Improving the water quality for local use of water resources and ecological state in the cross-border rivers Koitajoki and Tohmajoki - TohmaKoita KA10010

## **FINAL REPORT**

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# 1 Sampling and data analysis in Finland and Karelia

## 1.1 Introduction to sampling activities

The main objective of the Work Package 1 was to evaluate annual variation in levels of the environmental load flowing from Finland to the Republic of Karelia in the cross-border rivers Koitajoki and Tohmajoki.

The chosen methods for the environmental monitoring of the rivers were water sampling and transplanting of aquatic moss species *Fontinalis dalecarlica*. *During the first year of the project, the mosses were transplanted from* the River Sukkulanjoki to the rivers Koitajoki and Tohmajoki. After the first year, it was observed that there were no significant differences in metal and suspended solids background concentrations between the the River Sukkulanjoki and the target rivers. This was probably caused by recent forestry activities in the River Sukkulanjoki area. Because of this, alternative moss collection locations were sought in the second year of the project. Tikanvirta, located in the upper reach of the River Koitajoki (ETRS-TM35FIN coordinates 6996431.94 N 724386.08 E), was chosen as a new collection site for *Fontinalis dalecarlica*, because the aquatic moss grows abundantly there, the location is under relatively low load from the catchment area, and it is easily reachable by vehicles.



1 The location of Tikanvirta in the upper reach of the River Koitajoki.

Aquatic mosses, for instance *Fontinalis antipyretica* have been widely used as bioindicator for metal pollution for almost four decades, because they tolerate metal pollution, are widely distributed, they live long and have high accumulation capacity. Aquatic mosses take metals straight from the water by adsorption and absorption through the cell surfaces. Metal concentrations in the youngest terminal parts reflect the most current growing conditions of mosses. Concentrations in the whole plant reflects long time exposure in the growing conditions of mosses (Vuori & Helisten 2010).

The analysed parameters from moss samples were chemical elements As, Cd, Co, Cr, Cu, Ni, Pb, Se, U, V, Zn Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, Sr, Ti. Suspended solids were also analysed from the mosses.

Transplanting the aquatic mosses was performed as described by Hokkanen (2016). Aquatic mosses were transplanted from the River Sukkulanjoki to the rivers Tohmajoki and Koitajoki for 14 days. The mosses were transplanted at the same place and time where and when water sampling was performed.



2 Incubation rack and aquatic mosses. © Hannu Hokkanen



3 Incubation rack and the aquatic mosses after transplantation in the stream. ©Juuso Pätynen



4 Moss racks after a 14-day incubation period in the River Tohmajoki. ©Juuso Pätynen

## 1.2 Watersheds of the rivers Koitajoki and Tohmajoki

#### 1.2.1 The River Koitajoki

At area of sampling site Koitajoki 13, forestry and ditching of peatlands are probably the most significant types of land use. Clear-cutting has been performed in various locations at the upstream area of the River Koitajoki and forest areas have been widely ditched in the upper watershed before the River Koitajoki flows to Republic of Karelia.

Based on available maps, there are some areas where there are signs of clear-felling and potential ditching of forest in watershed of the River Koitajoki in Republic of Karelia. There are not observable signs of large-scale ditching of peatlands or peat production. Based on literature and map examination, Karelian watershed of the River Koitajoki seems to generally be in almost natural state.

When the River Koitajoki flows back to Finland in Möhkö village, which belongs to municipality of Ilomantsi, ditching and other forestry practices become more intensive again. When the river flows forward, there are also peat production areas in vicinity of the River Koitajoki; and Pamilo Hydroelectric Power Plant.

#### 1.2.2 The River Tohmajoki

In Finnish River Tohmajoki watershed the most common land use practices are agriculture, ditching of peatlands and forestry. Most of the vicinity of Tohmajoki is ditched, especially area of Tohmajoensuo, and there are several clear-felling areas. The river is dammed at the upper reach.

Based on map examination, in Karelian River Tohmajoki watershed the land use practices seem to be quite similar to Finland. The river has been dammed in Akhinkoski that is near Ruskeala. Settlements of Ruskeala, Rytty and Helylä are located along the river. The wastewater released from these settlements are probably the most significant type of load to the River Tohmajoki.

### 1.3 Collection of moss and water samples from the River Koitajoki in Finland

There were two sampling sites: one on the upper reach, where the River Alajoki (marked in the Finnish Vesla database as the sampling site Koitajoki 13) joins with the River Koitajoki, and one in the lower reach in Möhkö (marked in the Finnish Vesla database as the sampling site Koitajoki 1 Möhkö). Locations are shown on the Figure 5. Originally sampling at the upper reach was planned to be performed at Tasaisenkangas, but the location was changed to Koitajoki 13 site, because COVID-19 pandemic decreased the number of available transportation services and Tasainenkangas became too distant location for the new schedules.



Sources: ©Esri, Sampling sites ©Finnish Environment Institute SYKE, watershed borders © SYKE, Water bodies defined by the Water Framework Directive© SYKE



6 Location of Koitajoki 1 Möhkö site.

## 1.4 Collection of moss and water samples from the River Tohmajoki in Finland and Republic of Karelia.

In Finland, sampling sites were located at the upper and lower reaches of the River Tohmajoki. Locations are shown on the Figure 7. Russian sampling points are shown in Figure 8.

In Republic of Karelia, moss sampling could not be performed because of legal restrictions set by legislation of Russian Federation.

1 Sampling plan table for the River the Tohmajoki. Water sampling (W) and Moss incubations (M).

	Finnish a	area of the Ri	ver Tohmajoki	Karelian area of the River Tohmajoki				
Year	1st	2nd 3rd quarter		1st quarter 2nd		3rd quarter	4th quarter	
	quarter	quarter			quarter			
2020	-	June (W	September	-	June (W)	September	December	
		& M)	(W & M)			(W)	(W)	
2021	April	June (W &	September	March (W)	June (W	No data	No data	
	(Ŵ) *	M) **	(W & M)		& metals)			

\* Moss sampling (M) was not performed due to lack of mosses after winter.

\*\*Moss sampling failed at upper reach of the River Tohmajoki due to vandalism.

2 Sampling plan table for the River the Koitajoki. Water sampling (W) and Moss incubations (M).

The River Koitajoki								
Year	1st quarter	2nd quarter	3rd quarter					
2020	-	June (W & M)	September (W & M) *					
2021	May (W) **	June (W & M)	October (W & M)					

\* Sampling site was changed from Tasainenkangas to Koitajoki 13 site.

\*\*Moss sampling was not performed due to lack of mosses after winter.



7 Finnish water and moss sampling sites on the River Tohmajoki region.



Sources: ©Esri, Sampling sites ©Finnish Environment Institute SYKE, watershed borders © SYKE,

Water bodies defined by the Water Framework Directive© SYKE; Russian sampling sites ©Karelvodakanal LLC 8 Russian water sampling sites at the River Tohmajoki region. There were seven sites for metal analyses. For physicalchemical water quality variables there were three sites: Matkaselkä, Rytty and Helylä.

# 2 Analysis of hydrochemical properties and pollutants from moss and water samples in the rivers Koitajoki and Tohmajoki.

2.1 Results in the River Koitajoki

#### 2.1.1 Water quality

#### Physical-Chemical variables

Turbidity decreased generally towards Möhkö site (Figure 9). Summer and autumn 2021 were dry and water level was unusually low in the River Koitajoki, which may have affected turbidity of water through observed suspended solid levels. In May 2021 soil was probably still frozen in the watershed, which decreased volume of effluents flowing to river.



Figure 9 Turbidity results in the River Koitajoki.

Observed total suspended solid levels decreased towards Möhkö site in all sampling times (Figure 10). It is possible that suspended solid concentrations are higher because of lower water level in summer and autumn 2021, although particle runoffs from the watershed probably decreased due to dry season. The lowest suspended solid levels were observed in spring when soil was probably still frozen.



Figure 10 Suspended solid results in the River Koitajoki.

Generally electrical conductivity in river water seems to be lower at Möhkö site (Figure 11). Potassium (K), sodium (Na), Calcium (Ca) and magnesium (Mg) had generally lower levels at Möhkö site, but differences were not conspicuous. Based on the electrical conductivity results, observed levels of these elements and sulphates were low in the River Koitajoki.



Figure 11 Conductivity results in the River Koitajoki.



Alkalinity of the river water decreased consistently towards Möhkö site (Figure 12). In summer and autumn 2021 alkalinity of water may have been higher at Koitajoki 13 site because of dry season, which probably decreased runoffs from the watershed.

Figure 12 Alkalinity results in the River Koitajoki.

The river water was generally slightly more acidic at Möhkö site (Figure 13). Dry season in summer autumn 2021 and may have runoffs decreased from the watershed, which may have increased pH of river water.







During the sampling time colour results were generally lower at

Möhkö site (Figure 14). September 2020 was a rainy season, which probably increased runoffs from the watershed and elevated colour of the river water.

Generally total nitrogen levels were lower at Möhkö site (Figure 15). September 2020 was a rainy season, which probably increased nitrogen runoffs from the watershed.



Figure 15 Total nitrogen results in the River Koitajoki.

Observed total phosphorus concentrations were either on the same level or lower at Möhkö site (Figure 16). The lowest phosphorus levels were observed in spring sampling round. The highest difference between Koitajoki 13 site and Möhkö site were observed in summer sampling round.



Figure 16 Total phosphorus results in the River Koitajoki.

Analysed Chemical Oxygen Demand ( $COD_{Mn}$ ) results decreased towards Möhkö site (Figure 17). September 2020 was a rainy season, which probably increased organic matter runoffs from the watershed.



In June 2021 dissolved organic carbon (DOC) was on same level (14 mg/l). Otherwise observed DOC levels were slightly lower at Möhkö site (Figure 18). September 2020 was a rainy season, which probably increased organic matter runoffs from the watershed.



Figure 18 DOC results in the River Koitajoki.

Observed total organic carbon (TOC) concentrations were either on the same level or lower at Möhkö site (Figure 19). September 2020 was a rainy season, which probably increased organic matter runoffs from the watershed.



Figure 19 TOC results in the River Koitajoki.

In October 2021 observed sulphur levels were Koitajoki 13 site: 490  $\mu$ g/l.; Möhkö site: 470  $\mu$ g/l. In other sampling times sulphur was under detection limit of the laboratory (400  $\mu$ g/l).

#### Metals

Iron (Fe) load in the River Koitajoki seems to decrease towards Möhkö site (Figure 20). The lowest iron levels were observed in spring sampling round when soil was probably still frozen.



Manganese (Mn), that is chemically a close relative to iron, did not show significant level differences, expect Ocober 2021, between Koitajoki 13 site and Möhkö site and its concentrations were generally low in the River Koitajoki (under 50 µg/l) (Figure 21). Autumn 2020 was a season, which rainy probably increased manganese runoffs from the watershed.



Figure 21 Manganese analysis results in the River Koitajoki.

During this sampling period a clear trend in sulphate  $(SO_4)$  load between Koitajoki 13 site and Möhkö site was not observed (Figure 22). Meltwaters from the watershed may be a cause for observed higher sulphate levels at Möhkö site in May 2021.



