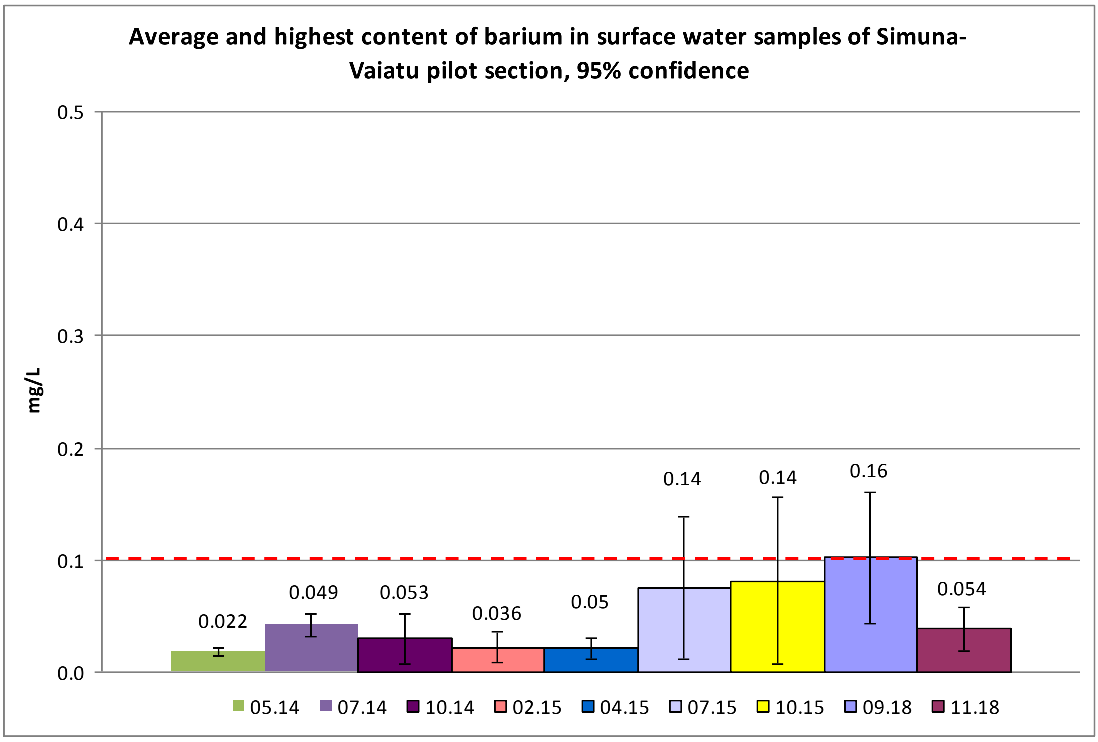


Figure 16. Observed content of barium in water samples of Narva-Mustajõe and Simuna-Vaiatu pilot sections (MAC-EQS for barium in surface water is 0.1 mg/L).

As can be seen from Figures 13-16 the content of selected trace elements in water samples is below environmental quality standards for lead and arsenic. The content of lead has decreased in water samples compared to those taken in 2011 i.e. before road construction. Still, it must be noted that the content of lead and other metals in water samples taken before 2014 are determined from the total sample content, whilst since 2014 the content of metals was determined from filtrated samples (0.45 µm).

Content of arsenic has not been affected by the road construction. Its content is minimal and can be considered as a natural background. The road construction has not affected the content on molybdenum in surface water of Narva-Mustajõe pilot section At the same time the content of molybdenum has increased in surface water of Simuna-Vaiatu pilot section during 2011-2018. Still, the content of molybdenum in water samples of Simuna-Vaiatu pilot is well below the national legal limit.

One element, which average concentration in surface water is close to or above national legal limits in both sections is barium (Figure 16), especially in Narva-Mustajõe section (Figure 17).

In order to establish a natural background level for barium content in surface water in the Narva-Mustajõe road area a surface water sample NM-0 was taken in 21.07.2015 outside the pilot section

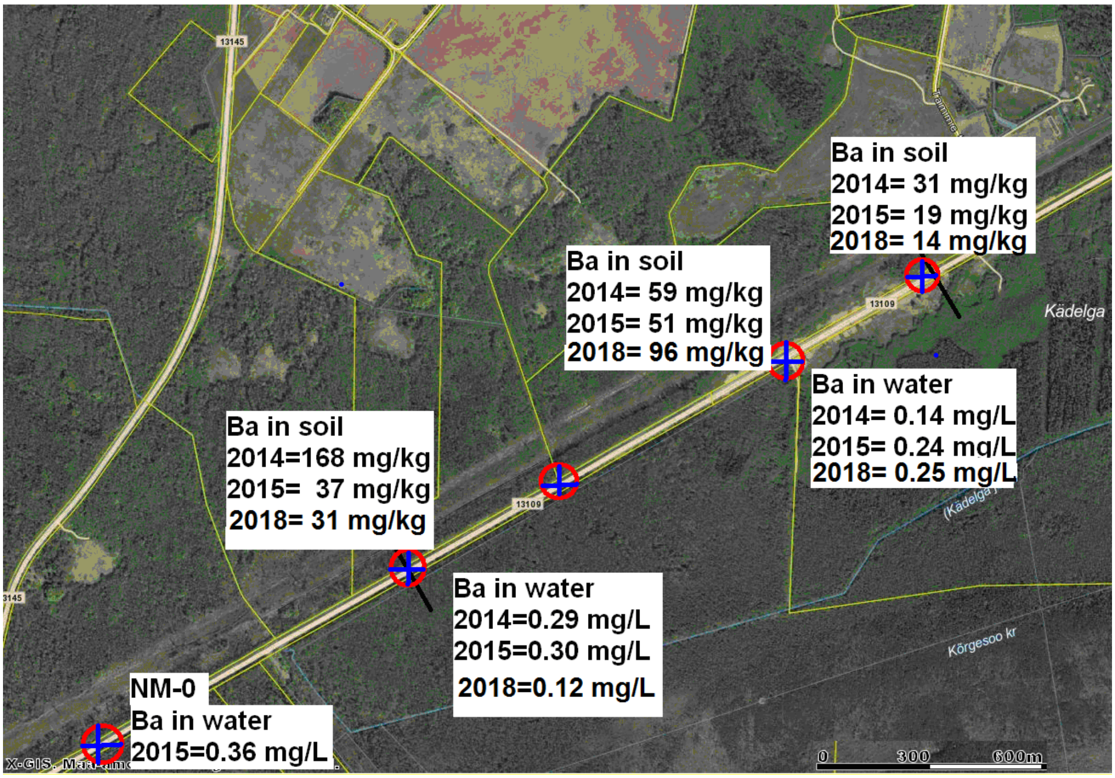


Figure 17. Barium content in soil samples and annual average barium content in surface water samples (except for NM-0).

It turned out that the content of barium in surface water outside the Narva-Mustajõe pilot section area was 0.36 mg/L. This is higher than mean concentrations of barium in surface water in the close vicinity of the pilot section area. This means that the natural background level of barium in the area is higher than national limits (0.1 mg/L).

The United States Environmental Protection Agency has set the maximum barium level in drinking water 2 mg/L[2]

[2] National Primary Drinking Water Regulations, EPA 816-F-09-004, May 2009

Second trace element, which concentration was observed above national environmental limits in surface water in 2018 monitoring is zinc (Tables 12 and 13, Figure 18).