Figure 22 Sulphate analysis results in the River Koitajoki.

Observed aluminium (Al) concentrations were either on the same level or lower at Möhkö site (Figure 23). Autumn 2020 was a rainy season, which probably increased aluminium runoffs from the watershed.



Arsenic (As) levels were generally lower at Möhkö site. Autumn 2020 was a rainy season, which possibly increased arsenic runoffs from the watershed (Figure 24).



Figure 24 Arsenic analysis results in the River Koitajoki.

Barium (Ba) seems to have a slight decreasing trend towards Möhkö site. Higher concentrations observed in September 2020 may be caused by a runoff peak during a rainy season.



Figure 25 Barium analysis results in the River Koitajoki.

At Möhkö site mercury (Hg) often had slightly higher aquatic levels than at Koitajoki 13 site (Figure 26). Autumn 2020 was a rainy season, which probably increased mercury runoffs from the watershed. Summer and autumn 2021 were dry seasons, which may have decreased mercury runoffs from the watershed.



Cadmium (Cd) does not seem to have a significant rising trend towards Möhkö site (Figure 27). Autumn 2020 was a rainy season, which may have increased cadmium runoffs from the watershed.



Figure 27 Cadmium analysis results in the River Koitajoki.

Potassium (K) seems to have a decreasing trend towards Möhkö site in this sampling period (Figure 28).



Figure 28 Potassium analysis results in the River Koitajoki.

Aquatic calcium (Ca) levels were lower at Möhkö site (Figure 29). Observed calcium levels were highest in autumn sampling rounds.







Figure 30 Cobalt analysis results in the River Koitajoki.

Autumn 2020 was a rainy season, which may have increased cobalt runoffs from the watershed.



Observed chrome (Cr) levels were lower at Möhkö site (Figure 31).

Figure 31 Chrome analysis results in the River Koitajoki.

Observed copper (Cu) levels were lower at Möhkö site (Figure 32). The highest copper levels were observed in September 2020, which was a rainy month.





Observed lead (Pb) levels were slightly higher at Möhkö site (Figure 33).

Figure 33 Lead analysis results in the River Koitajoki.

Observed magnesium (Mg) levels were lower at Möhkö site (Figure 34).



Figure 34 Magnesium analysis results in the River Koitajoki.

Sodium (Na) levels were generally lower at Möhkö site (Figure 35); in May 2021 sodium levels were on same level (0,8 mg/l).



Figure 35 Sodium analysis results in the River Koitajoki.

At Möhkö site observed nickel (Ni) concentrations were slightly lower than at Koitajoki 13 site (Figure 36). Autumn 2020 was a rainy season, which may have increased nickel runoffs from the watershed.



Figure 36 Nickel analysis results in the River Koitajoki

Selenium (Se) was under detection limit of the laboratory  $(0,1 \mu g/l)$  in all sampling times.

Generally observed Zinc (Zn) differences were not significant (Figure 37). Rainy season in September 2020 probably increased runoffs generally.



Figure 37 Zinc analysis results in the River Koitajoki.

At Möhkö site observed strontium (Sr) concentrations were lower than at Koitajoki 13 site (Figure 38). September 2020 was a rainy season, which probably increased strontium runoffs from the watershed.



Figure 38 Strontium analysis results in the River Koitajoki.

Titanium (Ti) levels were lower at Möhkö site, although excluding September 2020 differences were under one  $\mu g/l$ . Highest observed levels were observed in autumn sampling rounds (Figure 39).



Figure 39 Titanium analysis results in the River Koitajoki.

Uranium (U) levels were lower at Möhkö site, although differences were minor excluding September 2020 (Figure 40). Rainy season in autumn 2020 and meltwater in spring 2021 may have increased uranium runoffs from the watershed.



Figure 40 Uranium analysis results in the River Koitajoki.

Observed vanadium (V) levels were lower at Möhkö site (Figure 41).



#### 2.1.2 Moss sample results in the River Koitajoki

#### Description of the method used - Samples from Koitajoki and Tohmajoki

The moss turfs were melted and rinsed several times with distilled water in the laboratory. 100 -110 shoot tips with length of 1-1.5 cm were cut from each moss turf for one parallel sample. The shoot tips were rinsed with distilled water and freeze-dried. The size of the dried samples varied between 27,1–45,4 mg. The samples were microwave digested with nitric acid. The whole sample was digested and that is why samples were not homogenized. After digesting, samples were moved to test tubes and diluted to 30 ml with deionized water.

Concentrations of bioaccumulated elements in transplanted aquatic moss *Fontinalis dalecarlica* samples were mainly higher at the River Koitajoki upper reach site (Koitajoki 13) (figure 42, table 3) than in the lower sampling site (Koitajoki 1 Möhkö). The clearest differences between the sampling sites were for iron (Fe), uranium (U), sodium (Na) and arsenic (As). Iron concentrations varied between 239–640 mg/kg at Koitajoki 13, but only between 32–86 mg/kg at lower sampling site Koitajoki 1 Möhkö and there was a statistically significant difference (p = 0,000). Uranium concentrations were between 0,0056–0,0090 mg/kg at upper reach site and between 0,0012–0,0037 mg/kg at lower sampling site differing statistically (p = 0,000). Sodium concentrations were also higher at Koitajoki 13 (p = 0,011) varying between 2,1–4,2 mg/kg, while concentrations in Koitajoki 1 Möhkö were 0,46–1,6 mg/kg. In addition, arsenic concentrations were significantly higher (0,05–1,3 mg/kg) at the upper site compared to the lower sampling site (0,015–0,074 mg/kg) (p = 0,014). Concentrations of these elements in water samples had the same trend although there were not significant differences between the sampling sites. There seems to be also higher copper (Cu), strontium (Sr) and vanadium (V) concentrations in the mosses at Koitajoki 13, but the amount of samples was too small for statistical testing. High concentrations of lead (Pb) were measured at both sampling sites (0,0087–0,070 mg/kg).

Variation in concentrations were larger at the upper Koitajoki sampling site. For example, aluminium, chrome and titanium had large variation. High concentratios were measured particulary in the moss samples of the autumn year 2020. Opposite to most other elements, the concentrations of barium, cobalt, manganese and sulphur seemed to be higher in the lower sampling sites (table 4). However, the sample number of cobalt, manganese and sulphur was very small (1–2 samples per site). In many cases the concentrations in the moss samples were higher in the reference area, which made it often impossible to get the accumulation of these elements after incubation. Same trend between the sampling sites was not observed in the water samples of these elements – the concentrations were either higher in the upper sampling site or about the same.





Figure 42. Variability in concentrations (mg/kg) of bioaccumulated elements in aquatic moss Fontinalis dalecarlica samples (blue boxplots) and water samples (brown boxplots) at the River Koitajoki sampling sites. Only elements with three samples per site are presented in figures. The boxes show first and third quartiles and median values (thick line), and whiskers show minimum and maximum values. Number of aquatic moss samples is three (3) at both sites. Number of water samples is three (3) at both sites. Number of water samples is three (3) at Koitajoki 13 and four (4) at Koitajoki 1 Möhkö, but six (6) for AI, P, Ca and Na at the latter site.

		Koitajoki	13		Koitajoki 1	Möhkö		
Element	Md/value	min	max	Ν	Md/value	min	max	Ν
Al	15	5,0	45	3	13	4,0	19	3
As	0,07	0,05	0,13	3	0,017	0,015	0,074	3
Ва	1,0	0,70	1,3	2	1,7	0,05	3,3	2
Са	78	48	109	2	36	1,4	71	2
Cd				0	0,0014			1
Со	0,11	0,057	0,15	2	0,19			1
Cr	0,034	0,024	0,18	3	0,018	0,0077	0,088	3
Cu	0,082	0,076	0,088	2	0,025			1
Fe	573	239	640	3	69	32	86	3
Hg	0,00060	0,0000	0,0012	2	0,0000			1
К	1,7			1	1,5			1
Mg	10	5,8	14	2	6,0			1
Mn	32			1	51			1
Na	2,1	2,1	4,2	3	1,4	0,46	1,6	3
Ni	0,028	0,011	0,046	2	0,022			1
Р	12	11	29	3	15			1
Pb	0,040	0,010	0,070	2	0,040	0,0087	0,070	2
S	11			1	13			1
Se	0,0020			1	0,00073			1

Table 3. Medians (Md), minimum and maximum concentrations (mg/kg) of bioaccumulated elements in aquatic moss Fontinalis dalecarlica samples at the River Koitajoki sampling sites. N = number of samples.

Sr	1,2	1,1	1,3	2	0,34	0,21	0,48	2
Ti	0,67	0,32	5,9	3	0,32	0,32	1,7	3
U	0,0059	0,0056	0,0090	З	0,0029	0,0012	0,0037	З
V	0,20	0,11	0,44	3	0,045	0,0064	0,084	2
Zn	0,70			1				0

Table 4. Medians	(Md), minimum a	nd maximum	concentrations	(mg/kg)	of elements	in water	samples a	at the
River Koitajoki sa	mpling sites. N =	number of sa	mples.					

		Koitajoki	13	Koitajoki 1 Möhkö				
Element	Md	min	max	Ν	Md	min	max	Ν
Al	140	130	260	3	130	120	200	6
As	0,85	0,72	1,4	3	0,68	0,63	0,69	4
Ва	6,7	6,0	13	3	5,6	4,7	9,0	4
Hg	0,0042	0,0031	0,0070	3	0,0036	0,0016	0,0082	4
Р	12	12	12	3	12	12	12	4
Cd	0,009	0,006	0,014	3	0,010	0,009	0,013	4
К	0,35	0,34	0,37	3	0,30	0,24	0,37	6
Са	1,8	1,4	2,4	3	1,3	0,9	1,6	6
Cl				0	0,2	0,2	0,2	2
Со	0,27	0,24	0,40	3	0,19	0,16	0,27	4
Cr	0,69	0,59	0,86	3	0,44	0,36	0,51	4
Cu	0,43	0,33	0,88	3	0,31	0,28	0,44	4
Pb	0,28	0,21	0,39	3	0,31	0,28	0,42	4
Mg	0,59	0,40	0,66	3	0,40	0,27	0,48	6
Mn	37	32	51	3	38	34	48	4
Na	0,9	0,8	1,2	3	0,9	0,6	1,0	6
Ni	0,63	0,60	1,6	3	0,47	0,35	0,87	4
Fe	1600	920	1800	3	920	850	1500	4
S	200	200	200	3	200	200	200	4
Se	0,05	0,05	0,05	3	0,05	0,05	0,05	4
Zn	1,5	1,3	5,1	3	2,6	1,6	4,2	4
Sr	16	13	24	3	10	8,0	14	4
Ti	2,7	2,5	5,2	3	2,2	2,1	3,1	4
U	0,067	0,050	0,096	3	0,032	0,027	0,037	4
V	1,3	0,94	1,3	3	0,68	0,63	0,84	4

## 2.1 Results in Finnish area of the River Tohmajoki

#### 2.2.1 Water quality

#### Physical-Chemical variables

During the sampling time, turbidity of the river water increased generally towards the lower reach. The highest observed difference was



from June 2021. The lowest difference was in September 2021 and upper reach was as an exception observed to be more turbid than the lower reach.

In summer sampling rounds observed conductivity increased towards the lower reach and decreased in other seasons.



Figure 44 Conductivity results in the River Tohmajoki.

Analysed pH values decreased consistently towards the lower reach. The highest pH differences were observed in autumn sampling round 2020, which may be caused by rainy season. September 2021 was quite dry, which probably decreased effluents from the watershed.



Figure 45 Acidity results in the River Tohmajoki.

Excluding April 2021, river water's ability to resist changes in acidity remained good at both the upper and lower reach of the River Tohmajoki. In April 2021 alkalinity had decreased under 0,2 mmol/1 (the guideline for "good" alkalinity class) at the lower reach.



Figure 46 Alkalinity results in the River Tohmajoki.

Colour of the water elevated generally towards the lower reach. The highest difference was in September 2020 and the lowest in June 2020.



Figure 47 Colour results in the River Tohmajoki.



Figure 48 Total suspended solid results in the River Tohmajoki.

Observed levels of Dissolved Organic Carbon (DOC) and Total Organic Carbon (TOC) varied between the sampling times being either on the same level, or 1-8 mg/l higher at the lower reach. The highest differences in DOC and TOC levels were observed in September 2020. The lowest differences were in summer sampling rounds.



Figure 49 DOC results in the River Tohmajoki.

Excluding September 2021, total suspended solid levels ((filter particle size  $0,4 \mu m$ , analysis code SS;F6;GVS)) increased towards lower reach of the River Tohmajoki.



Figure 50 TOC results in the River Tohmajoki.

Observed Chemical Oxygen Demand (COD<sub>Mn</sub>) elevated consistently towards the lower reach, difference range being within 2,0 - 14 mg/l. The lowest difference was in June 2021 and the highest September 2020.



Figure 51 CODMn results from the River Tohmajoki.

Biological Oxygen Demand (BOD5-ATU) had more variation in results, when compared to Chemical Oxygen Demand results.

BOD5 results were more often higher at the lower reach, but in June and September 2021 the upper reach was observed to have higher Biological Oxygen Demand results.



Figure 52 BOD5 results from the River Tohmajoki.

Observed total nitrogen levels generally increased towards the lower reach. In June 2021 upper reach had as an exception 10  $\mu$ g/l higher total nitrogen levels than was observed in the lower reach. The highest nitrogen levels were observed in April 2021.

Total phosphorus levels elevated

mostly towards the lower reach,

however there were two aberrations: April 2021 and September 2021.



Figure 53 Total nitrogen results from the River Tohmajoki.



Figure 54 Total phosphorus results from the River Tohmajoki.

In summer observed sulphur (S) levels increased towards the lower reach; and during other seasons decreased.



Figure 55 Sulphur results from the River Tohmajoki.

Observed differences in sulphate  $(SO_4)$  concentrations were 0 - 1 mg/l and sulphate levels did not show clear differences between the upper and lower reaches



Figure 56 Sulphate results from the River Tohmajoki.

#### Metals

During the sampling period, iron (Fe) levels elevated consistently towards the lower reach, excluding April 2021 when observed iron levels were both 1200  $\mu$ g/l at the upper and at the lower reach.



Figure 57 Iron results from the River Tohmajoki.

In April 2021 manganese (Mn) levels were higher at the upper reach than at the lower reach; same was in September 2021, although the difference was minor. Otherwise, analysed manganese levels increased towards the lower reach of the River Tohmajoki.



Figure 58 Manganese results from the River Tohmajoki.

Observed aluminium (Al) load increased consistently towards the lower reach. The highest Al levels were observed in September 2020 and May 2021.



Figure 59 Aluminium results from the River Tohmajoki.



Figure 60 Arsenic results from the River Tohmajoki.

Barium (Ba) load was not observed differ significantly between upper and lower reaches of the River Tohmajoki. Range of differences was within  $0 - 2 \mu g/l$ .



Figure 61 Barium results from the River Tohmajoki.

Observed arsenic (As) load increased consistently towards the lower reach.

Observed mercury (Hg) levels elevated generally towards the lower reach. As an exception analysed mercury levels were  $0,0007 \mu g/l$  at both upper and lower reach in June 2020.

Cadmium (Cd) levels elevated

generally towards lower reach but

there were two occasions when

concentrations were either on same level or slightly higher at the upper

reach (June 2020 and 2021).



Figure 62 Mercury results from the River Tohmajoki.

0,017 CADMIUM MICROGRAM/L 0,014 0,014 0,011 0,011 0,009 0,01 0,008 TOHMAJOKI 9 UPPER REACH TOHMAJOKI LOWER REACH TOHMAJOKI LOWER REACH TOHMAJOKI LOWER REACH TOHMAJOKI 9 UPPER TOHMAJOKI 9 UPPER TOHMAJOKI 9 UPPER TOHMAJOKI 9 UPPER TOHMAJOKI LOWER TOHMAJOKI LOWER REACH REACH REACH REACH REACH REACH REACH 23.9.2020 28.4.2021 22.6.2021 20.9.2021 SAMPLING SITE AND DATE

Figure 63 Cadmium results from the River Tohmajoki.

Potassium (K) did not show clear increasing nor decreasing trend towards the lower reach: at times the upper reach had higher levels, sometimes the lower reach.



Figure 64 Potassium results from the River Tohmajoki.

Calcium (Ca) showed decreasing trend towards the lower reach more often than rising.



Figure 65 Calcium results from the River Tohmajoki.



Figure 66 Cobalt results from the River Tohmajoki.



Cobalt (Co) was observed to have a

rising trend towards the lower reach.

Chrome (Cr) showed increasing trend towards the lower reach.

Based on the results there does not seem to be significant difference in copper (Cu) load of the upper and lower reach of the River Tohmajoki.

Figure 68 Copper results from the River Tohmajoki.

Lead (Pb) showed increasing trend towards the lower reach, although volume of differences variated between sampling rounds.



In summer magnesium (Mg) load increased towards the lower reach; and during other seasons decreased.



In summer observed sodium (Na) load increased towards the lower reach; and during other seasons it decreased.

Nickel (Ni) showed a rising trend towards the lower reach. However, there was variation in volume of level differences.



Figure 72 Nickel results from the River Tohmajoki.

Selenium (Se) levels were under detection limit of the laboratory in all sampling times.



Based on the observed levels strontium (Sr) seems to have slightly decreasing trend towards the lower reach.

rising trend towards the lower reach.

Figure 74 Strontium results from the River Tohmajoki.



Titanium (Ti) showed increasing trend towards the lower reach.

Figure 75 Titanium results from the River Tohmajoki.

There was not a clear trend in uranium (U) concentrations between the upper and the lower reach and differences were small.



Figure 76 Uranium results from the River Tohmajoki.



Vanadium (V) showed increasing trend towards the lower reach.
#### 2.1.2 Moss sample results in the River Tohmajoki

Aluminium (Al), arsenic (As), manganese (Mn), sodium (Na), titanium (Ti) and uranium (U) concentrations in transplanted *Fontinalis dalecarlica* samples seemed to be slightly higher at the River Tohmajoki lower reach sampling site (figure 78, table 5). However, only sodium concentrations were statistically higher at the lower site (p = 0.022). Sodium concentrations varied between 0.84–4.8 mg/kg at the lower site and between 0.26–1.5 mg/kg in the upper site. The concentrations of arsenic and titanium were clearly higher in the water samples at the lower sampling site of the River Tohmajoki and there were statistical differences (for As p =0.008 and for Ti p = 0.018).

On the contrary, the concentrations of copper (Cu) and selenium (Se) seemed to be slightly higher in mosses at the River Tohmajoki upper reach sampling site, but they did not differ statistically. High concentrations of cadmium (Cd), copper (Cu) (and potassium (K) was measured at both the upper and the lower reach sampling sites.

In general, the concentrations of elements were higher during the first sampling year in moss samples possibly due to high discharge in the river after several days of rain.







Figure 78. Variability in the concentrations of bioaccumulated elements in aquatic moss Fontinalis dalecarlica samples (blue boxplots) and water samples (brown boxplots) at the River Tohmajoki sampling sites. Only elements with at least three samples per site are presented in figures. The boxes show first and third quartiles and median values (thick line), and whiskers show minimum and maximum values. Number of water moss samples is three (3) at Tohmajoki upper reach and mainly four (4) at Tohmajoki lower reach, however three (3) for Cu, Mn, P at the latter site. Number of water samples is five (5) at River Tohmajoki both sites.

	Tohmajoki upper reach				Tohmajoki lower reach			
Element	Md/value	min	max	Ν	Md/value	min	max	Ν
Al	8	2	30	3	21	7	31	4
As	0,011	0,0021	0,028	3	0,013	0,0000	0,035	4
Ва	1,5			1	0,21	0,042	0,37	2
Са	146	137	273	3	168	120	212	4
Cd	0,012			1	0,0066	0,0046	0,0085	2
Со	0,055			1	0,20	0,042	0,36	2
Cr	0,033	0,016	0,11	3	0,052	0,010	0,089	4
Cu	0,49	0,22	0,56	3	0,24	0,046	0,55	3
Fe	65			1	114	29	219	4
Hg	0,0024			1	0,00024			1
К	29			1	22			1
Mg	7,8	0,78	14	3	8,4			1
Mn	18	17	92	3	52	33	125	3
Na	0,48	0,26	1,5	3	1,8	0,84	4,8	4
Ni	0,46	0,081	1,3	3	0,45	0,13	1,1	4
Ρ	8,9	6,4	12	3	4,6	1,5	26	3
Pb	0,017			1				0
S	4,8			1	7,5			1
Se	0,0047	0,0037	0,0055	3	0,0042	0,0018	0,0061	4
Sr	0,60	0,23	1,0	2	0,20	0,11	0,56	3
Ті	0,48	0,47	1,9	3	1,2	0,12	2,5	4
U	0,0094	0,0050	0,016	3	0,013	0,0072	0,016	4
V	0,0063	0,0016	0,011	2	0,037	0,035	0,038	2
Zn	2,1			1				0

Table 5. Medians (Md), minimum and maximum concentrations of bioaccumulated elements in aquatic moss Fontinalis dalecarlica samples at the River Tohmajoki sampling sites. N = number of samples.

Table 6. Medians (Md), minimum and maximum concentrations (mg/kg) of elements in water samples at the River Koitajoki sampling sites. N = number of samples.