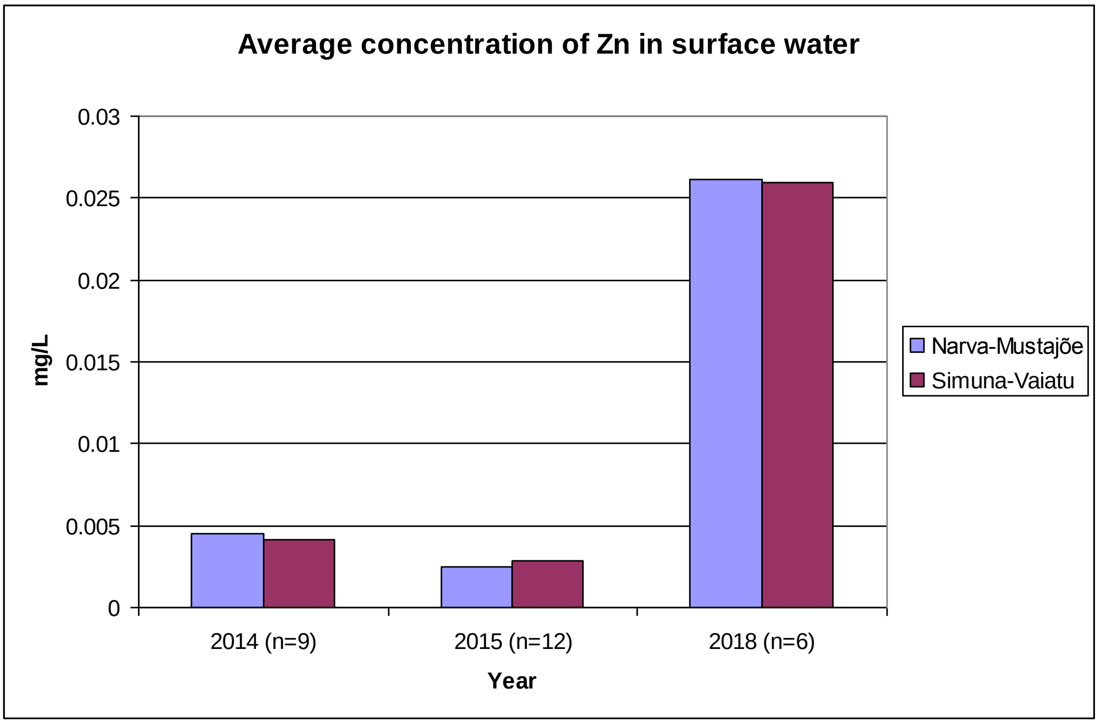


Figure 18. Average concentration of zinc in surface water samples during follow-up monitoring- values below LOQs are halved.

Road construction, maintenance and traffic affect surrounding environment including leaching of Zn to aqueous environment. Similar findings can be found in literature [12, 13]. This phenomena is not related specifically to the use of oil shale ash.

6. Data analysis

For deriving hidden information from the collected data a simple bivariate statistical approach was used. Surface water data from previous and current sampling campaigns was used - totally nine sampling episodes for each point. Bivariate correlations between selected parameters in water sampling points of Narva-Mustajõe and Simuna-Vaiatu pilot sections are presented in Appendix 5.

In Narva-Mustajõe pilot section sampling points NM1 and NM2 there is a tendency of electric conductivity of surface water to be higher when content of content of sulfates and chlorides increases.

Also there is a similar positive correlation between the electric conductivity of surface water with the content of sulfates and chlorides as well as with molybdenum and barium in monitoring point SV2 in Simuba-Vaiatu pilot section.

7. Conclusions

On the basis of follow-up environmental monitoring conducted in 2018 following conclusions can be drawn:

- The content of all selected trace elements in soil samples remained below national environmental quality limits in both pilot sections- The road construction **has not affected the soil quality** and the soil is in good conditions in both pilot sections.
- The content mercury, cadmium, lead and nickel was below limit of detection (LOQ) in all water samples taken in 2018.
- Among hazardous substances following anions and elements were detected: fluoride, arsenic, barium, copper and zinc. **Average content of barium and zinc was found in several water samples above national environmental quality standards** (0.1 and 0,01 mg/L, respectively) in both pilot sections.
- The natural level of barium in surface and groundwater in East-Estonia is generally above national environmental quality standards and is most probably not affected by the use of OSA in road construction [11].
- Natural background level of barium as well as sulfates and chlorides is many times higher in surface water of Narva-Mustajõe pilot section compared to Simuna-Vaiatu section.
- No significant correlation between barium content and other variables was observed in Narva-Mustajõe pilot section. In Simuna-Vaiatu pilot section the content of barium as well as molybdenum correlated with electric conductivity of water samples in SV2 and SV3
- Content of zinc has decreased in soil samples of both pilot sections compared to the pre-construction monitoring results or natural background.
- Concentration of zinc in surface water has increased. Leaching of zinc from road bank soil could be one of the source for elevation in zinc content in surface water of both pilot sections. Other causes could be road maintenance and traffic emissions. Content of zinc should me monitored in future monitoring programs.
- The road construction has not affected the natural level of pH or electric conductivity of surrounding surface water. Electric conductivity of water is directly connected to dissolved solids or salts. Also **content of chlorides and fluoride is similar to natural background level** or with the observations made before road construction.
- The results of sulfate content in surface water samples in comparison with observations made in pre-construction monitoring leave us believe that the **road construction has raised the sulfate content in surrounding surface water in both sections.**.
- In 2011 no sulfates were found in surface water samples of both pilot sections, whilst during follow-up monitoring program in 2014, 2015 and 2018 the elevation in average sulfate content in surface water can be observed in both pilot sections. Natural level of sulfate in Estonian surface water is 20-50 mg/L. In Narva-Mustajõe the mean content of sulfates in surface water fluctuates around 100 mg/L and in Simuna-Vaiatu around 40 mg/L (Figure 11).

- It is recommended to **continue to monitor the EC, concentrations of sulfates, chlorides, barium and zinc** in nearby surface water in future monitoring campaigns until their content has stabilized.
- In Simuna-Vaiatu pilot section the monitoring of surface water could be automated by measuring EC values of the ditch water near to the established road monitoring station (Picture 2). EC is in turn directly correlated with the content of salts in surface water as well as with barium and molybdenum (Table 25) in monitoring point SV2.

Picture 2. Road monitoring station at Simuna-Vaiatu pilot section (near monitoring point SV2).

8. References

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Appendix 1 Accreditations

Appendix 2 Sampling reports and results of analysis for 18.09.2018 and 04.11.2018 sampling campaigns

Appendix 3 Results of previous monitoring programs

Appendix 4 Terms of Reference of the Contract

Appendix 5 Bivariate correlations

Table 5-1. Pearson's bivariate correlations between selected parameters in NM1 during 2014-2015 and 2018 (blue at significance level p< 0.05, red at significance level p>0.01).

	Air temp.	Water temp.	pH	EC	Cl-	SO42-	F-	Ba
Air temp. oC	1.000							
Water temp. oC	**0.915**	1.000						
pH	0.371	0.442	1.000					
EC	-0.241	-0.503	-0.612	1.000				
Chlorides	-0.434	-0.455	0.009	0.331	1.000			
Sulfates	0.032	-0.197	-0.561	**0.916**	0.133	1.000		
Fluoride	0.453	0.299	0.354	0.298	0.165	0.398	1.000	
Barium	0.164	0.151	0.506	-0.420	-0.514	-0.511	-0.019	1.000

Table 5-2. Pearson's bivariate correlations between selected parameters in NM2 during 2014-2015 and 2018 (blue at significance level p< 0.05, red at significance level p>0.01).