	Tohmajoki 9 padon yläp.				Tohmajoki alaosa			
Element	Md	min	max	Ν	Md	min	max	Ν
Al	84	51	170	5	110	88	220	5
As	0,35	0,28	0,36	5	0,39	0,36	0,49	5
Ва	16	15	17	5	16	15	18	5
Hg	0,0011	0,0007	0,0020	5	0,0017	0,0007	0,0025	5
Ρ	12	12	12	5	12	12	12	5
Cd	0,011	0,008	0,017	5	0,014	0,010	0,022	5
К	2,0	1,9	2,1	5	1,9	1,7	2,1	5

Са	9,0	8,6	9,2	5	8,6	7,6	9,3	5
Со	0,18	0,16	0,53	5	0,43	0,32	0,99	5
Cr	0,35	0,25	0,39	5	0,48	0,35	0,54	5
Cu	1,6	1,5	1,6	5	1,5	1,4	1,6	5
Pb	0,12	0,11	0,14	5	0,18	0,13	0,22	5
Mg	2	2,0	2,2	5	2	1,9	2,3	5
Mn	85	76	140	5	110	82	210	5
Na	2,83	2,6	2,9	5	2,7	2,4	2,9	5
Ni	3,4	2,9	3,5	5	3,7	3,1	4,0	5
Fe	700	570	1200	5	1300	1000	1800	5
S	5600	4800	6000	5	5500	4800	6200	5
Se	0,05	0,05	0,05	5	0,05	0,05	0,05	5
Zn	1,7	1,2	3,0	5	2,4	1,9	4,4	5
Sr	41	38	42	5	38	34	41	5
Ті	2,2	1,6	2,7	5	2,8	2,6	4,3	5
U	0,053	0,047	0,059	5	0,052	0,049	0,056	5
v	0,37	0,33	0,47	5	0,63	0,49	0,72	5

#### 2.3 Water quality results from Karelian side of the River Tohmajoki

There were three water quality sampling points at the area of the Republic of Karelia. The sampling sites were located at settlements of Matkaselkä, Rytty and Helylä (Figure 8). Matkaselkä is located at the Karelian upper reach of the River Tohmajoki. Helylä is located at the lower reach just before the River Tohmajoki flows to Lake Ladoga. Besides these, there were seven sampling sites for metal analyses, which have their own chapter.

Due the suspension of project it was not possible to get all the activities done by planned way.

#### Physical-Chemical variables

#### Acidity

During the sampling periods, it was observed that the river water becomes consistently more alkaline (pH value in the river water rises) the closer the River Tohmajoki flows to the Lake Ladoga. In every sampling round the lowest pH results were in Matkaselkä site and the highest in Helylä site.



Figure 79 Acidity analysis results in 2020.



Figure 80 Acidity analysis results in 2021.

#### Suspended solids

Suspended solid levels were observed to elevate towards the Lake Ladoga. Due to current political circumstances, it is not known which filter size has been used by the Russian laboratory. Because of this Finnish and Russian results should be compared with caution.



Figure 81 Total suspended solid analysis results in 2020.



Figure 82 Total suspended solid analysis results in 2021.

#### Biological Oxygen Demand with a five-day incubation time (BOD5)

Observed Biological Oxygen Demand (BOD5) rose generally towards settlement of Helylä. There were some exceptions caused by seasonal variation.



Figure 83 BOD5 analysis results in 2020.



Figure 84 BOD5 analysis results in 2021.

#### Nitrogen

Observed total nitrogen levels rose generally towards Helylä site. There were some exceptions caused by seasonal variation.



Figure 85 Total nitrogen analysis results in 2020.





#### Phosphorus

Total aquatic phosphorus levels rose generally towards Helylä settlement. In Matkaselkä site the highest observed phosphate level was 50  $\mu$ g/l (September 2020). In other sampling times phosphate levels were under detection limit of the laboratory at Matkaselkä site.



Figure 87 Total phosphorus analysis results in 2020.





#### Sulphate

In Matkaselkä site the highest observed sulphate levels were 10 (September 2020) and 12,2 (June 2021) mg/l. In other sampling rounds sulphate levels were under detection limit of the laboratory.

In Rytty site the highest observed sulphate level was 13,7 mg/l in June 2021. In other sampling rounds sulphate levels were under detection limit of the laboratory.

In Helylä site the highest observed sulphate level was 12,2 mg/l in June 2021. In other sampling rounds sulphate levels were under detection limit of the laboratory.



Figure 89 Sulphate analysis results in 2020.



Figure 90 Sulphate analysis results in 2021.

Oil products were not detected in any sampling rounds.

#### Turbidity

Turbidity of the river water increased towards Helylä site in all sampling rounds.







Figure 92 Turbidity analysis results in 2021.

#### Colour

Colour of the river water increased generally towards Helylä site at least slightly. However, seasonal variation was significant and there were some exceptions.



Figure 93 Colour analysis results in 2020.



Figure 94 Colour analysis results in 2021.

#### Chemical Oxygen Demand COD(Mn)

COD<sub>Mn</sub> was analysed in the delta of the River Tohmajoki in September/October 2020. Analysed Chemical Oxygen Demand was 18,4 mg/l. In Finnish lower reach of the River Tohmajoki highest observed CODMn value was 28 mg/l in September 2020.



Figure 95 CODMn analysis results from Finnish part of the River Tohmajoki.

#### Metals

Metals were analysed from seven sampling sites in Karelian area of the River Tohmajoki at the end of June 2021. The running numbers of the sampling sites rose towards the Lake Ladoga. Aluminium, iron, and manganese were the only metals whose concentrations were above detection limit of the laboratory.

#### Aluminium (Al)

The lowest aluminium level (112  $\mu$ g/l) was in the Karelian sampling site 1; and the highest (131  $\mu$ g/l) in the 2<sup>nd</sup> sampling point in settlement of Ruskeala. In the rest five sampling sites results varied between 121  $\mu$ g/l (Point 6) and 130  $\mu$ g/l (Point 4). When compared to the first sampling point, sampling sites down the river had generally higher aluminium levels. Hovewer, aluminium levels were not always observed to elevate in a linear manner towards the lower reach.



Figure 96 Aluminium analysis results from Karelian part of the River Tohmajoki.

Iron (Fe)

The lowest iron level (654 µg/l) was observed in the 2nd sampling point (Ruskeala); and the highest (716 µg/l) in the 3rd sampling point. In this sampling time iron levels did not show clear differences between upper and lower reach of the River Tohmajoki in the Republic of Karelia.



Figure 97 Iron analysis results from Karelian part of the River Tohmajoki.

#### Manganese (Mn)

The lowest manganese level (42 µg/l) was analysed in the 1st sampling point; and the highest (95 µg/l) in the 6<sup>th</sup> sampling site. Generally sampling sites located in the lower reach had higher observed manganese levels than the 1<sup>st</sup> sampling site. However, manganese levels were not always observed to elevate in a linear manner towards the lower reach.



Figure 98 Manganese analysis results from Karelian part of the River Tohmajoki.

## 3 Assessment of environmental load from Finland to Republic of Karelia

Environmental load from Finland to Republic of Karelia was assessed with Finnish SYKE-WSFS-Vemala 1 Water model system. Chosen variables for the model were total nitrogen, total phosphorus, and suspended solids, because their results are best checked.

#### 3.1 The River Koitajoki

At the area of sampling site Koitajoki 13 total nitrogen load is originated from:

- 3% from agriculture.
- Natural leaching from forests 82%.
- Forestry activities (logging, fertilization, maintenance of ditches) 10%.
- 1% from point load and fallout 3% (VEMALA V1).

Based on VEMALA V1 simulations, annual sum of estimated nitrogen load has been 70 - 110 tons in years 2016 - 2021 (Figure 97).



99 Annual sum of nitrogen load at area of Koitajoki 13 site.

Based on VEMALA V1 simulations, nitrogen and phosphorus loads are at the highest level in spring, when snow is melting. Second but lower peak occurs in rainy autumn months (Figures 100 and 102). As expected, the loads are at the lowest level in winter months and then during summer.



100 Simulated seasonal variation in nitrogen load at area of Koitajoki 13 site.

Total phosphorus is originated from:

- 7% from agriculture.
- 16% from forestry.
- Natural leaching from forests 75%.
- 1% fallout (VEMALA V1).

Based on VEMALA V1 simulations, annual sum of estimated phosphorus load has been approximately 3,5 - 5,3 tons in years 2016 - 2021 at area of Koitajoki 13 site (Figure 101).



101Annual sum of phosphorus load at area of Koitajoki 13 site.



102 Simulated seasonal variation in phosphorus load at area of Koitajoki 13 site.

03-Mar-22 10:46:45 Filename=basinstationload2724985 6984802 20 Total suspended solid (F6) load is originated from:

- 1% is from agriculture.
- Natural leaching from forests 99%. (VEMALA V1).

Based on VEMALA V1 simulations, annual sum of estimated suspended solid load has been approximately 880 - 1500 tons in years 2016 - 2021 at area of Koitajoki 13 site (Figure 13). Based on VEMALA V1 simulations, suspended solid load is at the highest level in spring, when snow is melting. Second but lower peak occurs in rainy autumn months (Figures 104). As expected, the loads are at the lowest level in winter months and then during summer.



103Annual sum of suspended solid load at area of Koitajoki 13 site.



104 Simulated seasonal variation in suspended solid load at area of Koitajoki 13 site.

#### 3.2 The River Tohmajoki

The annual total nitrogen loads that left Finnish part of the River Tohmajoki were approximately 50 - 68 tons between years 2016 and 2021 (Figure 105). Based on V1 simulations, the nitrogen load is generally at the highest level in spring, after snow starts to melt. The second but lower peak occurs during rainy season in autumn. The lowest simulated load level is during winter months and the second lowest in July and August (Figure 106).



105 Annual total nitrogen load in Finnish Tohmajoki lower reach site.



106 Seasonal variation in total nitrogen load in Finnish Tohmajoki lower reach site.

At Tohmajoki lower reach site total nitrogen load is originated from:

- 18% from agriculture.
- Natural leaching from fields 8% and forests 47%.
- Forestry activities (logging, fertilization, maintenance of ditches) 11%.
- Drainage waters 3%.
- Sparce population and holiday homes 2%.
- 12% from point load and fallout (VEMALA V1).

The annual total phosphorus load was 1,6 - 2,0 tons between years 2016 and 2021 (Figure 105). In V1 simulations phosphorus shows similar temporal trend with nitrogen, load peaks being at spring and autumn, when flow rate is at its highest due to melting snow and autumn rains (Figure 108).



107Annual total phosphorus load in Finnish Tohmajoki lower reach site.



108 Seasonal variation in total phosphorus load in Finnish Tohmajoki lower reach site.

At Tohmajoki lower reach site total phosphorus load is originated from:

- 57% from agriculture.
- Natural leaching from fields 3% and forests 15%.
- Forestry activities (logging, fertilization, maintenance of ditches) 9%.
- Drainage waters 7%.
- Sparce population and holiday homes 4%.
- 5% from point load and fallout (VEMALA V1).

For suspended solids (F6) annual total loads were approximately 250 - 420 tons between years 2016 and 2021 (Figure 109). A difference to nitrogen and phosphorus load simulations is that spring seems to be more dominant season for suspended solids load. The load does increase in autumn, but in much lower scale than with total nitrogen and phosphorus loads (Figure 110).



109 Annual total load of suspended solids in Finnish Tohmajoki lower reach site.



110 Seasonal variation of suspended solid load in Finnish Tohmajoki lower reach.

At Tohmajoki lower reach site suspended solid (F6) load is originated from:

- 40% from agriculture.
- Natural leaching from fields 6% and forests 53% (VEMALA V1).

### 4 Discussion and conclusions

#### 4.1 The River Koitajoki

#### 4.1.1 Water Quality

#### Metals

Based on the analysis results, general trend seems to be that observed aquatic metal concentrations decrease while River Koitajoki flows in territory of Republic of Karelia. Lead, mercury, and zinc were observed to be expections and their observed levels elevated slightly between sampling points Koitajoki 13 and Koitajoki 1 Möhkö.

The most notable metal was iron (Fe), whose observed levels were  $70 - 680 \mu g/l$  lower at sampling point Koitajoki 1 Möhkö than at Koitajoki 13 during the sampling rounds performed in years 2020 and 2021. Observed iron levels were generally typical for peatland river areas. However, it was interesting how iron levels decreased by even several hundreds of micrograms per litre while Koitajoki flows in Republic of Karelia. This may indicate that dilution effect from other rivers and streams flowing to Koitajoki combined with potential self-purification processes lower levels of iron (and other metals) closer to what they might be in river's natural state. However, confirmation of this trend requires a longer monitoring period. As a whole iron levels seem to be typical for swampy watersheds in Koitajoki.

At Möhkö observed iron load did not show aberrations from concentration range that was observed between years 2000- 2021 (Hertta database). In the area of sampling point Koitajoki 13, a longer time examination was not possible due to lack of suitable monitoring data.

The upper part of Finnish area of Koitajoki (before the river flows to Republic of Karelia) is heavily affected by ditching of peat lands and large-scale cutting of forests for the needs of forestry. This kind of treatment of peat lands is known to increase iron transport in catchment areas (Heikkinen et al. 2021). It must be noted that heavy land treatment generally increases environmental load in waterbodies, although it can be lowered with proper buffer zones and land treatment techniques.

According to literature review by Project PuuMaVesi and based on map examination, Russian side of Koitajoki area is more in natural state (Project PuuMaVesi literature review in Finnish: Puuaineksen lisäyksen mahdollisuudet ravinteiden pidättäjänä ja eliöstön monipuolistajana kuormitetuissa vesistöissä: kirjallisuuskatsaus), which probably increases the river's self-purification capacity compared to Finnish parts of Koitajoki.

Iron has complex environmental chemistry that is not yet fully understood. Iron has a role in brownification of waterbodies, which has been observed in Northern Europe during last 30 years (Sarkkola et al. 2013). According Sarkkola et al. 2013, brownification may change function of aquatic ecosystems in several ways:

- 1) By reducing amount of sunlight available to primary producers,
- 2) By increasing temperature of water by higher absorption of sunlight, especially in lakes. This may impair species that require cold and clear water and decrease oxygen levels in water.
- 3) Increased iron load may also cause direct toxic effects to the biota if organisms are adapted to lower iron levels in their habitat.
- 4) Browner surface waters may also channel more greenhouse gases to atmosphere.
- 5) In terms of human usage, brownification of waterbodies increases drinking water production costs and decreases cultural and recreational values of waterbodies (Wit et al. 2016).
- 6) Iron may act as vector for toxic metals like arsenic, lead, mercury, and vanadium with dissolved organic matter (Kritzberg 2019).

Aluminium (Al) was observed to have second highest aquatic metal levels after iron. Currently aluminium does not have an official environmental quality standard in European Union. Only guidelines for drinking water: maximum allowable concentration 200  $\mu$ g/l and recommendation <100  $\mu$ g/l (World Health Organization). Like for most metals, toxicity of aluminium is dependent on which chemical form it occurs in

environment. Occurrence of toxic forms of metals generally increases in acidic waters. Aluminium occurs in toxic form to the fish, if pH of water is lower than 6,0 or greater than 8,0, the gill being main target of toxicity (Wilson 2011).

Based on the observed acidity range of water and aluminium levels during the sampling period, aluminium toxicity to the fish might be theoretically possible in Koitajoki, if water is acidic enough and there is not enough dissolved organic matter to bind metals from water and decrease their bioavailability and toxicity to biota (Wilson 2011). In other words, in terms of observed acidity range and concentrations aluminium toxicity to the (young) fish may be possible in Koitajoki, but in practice it is near impossible to predict, because in nature there are so many factors, like levels of dissolved organic matter, in the equation. Meaning monitoring of status of the river is pretty much all that can be done before something occurs. At Möhkö observed aluminium load was generally on same level than it has been recorded to be between years 2000 - 2021 (Hertta database).

Based on water sampling, none of the observed aquatic levels of priority metals, mercury (Hg), lead (Pb), nickel (Ni) and cadmium (Cd) were near their environmental quality standards set by the Water Framework Directive (Directive 2000/60/EC). Based on this, their observed aquatic levels were on safe level in River Koitajoki. However, water samples represent water quality only at the sampling moment and do not take into account metal bioaccumulation to food webs, which is long time process. The overall picture is better gotten from metal levels in aquatic mosses that represent a 14 - day- period. A continuous longer time monitoring data was not found from Hertta database for the priority metals at Möhkö.

#### Physical-chemical properties of river water

Together with metal and especially iron results, observed lower turbidity, colour of the water, total suspended solids and total nitrogen levels may indicate that potential dilution caused by streams flowing to Koitajoki and the river's self-purification processes are together cleansing water from the effects of Finnish land-use while River Koitajoki flows in Republic of Karelia. As said before, a longer systematic monitoring plan is needed for confirming this.

Colour, total nitrogen levels and Chemical Oxygen Demand are typical for humic or very humic waters in River Koitajoki (Oravainen 1999, Vedenlaatuluokituksen raja-arvot ja lähteet, Haakana 2018).

Observed total phosphorus levels were more or less at same level at sampling points Koitajoki 13 and Koitajoki 1 Möhkö. In summer 2021 phosphorus was 5,0  $\mu$ g/l lower than at Koitajoki 13, which might indicate that there may be greater differences in summer, when primary production is active.

In summer observed acidity (pH) was quite typical for humic peatland rivers during the sampling period, some 6,0. At Koitajoki 1 Möhkö pH was slightly lower than at Koitajoki 13, which is not surprising for a peatland river.

At Möhkö observed acidity of river water seems to continue a longer trend: Between years 2000-2021 pH of river water has varied within 4,87 - 6,45 at Möhkö (Hertta database). If pH of water drops under 5,0, the most vulnerable aquatic organisms, like fry, will die. Based on analysis results and Hertta database, low pH may be a risk for vulnerable organisms in autumn, winter, and spring in River Koitajoki. Acidity may also increase toxicity of metals during those seasons.

Observed alkalinity (water's ability to resist acidification) of the river water has mostly been poor (< 0,1 mmol/l) at Möhkö between years 2000-2022, meaning melt water may probably lower acidity of river water under pH 5,0 in spring.

#### Conclusions

River Koitajoki is an interesting case for a river: The watershed at the area of Koitajoki 13 has been heavily influenced by ditching of peatlands and forestry activities like clear-cutting. There has been peat production at the watershed of River Alajoki that flows to Koitajoki at the location of Koitajoki 13. At area of Koitajoki 1 Möhkö the watershed has been influenced by ditching of peatlands for forestry purposes. Meanwhile Russian watershed is more in natural state, although there are some harvested areas and roads based on map

examination. Visible large-scale ditching of peatlands has not been performed in Karelian area of Koitajoki based on satellite maps.

According to literature review published by project PuuMaVesi (2020), in Karelian watershed of Koitajoki average wood volume is 332 m3 ha<sup>-1</sup> and 17 m3 ha<sup>-1</sup> in Finnish watershed. Difference is caused by extensive clear-cutting practices in Finnish watershed. Locally differences in wood volume might be even hundredfold between Finland and Karelia. Because of greater wood volume in the watershed, it might be possible that amount of sunken wood in river is greater in Karelia than in Finland. Sunken wood offers habitats for aquatic plants and microbic biofilms that act as part of river's self-purification processes: binding nutrients, suspended solids, metals, and organic matter from water. This might explain observed water quality differences between sampling points Koitajoki 13 and Koitajoki 1 Möhkö. Sunken wood also offers habitats for the fish.

As stated before, based on water sampling aquatic metal concentrations seemed to lower generally between sampling points Koitajoki 13 and Koitajoki 1 Möhkö. Iron may be partly reason for this because it acts as vector for toxic metals like arsenic, lead, mercury, and vanadium with dissolved organic matter (Kritzberg 2019). In other words, decreasing iron levels may directly or indirectly decrease aquatic concentrations of other metals also, which may have been seen in water quality of Möhkö. It must be noted that a two-year project is too short time for this observation to be confirmed, and its verification needs further studies.

Based on observed priority metal results from water sampling and Hertta database, levels of mercury (Hg), lead (Pb), nickel (Ni) and cadmium (Cd) were clearly under their environmental quality standards for water phase. However, water samples represent water quality only at the sampling moment, whereas aquatic moss samples represent a 14- day- time - period, which is better for assessing the big picture. For water samples there was also the lack of continuous longer time monitoring, which too hinders risk assessment for metals.

It must be also noted that in humic waters, as peatland rivers like Koitajoki, mercury occurs readily as hydrophobic methylmercury that accumulates in food webs to the fish. In water samples observed mercury levels represent its inorganic form that is less harmful to the biota. Because observed levels of mercury in fish have remained high and expert assessed long-range transboundary air pollution by flame retardants, River Koitajoki has been chemically classified in "worse than good" status (Hertta database). Large predator fishes have the highest mercury levels, which is why their consumption is recommended to be avoided. In Finland waterbodies are classified either as "good" or "worse than good" based on if any of the EU priority substances exceed its environmental quality standards stated by the Water Framework Directive.

Based on water quality results, it is possible that Finnish land-use has increased environmental loads higher than they would naturally be at area of Koitajoki 13; and water quality of Koitajoki then recovers while the river flows through Karelian area that is more in natural state. There is also possibility of dilution due to other rivers flowing to River Koitajoki. Most likely both dilution and river's self-purification processes are affecting the water quality at Möhkö. The most notable differences are in water's turbidity, iron, total suspended solid and nitrogen levels.

#### 4.1.2 Moss samples

In general, the element concentrations were higher at the River Koitajoki upper reach sampling site (Koitajoki 13) compared to the lower site (Koitajoki 1 Möhkö). There were statistical differences in the concentrations of iron, uranium, sodium and arsenic between the two sampling sites. The concentrations in the moss samples reflect the respective concentrations in water. Also Vuori et al. (2003) have reported elevated metal concentrations in aquatic moss samples in the upper reach of Koitajoki about twenty years earlier. There was greater variation in the moss concentrations in the upper Koitajoki compared to middle reaches of the river in Russian Karelia, most likely due to long history of forestry activities in combination with specific geochemical features') in the basin of the upper part of the river.