	Air temp.	Water temp.	pH	EC	Cl-	SO42-	F-	Ba
Air temp. oC	1.000							
Water temp. oC	**0.918**	1.000						
pH	-0.143	-0.405	1.000					
EC	-0.037	-0.134	0.168	1.000				
Chlorides	0.314	0.175	0.195	**0.820**	1.000			
Sulfates	-0.003	-0.161	-0.196	-0.117	-0.195	1.000		
Fluoride	0.375	0.622	**-0.718**	-0.196	-0.280	0.089	1.000	
Barium	0.230	0.131	-0.057	**0.643**	0.559	0.445	0.196	1.000

Table 5-3. Pearson's bivariate correlations between selected parameters in NM3 during 2014-2015 and 2018 (blue at significance level p< 0.05, red at significance level p>0.01).

	Air temp.	Water temp.	pH	EC	Cl-	SO42-	F-	Ba
Air temp. oC	1.000							
Water temp. oC	**0.901**	1.000						
pH	-0.099	0.195	1.000					
EC	-0.616	-0.520	0.221	1.000				
Chlorides	-0.448	-0.512	-0.223	**0.741**	1.000			
Sulfates	0.105	-0.188	**-0.697**	0.208	0.489	1.000		
Fluoride	**0.775**	0.614	-0.573	-0.368	-0.065	0.608	1.000	
Barium	-0.572	**-0.721**	0.038	0.444	0.542	0.032	-0.587	1.000

Table 5-4. Pearson's bivariate correlations between selected parameters in SV1 during 2014-2015 and 2018 (blue at significance level p< 0.05, red at significance level p>0.01).

	Air temp.	*Water temp.*	*pH*	*EC*	*Cl-*	*SO42-*	*F-*	*Ba*	*Mo*
Air temp. oC	1.000								
Water temp. oC	0.901	1.000							
pH	0.158	0.116	1.000						
EC	-0.093	-0.100	-0.251	1.000					
Chlorides	0.252	0.235	-0.344	0.370	1.000				
Sulfates	0.012	0.004	-0.443	0.882	0.577	1.000			
Fluoride	0.667	0.601	0.160	0.365	0.691	0.434	1.000		
Barium	0.115	0.055	-0.644	0.583	0.476	0.764	0.308	1.000	
Molybdenum	0.281	0.201	-0.453	0.204	0.917	0.530	0.597	0.629	1.000

Table 5-5. Pearson's bivariate correlations between selected parameters in SV2 during 2014-2015 and 2018 (blue at significance level p< 0.05, red at significance level p>0.01).

	Air temp.	*Water temp.*	*pH*	*EC*	*Cl-*	*SO42-*	*F-*	*Ba*	*Mo*
Air temp. oC	1.000								
Water temp. oC	0.922	1.000							
pH	0.704	0.690	1.000						
EC	0.620	0.463	0.387	1.000					
Chlorides	0.356	0.176	-0.088	0.854	1.000				
Sulfates	0.339	0.173	-0.138	0.832	0.981	1.000			
Fluoride	0.649	0.481	0.250	0.930	0.928	0.904	1.000		
Barium	0.543	0.570	0.535	0.821	0.507	0.496	0.617	1.000	
Molybdenum	0.598	0.465	0.106	0.825	0.846	0.904	0.904	0.531	1.000

Table 5-6. Pearson's bivariate correlations between selected parameters in SV3 during 2014-2015and 2018 (blue at significance level p< 0.05, red at significance level p>0.01).

	Air temp.	*Water temp.*	*pH*	*EC*	*Cl-*	*SO42-*	*F-*	*Ba*	*Mo*
Air temp. oC	1.000								
Water temp. oC	0.965	1.000							
pH	0.691	0.795	1.000						
EC	0.716	0.560	0.278	1.000					
Chlorides	0.596	0.453	0.162	0.750	1.000				
Sulfates	0.875	0.773	0.463	0.799	0.600	1.000			
Fluoride	0.896	0.814	0.531	0.782	0.544	0.988	1.000		
Barium	0.302	0.134	-0.126	0.727	0.899	0.369	0.292	1.000	
Molybdenum	0.835	0.769	0.466	0.658	0.469	0.971	0.973	0.199	1.000