Diffuse and point loading due to land use is found to affect the amount of iron and aluminium (Karjalainen et al 2015) and several other metals (Vuori & Helisten 2010) bioaccumulated in aquatic mosses. Forestry and peat production, especially ditching of peatland affects the loading of these metals (Karjalainen et al 2015, Marttila et al 2018). Iron can be an important determining factor for arsenic in streams (Wällstedt et al. 2010).

After Virtanen (2004), iron compounds can bind arsenic in surficial peat layer of drained mires. Higher arsenic contents have been found in surface peat layer of old peatland forests than in more recently ditched mires. Arsenic is bound with iron especially on meso-eutrofic to eutrofic mires. Despite of rather high concentrations of arsenic in transplanted mosses at the upper reach of the River Koitajoki, the concentrations are clearly lower than those measured near mine areas in northern Finland (Ahkola et al. 2019).

High concentrations of lead (Pb) were measured at both sampling sites. Vuori et al. (2003) reported higher lead concentrations in *Fontinalis* at the middle reaches of the River Koitajoki compared to the upper reaches. However, Vuori et al. mentioned even higher concentrations measured in other studies concerning polluted and unpolluted areas (e.g. Vuori et al 1998b).

#### 4.2 The River Tohmajoki

#### 4.2.1 Water Quality trends in Finland and Republic of Karelia

#### Metals

Iron (Fe) seems to be the most notable metal in Finnish area of Tohmajoki in terms of level differences and general concentrations. Iron levels increased consistently towards the lower reach, expect in April 2021 observed iron loads were on same level (1200  $\mu$ g/l). Otherwise, observed iron concentrations at the lower reach were two- or threefold compared to the upper reach. There was variation in levels of manganese (Mn), that is a chemical relative to iron, but they elevated more often towards the lower reach than decreased. The highest rise in Mn levels towards the lower reach was 134  $\mu$ g/l in September 2020. Aluminium (Al) was the second notable metal after iron in terms of elevating concentrations and general levels in water.

Some metals elevated slightly but consistently towards the lower reach. These included arsenic (As), mercury (Hg), cadmium (Cd), cobalt (Co), chrome (Cr), lead (Pb), nickel (Ni), zinc (Zn), vanadium (V), and titanium (Ti). In water samples, observed levels of priority metals: mercury, lead, and cadmium, and nickel were lower than their environmental quality standards for inland surface waters. However, better big picture is gotten from their concentrations in moss samples, since they represent longer period than water samples. Also, in peatland rivers like Tohmajoki mercury occurs readily as hydrophobic methylmercury, which accumulates in food webs. In water samples most of observed mercury is in inorganic form that is less harmful to the biota than the organic form.

Other slightly increased metals do not have EU directive nor national legislation based environmental quality standards in Finland at the writing moment (Water Framework Directive and Government Decree 23.11.2006/1022 on Substances Hazardous and Harmful to the Aquatic Environment.). Their levels seem to be normal background levels at the upper reach of Tohmajoki, and their elevations towards the lower reach do not seem to be conspicuously high.

Other metals had more variation in their level trends: sometimes they increased towards the lower reach, at times they decreased. Observed barium (Ba) and copper (Cu) levels were approximately on same level, one microgram per litre higher or lower, at both reaches. Strontium (Sr) was observed to be either on same level or  $1,0 - 4,0 \mu g/l$  lower in the lower reach. Uranium (U) levels were generally low, sometimes a bit higher. at times lower at the lower reach of Tohmajoki,

#### Physical-chemical properties of river water

Turbidity increased notably towards the lower reach, excluding September 2021 when observed turbidity was 0,2 FNU higher at the upper reach. Turbidity probably correlates with total suspended solid levels, which generally were considerably higher at the lower reach. The difference was consistently visually perceived from the moss samples after a 14 - day - incubation time in the river: the mosses were consistently more intensively covered by mud at the lower reach. Colour value of the river water was generally higher at the lower reach, which is natural for peatland rivers. Colour of water may be increased by iron and other dissolved matter leached from the watershed.

Dissolved Organic Carbon and Total Organic Carbon were either on same level or higher at the lower reach. Their levels probably correlate with Chemical Oxygen demand ( $COD_{Mn}$ ) and Biological Oxygen Demand ( $BOD_5$ ) since higher levels of decomposing organic matter consumes more oxygen in water. Their highest differences were observed in September 2020. In September 2020 there were several rainy days before sampling started, which probably increased runoffs (and total environmental load) from Finnish watershed of Tohmajoki.

Electrical conductivity, magnesium (Mg), and sodium (Na) had increasing trend during summers and decreasing trend in other seasons. This is probably caused by effluents from agriculture lands, where fertilizers are used during summer. In other seasons electrical conductivity was higher at the upper reach, which is probably influenced by Lake Tohmajärvi. In Tohmajoki electrical conductivity was generally typical for lakes in natural state but low for typical river water (Haakana 2018). In Finland common bedrock types are generally poorly weathering, which also decreases alkalinity of waterbodies (Oravainen 1999).

Acidity of river water decreased slightly but consistently towards the lower reach of Tohmajoki, which is probably caused by effluents from the peatlands surrounding Tohmajoki. Observed acidity range was typical for Finnish waterbodies. By observed alkalinity River Tohmajoki has good or satisfactory ability to resist pH changes (Oravainen 1999). During summer observed alkalinity increased towards the lower reach, which may be affected by effluents from agriculture lands.

Total nitrogen levels were within typical levels for humus waters in Tohmajoki and increased generally towards lower reach (Oravainen 1999). Based on checked calculations made in Vemala model, nitrogen load from watershed (agriculture) to Tohmajoki is significantly higher than what it would naturally be (Hertta database). Forestry may also elevate nitrogen load to Tohmajoki, especially at recently cultivated land-areas.

For humus waters natural range of total phosphorus levels is  $10 - 15 \mu g/l$  (Oravainen 1999). In Tohmajoki observed concentrations were higher: at the upper reach range was  $19 - 26 \mu g/l$  and at the lower reach  $18 - 30 \mu g/l$ . It has been earlier reported that agriculture and forestry have considerably elevated phosphorus load above its natural level in area of Tohmajoki (Hertta database). Observed dissolved phosphate, that is directly usable to the plants, level range was higher at the lower reach.

Observed sulphate levels did not differ significantly between the upper and lower reach of Tohmajoki. In River Tohmajoki sulphate levels seem to be average (15 mg/l) for Finnish lakes, which might be influenced by Lake Tohmajärvi (Kauppi et al. 2013).

#### **Republic Of Karelia**

In Karelian part of River Tohmajoki the most notable changes in water quality were observed in suspended solid levels. Their levels increased generally the closer River Tohmajoki flows to Lake Ladoga, reaching their peak after settlement of Helylä. In Karelia the main sources of suspended solids are poorly treated wastewaters released from settlements along the river, especially Helylä. Effects of wastewater releases were observed as odour of sewer and very turbid water near the estuary of Tohmajoki at Soikkasenlahti Bay in 2019.

Effects of wastewater releases could be perceived also from elevated Biological Oxygen Demand (BOD<sub>5</sub>) results and levels of total nitrogen and total phosphorus, which at their highest were considerably higher than their Finnish peak concentrations.

#### Metals

In Republic of Karelia analysed metals were chosen by their potential toxicity to biota (aluminium, cadmium, nickel, mercury, and lead) and effect on raw water quality available to be used by settlements (iron and manganese).

Only aluminium (Al), iron (Fe) and manganese (Mn) levels were high enough to be detected by the Russian laboratory. Analysis results were probably affected by the long dry season that occurred in Republic of Karelia in summer 2021, and likely decreased runoffs from Karelian watershed of Tohmajoki. Meanwhile there were some rainy days in Finnish area of Tohmajoki in June 2021 (Finnish Meteorological Institute's

survey station, ID "Tohmajärvi Kemie"), which may have increased runoffs from Finnish watershed. It may also be possible that river water is diluted while River Tohmajoki flows through lakes Rämeenjärvi and Ruskojärvi, which may result in lower metal and suspended solid levels than in Finnish lower reach of the river.

These may explain considerable rise in iron levels at Finnish area of Tohmajoki; and lower iron levels in Karelia that were more or less at same scale with Finnish upper reach of Tohmajoki. Same kind of decrease could be seen with manganese. Aluminium levels were slightly higher in Karelia than in Finland, but differences were within 20 micrograms per litre when compared to Finnish lower reach. In Karelia sampling was performed at the end of June 2021, and in Finland on June 22, 2021.

#### 4.2.2 Moss samples

Some metal concentrations (Al, As, Mn, Ti and U) were slightly higher in transplanted *Fontinalis dalecarlica* moss samples at the lower sampling site, but clear differences were not found between the two sites. Only sodium concentrations of all the studied elements were statistically higher at the lower site. There was less difference between the metal concentrations at the upper and the lower sampling sites of the River Tohmajoki compared to the River Koitajoki perhaps due to shorter distance of the sites. However, the effect of forestry, especially the extent of ditched peatlands, can be seen in the concentrations of many metals also at the lower reach sampling site of the River Tohmajoki. At Tohmajoki, part of the loading of studied elements is originated from agriculture as the proportion of agriculture as origin of suspended solids is 40%, total phosphorous 57 % and total nitrogen 18 % (chapter 3.2). This may be partly responsible for the high potassium and sodium concentrations.

#### 4.3. Conclusions

In Finland there are widely ditched areas in vicinity of Tohmajoki. Especially area of Tohmajoensuo has been heavily drained for forestry purposes and there are several clear-cutting areas in vicinity of the river. Based on the map, there have been left 5,0- 20 metres wide buffer zones between the cutting areas and the river.

Based on map examinations, there also seem to be drained forest and swamp areas in vicinity of Tohmajoki in Republic of Karelia. Clear-cutting areas may also be observed in relative vicinity of Tohmajoki, although their buffer zones are generally ranging from 50 meters to several hundred meters, which is considerably wider than observed in Finnish area of Tohmajoki.

In Finland observed levels of priority metals (mercury, cadmium, nickel, lead) were under their environmental quality standards in water samples. The highest observed nickel concentration  $(3,7 \ \mu g/l)$  was close to nickel's annual average (AA-EQS) standard 4,0  $\mu g/l$ . However, this is still considered to be on a safe level. Maximum Allowable Concentration for nickel is  $34 \ \mu g/l$ , whose exceeding is considered a warning signal. Due to lack of consistent monitoring data, better big picture about the load of priority metals may be gotten from the moss samples.

Based on the observed aquatic levels, **iron, dissolved organic matter (DOM) and suspended solids** may be indirectly the most significant water quality variables affecting ecological and chemical state of Tohmajoki. Iron and dissolved organic matter may act as vectors for toxic metals like arsenic, lead, mercury, and vanadium. This means that higher aquatic levels of iron and dissolved organic matter may also elevate metal levels generally in a waterbody. (Kritzberg 2019).

Increasing iron, dissolved organic matter, and suspended solid levels may promote brownification of a waterbody (Sarkkola et al. 2013), whose indirect side-effect may be increased formation of highly toxic and bioaccumulative methylmercury in a waterbody due to changes in microbial activity. Ongoing climate change is expected to increase annual precipitation in Finland (and probably Republic of Karelia also), which probably increases runoffs from watershed of Tohmajoki in the future.

Currently chemical status of River Tohmajoki is assessed to be "worse than good" in Finland due to methylmercury accumulation to the fish; and long-range transboundary air pollution by flame retardants, PBDE compounds, (Hertta database). Flame retardants accumulate in food webs, like to the fish, and may cause hormonal disorders in humans and they are widely used in electronics, which is why they are being monitored.

By ecological status Finnish part of Tohmajoki is classified to be in "satisfactory" condition due to heavily changed river morphology (70% of the riverbed has been cleared from rocks and sunken wood; Tohmajoki has been dammed at the upper reach) and scattered load from forestry, agriculture, and long-range transboundary air pollution (Hertta database).

Finnish part of River Tohmajoki is not a significant source of usage water for settlements, unlike in Republic of Karelia. In Finland most of the challenges of Tohmajoki are related to recreational purposes like fishing (methylmercury and suspended solids), management of climate change, and collapse of biodiversity in terrestrial and aquatic ecosystems.

Sustainability of Finnish forestry practices has been under a heavy debate in perspectives of climate change and biodiversity loss during recent years. Especially peatland forests have been a subject of discussion since in recent years studies have indicated that greenhouse gas emissions are higher at peatlands than at mineral soils (Nieminen et al. 2018).

Drained peatland forests have been proven to be greater source of nutrients, suspended solids, and total and dissolved organic carbon for water systems than undrained peatlands or mineral soil forests. Because of this, it has been widely discussed if continuous cover forestry can be economically and environmentally feasible management option for clear cutting on drained boreal peatlands. Based on recent studies it can be, at least on some peatland forests (Nieminen et al. 2018). This discussion is important for area of Tohmajoki since there are drained peatland forests at vicinity of the river and clear cutting has been practiced there.

In Republic of Karelia ecological and chemical state of Tohmajoki has had more direct and concrete influence on people's lives since it has negatively affected quality of usage water in local settlements like village of Ruskeala and town of Sortavala. The most significant variables degrading river water quality in Republic of Karelia were observed to be dissolved organic matter and suspended solids that increase cost of usage water treatment, iron and manganese that makes water's taste and colour distasteful and may irritate stomach, and phosphorus that may cause algal blooms and other phenomenon related to eutrophication of a water system.

In summary, the most notable differences between Finnish and Karelian parts of Tohmajoki were observed in maximum nitrogen, phosphorus, dissolved organic matter, and suspended solids levels, which were generally higher in Karelian part of Tohmajoki. In Matkaselkä observed load was generally at similar level or lower than in Finnish upper reach, which is probably caused by dilution in Lake Ruskojärvi. Observed nitrogen, phosphorus, dissolved organic matter, and suspended solids levels elevated towards Lake Ladoga, peaking in Helylä settlement.

## 5 Plans for monitoring the physical and chemical state of the rivers

Project TohmaKoita has produced analysis data on current physical- chemical states of the rivers Tohmajoki and Koitajoki. In the future, this information can be used as basis for determining if performed water protection or purification measures, either those that were proposed in this report or others, affect water quality in the rivers.

Transplantation of aquatic mosses like *Fontinalis antipyretica* is suggested as the monitoring method for suspended solids and metals. Moss sampling can be combined with water sampling that can be performed either at the time of transplantation of moss racks to the river, or at the time when moss racks are lifted from the river.

Transplantation of aquatic mosses like *Fontinalis antipyretica* was observed to be relatively effortless and cost-effective method to monitor suspended solid and metal load in the River Tohmajoki. One of the advantages is that the sampling personnel may get a tentative picture about suspended solid load of the river through visually comparing mosses transplanted in different parts of the river. At the sampling sites Koitajoki 13 and Koitajoki 1 Möhkö transplantation of moss racks was relatively effortless, and the sites were easy to reach with vehicles.

For the sampling personnel, the main challenges of the method are:

1) Finding a river clean enough, where mosses can be harvested for monitoring activities. Tikanvirta was used for this purpose by project TohmaKoita in 2021 (Figure 1).

2) Lifting the moss racks carefully and slowly enough to minimize lost volume of suspended solids from the mosses after a 14- day-incubation time. The working conditions are especially challenging at the lower reach of the River Tohmajoki due to muddy river bottom and heavy moss racks.

3) Availability of aquatic mosses in April or May. In May 2021 growth of aquatic mosses had not yet started in Tikanvirta, which was chosen as new harvesting location due to increased environmental load in River Sukkulanjoki that was the harvesting location in 2020. At the beginning of June 2021 *Fontinalis antipyretica* growth was suitable for harvesting without causing significant damage for the moss growth. At the end of September 2021, the moss growth was decomposing in shallow parts of the river for unknown reason. In deeper parts of the river the mosses were healthy.

4) Assessing adequate amount of aquatic moss per sample, which can be learnt only by experience and feedback from the laboratory.

5) Vandalism risk during 14-day-incubation time. The risk can be tried to mitigate by communication with landowners and placing info cards to binding ropes.

According to VEMALA V1 simulations, suspended solid load is generally at highest in April or May, when snow melts, and spring flood occurs in the River Tohmajoki. Second but lower load peak comes in September or October, depending on when autumn flood occurs. Based on this monitoring should be performed at least in spring, if there are aquatic mosses with fresh green parts available at the time, and in autumn. If there are sufficient resources, moss sampling could also be performed around the time of Midsummer. If aquatic mosses are not available in spring, then moss sampling could be performed during summer and autumn.

At the area of Koitajoki 13 site, suspended solid load is also generally at highest in April or May. According to VEMALA V1 simulations, the second load peak is higher than it is in the River Tohmajoki, but still lower than the simulated spring peak.

According to final report of project PuuMaVesi, purification processes of sunken wooden structures should begin a growing season or two after installation. Moss sampling would be an efficient method to monitor development of suspended solid and metal load before and after installation of the wooden purification plants. For the River Tohmajoki one potential sampling site is Tohmajoki lower reach that was used by project TohmaKoita, since it is located at the end of the river in Finland and is reachable with vehicles. (Figure 7). The site is located on private property, so the landowner must be consulted for permission before potential activities.

# 6 Proposals for measures needed to ensure the quality of water and ecosystem

#### 6.1 The River Tohmajoki

In Finnish catchment area of River Tohmajoki most of the environmental load is nonpoint source pollution from agriculture and forestry at ditched peatlands (Hertta database). Meanwhile in Republic of Karelia, poorly treated wastewater releases have greater impact to the water quality in Tohmajoki, though nonpoint source pollution from agriculture and forestry is likely also present. Planning and preparation of measures to terminate wastewater releases have been started for Helylä village, which is the worst point source of wastewaters for Tohmajoki.

Most of the Finnish forests are commercial forests that are used for forestry, and some 90% of Finnish commercial forests are PEFC certificated. Some 10% of Finnish commercial forests are FSC certificated (Ministry of Agriculture and Forestry of Finland). Forest certifications set certain minimum standards for forestry practices, for example minimum width for a buffer zone between a cutting area and a waterbody. Buffer zones are required for waterbodies by Finnish forest law, but it does not state minimal widths.

In February 2022 PEFC standard recommends that water systems and springs should be left with buffer zones, whose minimum width is always five metres and averagely at least 10 metres. Earlier required width of a buffer zone for waterbodies was five metres, so protection of aquatic ecosystems was improved in update of PEFC standard. Open bogs in their natural state, and swamps waiting to regain their natural state, should be left with at least 10 metres wide buffer zone.

The objectives of a buffer zone are to: 1) Manage loads of nutrients and suspended solids caused by forestry practices. 2) Protect biodiversity of nature by leaving relatively intact forest areas. PEFC allows light selection felling that leaves trees of different size, emphasising broad-leaved trees, at the area of buffer zone (PEFC Finland 2021).

In 2019 and 2020 PEFC standard was being updated, and changes to the standard were published in April 2021. Finnish Environment Institute and Centres for Economic Development, Transport and the Environment criticised that the suggested changes emphasized too much on economical angles of forestry at the cost of ecological sustainability in forest and aquatic ecosystems. In the end Finnish Environment Institute and Centres for Economic Development, Transport and the Environment decided not to approve PEFC standard. Criticized points were for example:

1) Decreased minimum area for prescribed burning, from five hectares to two hectares, to create habitats for species that require wildfires.

2) In their surveillance, ELY centres had observed unnecessarily heavy tilling of soil in PEFC certificated commercial forests, which decreases cost-effectiveness of forestry to forest owners, and worsen environmental impact like runoffs of nutrients, harmful metals, and suspended solids to water systems.

3) Auditing of the PEFC standard was described to be partly impossible because of vaguely stated criteria, and violations were likely to be unnoticed due to lack of supervision (EPOELY/575/2021: Justification for the withdrawal of ELY Centres from the PEFC Standards Working Group. Published on March 26, 2021).

Compared to PEFC, Finnish FSC standard sets stricter minimum requirements for widths of buffer zones:

- 1) All ponds and lakes have always at least 10 metres wide buffer zone.
- 2) Streams, brooks, rivers, and seashores have always at least 15 metres wide buffer zone.
- 3) Cutting, tilling of soil, ditching and removal of tree stumps is not allowed in buffer zone.
- 4) Streams, brooks, and rivers, that are classified to be in natural or almost natural state, should be left with at least 20 metres wide woody riparian protection zone. This does not apply to all forest sectors, for example seedlings (FSC Finland 2022: Protection zones).

For comparison, in Russian Federation width of the buffer zone if dependent on length of a river or stream; and is at minimum 50 metres and 200 metres at maximum. Lakes and reservoirs require 50 metres wide buffer zone, and for seashores 500 metres is required (Water Code of the Russian Federation, January 1, 2007). In Russian Federation most of the forests are state owned, whereas in Finland forests are mostly privately owned.

Effectiveness of PEFC and FSC in the protection of headwater stream ecosystems was discussed by Jyväsjärvi et al. 2020. In their study Jyväsjärvi et al. 2020 stated as follows: "The riparian buffer retention measures of either certificate are, however, poorly supported by scientific evidence. Several lines of evidence suggest that the protection of environmental conditions, key ecosystem processes and stream biodiversity requires 30-m wide riparian buffers (Sweeney and Newbold, 2014) and safeguarding the riparian plant and wildlife biodiversity may necessitate even more extensive (> 40 m) buffers (Marczak et al., 2010; Selonen & Kotiaho, 2013)."

Based on the minimal requirements for widths of buffer zones, FSC standard is better at protecting stream biodiversity and ecosystem functioning than PEFC standard. However, finding a compromise that is sustainable both ecologically, socially, and economically is not a simple matter, especially in a country as covered by water bodies as Finland. Currently progress is going towards flexible buffer zones: Buffer zones are wider in locations that have particularly high biodiversity, for example wetter areas, or are in other ways important ecologically, hydrologically, or biochemically. There is still the question: What is the minimum width for a buffer zone? Based on latest available studies, it should be at least 15 metres, preferably 25 -30 metres, if the goal is to protect stream and riparian forest biodiversity and improve ecological and chemical status of water bodies (Jyväsjärvi et al. 2020).

Based on literature reviewed by Jyväsjärvi et al. (2020), careful thinning (30 %) can be allowed in 30 metres wide riparian buffer zone without threatening diversity of riparian plant communities (Olden et al. 2019). According Kreutzweiser et al. (2010) partial harvesting of >30 metres wide riparian buffer does not pose major risks to stream biodiversity and ecosystem functioning. Partial harvesting may improve biodiversity of the riparian forest by decreasing predominance of coniferous trees and enhance biodiversity by food webs. Small-scale harvesting of riparian forest may also emulate patchy disturbance that is typical for natural forest succession (Jonsson et al. 2017, Sibley et al. 2012). Jyväsjärvi et al. (2020) emphasized that partial harvesting requires at least 15 metres wide buffer zone, and preferably 25 – 30 metres wide.

#### 6.1.2 Recommendations for Finnish area of Tohmajoki

Based on the literature reviewed by Jyväsjärvi et al. 2020, there are arguments for exploration of opportunities for continuous cover forestry practises, and at least 15 metres, preferably 25-30 metres, wide buffer zones at area of Tohmajoensuo, because there the river is surrounded by ditched peatland forests, which are known to be considerable sources of iron, nutrients, organic matter, and suspended solids to waterbodies (Nieminen et al. 2018). According Jyväsjärvi et al. 2020's literature review, careful thinning (30%) does not pose significant risks for biodiversity in 30 metres wide buffer zone. Based on map examination, the current buffer zones between logging areas and the River Tohmajoki are generally 10 - 20 metres wide.

In peatlands the most severe problems of even-aged management are: 1) Larger scale disturbance of soil surface, which releases nutrients and suspended solids from the soil. 2) Rising water table level in soil because of decreased tree transpiration that is caused by clear-cutting. Rising water table level may increase need for ditch cleaning, which is currently considered to be the most harmful forestry operation affecting surface water quality in Finland (Finer et al. 2010 according Leppä et al. 2020).

Based on literature review by Leppä et al. 2020, clear- cutting may increase methane (CH4) emissions from the peatland, especially if water table level rises higher than 30 cm below the soil surface. Whereas too low water table level may increase emissions of carbon dioxide (CO2) and nutrients due to decomposing peat. Other effects of rising water table level are elevated exports of iron, dissolved organic carbon, nitrogen, and phosphorus from the soil to waterbodies. As was discussed earlier, iron may act as carrier for other metals, meaning emissions of other metals may also increase with iron. Due to these reasons possibilities of continuous cover forestry have been researched on peatland forests.

Leppä et al. 2020 concluded that continuous cover forestry practise could be used as a tool to control water table levels and manage climate and environmental impact caused by forestry in boreal drained peatland forests. However, planning and execution must be done carefully, because selective cutting seems to work better in southern Finland currently. However, it is possible that potential of continuous cover forestry will increase in future climate (Leppä et al. 2020).

Continuous cover forestry could be economically feasible at least on some peatland forests, since continuously maintaining a tree stand with significant transpiration and interception capacity would decrease the need for ditch network maintenance, and fewer investments are needed to establish the forest stand and sustain its growth, although tree growth might be lower than in even-aged management (Nieminen et al. 2018).

Currently most of Finnish commercial forests are dominated by Norway spruce (*Picea abies*) or Scots pine (*Pinus sylvestris*). Only 14% of Finnish forests are mixed forests. Naturally proportion of mixed forests would be much higher (WWF Finland). Recent studies have indicated that current monoculture practise has become quite risky, because climate change is expected to increase probabilities for of extremes of weather like drought, and occurrence of wood pests and diseases in Finland, increasing risk of large-scale damages in commercial forests dominated by one or two tree species.

Because of this Finnish forestry recommendations have started to favour growing of mixed forests where it is possible more than in the last decades (Tapio: Recommendations for forestry 2022). Another reason for increasing portion of mixed forests is that they have higher biodiversity than monocultures of Norway spruce or Scots pine, which increases possibilities for recreational activities like hunting and picking berries and mushrooming. Allowing growth of broad-leaved tree species where environment is suitable for them would be a good way to protect biodiversity of nature at area of the River Tohmajoki, increase number of available ecosystem services to the local population, and manage forest damage risks caused by pests and climate change. Partial harvesting could be used to decrease predominance of coniferous trees and create room for broad-leaved trees in commercial forests.

According to Hertta database, more than 70% of bottom of the River Tohmajoki has been cleared from rocks and wood to increase flow rate in the river. This has probably decreased number of available habitats for aquatic organisms, decreasing biodiversity in the river ecosystem. Potential method for repairing this damage and purify river water could be carefully planned introduction of sunken wood structures to banks of the River Tohmajoki, and ditches leading to the river.

In 2018- 2020 project PuuMaVesi, directed by Finnish Environment Institute, studied could sinking wood into streams, ditches and settling pools be used to manage environmental impact forestry to waterbodies. The project results were promising. Sunken wood structures were stated to create habitats to aquatic organisms like insects and fish fry and retain nutrients, metals, and organic matter from water via increased growth of microbial biofilms and aquatic plants. Additionally wood structures may decrease erosion via retaining soil particles and slowing flow rate of water. Pine was observed to be the best growing surface for aquatic plants and microbial biofilms due to its rough bark. Other benefits were that pine is more durable under water than hardwood and it contains lesser amounts of protective substances that may be harmful to biota. The method could also work for nutrient and suspended solid effluents originated from agriculture.

The research is continued in on-going project PuuValuVesi, which aims to clarify is it possible to mitigate harmful effects of climate change to watersheds and nature via increasing amount of sunken wood in waterbodies. Since wood has been widely used in restoration of river ecosystems, it might be worth consideration to try in River Tohmajoki also, especially since the method is quite cost-efficient and long-lasting, depending on the used wood species. For example, used Christmas trees have been sank into streams to purify water.

#### 6.2 The River Koitajoki

Currently upper reach of Koitajoki (Hertta database code Koitajoki yläjuoksu 04.922\_y01 Joki) is classified to be ecologically "good" state and chemically "worse than good state". Chemical state is worsened by mercury and PBDE fallouts (Hertta database). Based on map examination, buffer zones of logging areas seem generally be around 20-30 metres or wider, which should be at least satisfactory for protection of water quality in upper reach of Koitajoki. However, scattered load is still possible via ditches. Like in River
Tohmajoki, using sunken wood structures in streams, ditches and settling pools might be a cost-efficient tool to manage scattered load originating from the watershed of Koitajoki.

Since Koitajoki is a peatland river and there are ditched peatland forests in vicinity of the river, same proposals (like utilization of continuos cover forestry practices in peatland forests) could also be considered there than at the area of Tohmajoki.

# 7 Preparing suggestions for using the results in updating or creating water protection or land-use management plans for the River Koitajoki and the River Tohmajoki.

### 7.1 The River Tohmajoki

According to VEMALA model V1 environmental load simulations and Hertta database, agriculture, forestry, and natural leaching from forests are the main sources of load to the River Tohmajoki. Dissolved organic matter, suspended solids and nutrients are stated to be the main load types in the River Tohmajoki (Hertta database). VEMALA's metal load models are still under development, so their environmental load simulations haven't been utilized in this report.

In the River TohmaKoita's analysis data, iron of all metals increased the most towards the lower reach of Tohmajoki. Increasing suspended solid load towards the lower reach of the River Tohmajoki was visually observed from moss samples after their 14-day- incubation times in the river. As was discussed earlier, increasing iron, dissolved organic matter, and suspended solid levels may generally elevate metal levels in a waterbody. Although any of the toxic metals were not observed to exceed their environmental quality standards for inland waterbodies, it is possible their load will elevate due to increasing precipitation in the future.

Overall, based on project's analysis results and moss sampling, there is not a doubt that human activities (in Finland agriculture and forestry, in Republic of Karelia particularly untreated wastewaters) affects water quality in the River Tohmajoki. In Republic of Karelia state of the River Tohmajoki deteriorates the closer to the Lake Ladoga the river flows due to untreated wastewaters from settlements. In Matkaselkä observed water quality was somewhat comparable to Finnish upper reach, probably because in both locations there are lakes upstream.

The most notable differences between Finnish and Karelian parts of the River Tohmajoki were observed in maximum nitrogen, phosphorus, dissolved organic matter, and suspended solids levels, which increased significantly between settlements of Matkaselkä and Helylä and were much higher than in Finnish lower reach of the River Tohmajoki. There are probably differences in laboratory standards between Finland and Russian Federation, so the results may not always be directly comparable. The greatest differences are probably in suspended solids, whose Russian filter size could not be clarified due to current political circumstances.

Suggestions for potential measures to mitigate load from land-use and protect quality of water and ecosystem services at the area of the River Tohmajoki have been discussed in the chapter "Proposals for measures needed to ensure the quality of water and ecosystem". Suggested sunken wood structures, if carefully planned and constructed in ditches, streams, and the riverbanks, might be a cost-efficient way to mitigate environmental load from land-use, since they offer habitats to surface growth and benthic fauna that filter

nutrients, humus, and metals from water and at the same time improve diversity of food webs in the ecosystem.

In Republic of Karelia, sunken wood structures might be a cost-effective method worth testing, do they mitigate effects of untreated wastewaters in the River Tohmajoki. Although they would likely be just a temporary solution to improve water quality a little bit before untreated wastewater releases were terminated from the settlements.

The water quality and moss sample data produced by the project TohmaKoita can be used as a comparison data, if proposed wooden water purification structures, or other water protection and purification measures, are installed or performed in the River Tohmajoki and the ditches in the river's watershed.

### 7.2 The River Koitajoki

According to VEMALA model V1 environmental load simulations and Hertta database, natural leaching from forests and forestry activities are the main sources of load at the area of Koitajoki 13 site. Area of Koitajoki 1 Möhkö site was not examined in VEMALA, because the objective was to assess the environmental load flowing from Finland to Republic of Karelia in the rivers Koitajoki and Tohmajoki, and the River Koitajoki returns to Finland at the area of Möhkö site.

The water samples collected from Koitajoki 1 Möhkö site showed generally lower concentrations in suspended solids, nutrients, and metals than water samples collected from Koitajoki 13 site. This might be partly caused by dilution of river water from streams flowing to the River Koitajoki in Republic of Karelia, but differences in land-use in the river basin probably also affects the water quality in Möhkö site.

Annual load of suspended solids was particularly high in VEMALA V1 simulations at Koitajoki 13 site: 880 -1500 tons in years 2016 -2021. Suspended solid load may be increased above the natural level by ditching of peatlands at the watershed of the River Koitajoki and the peat production area at the watershed of the River Alajoki. There are water protection structures like settling pools at the location of the peat production area, which probably decrease suspended solid load to the river.

There are peatland forests in the watershed upstream from Koitajoki 13 site and based on map examination, some clear-cutting has been performed there. In the light of the reviewed literature in this report, there are indications that clear-cutting is somewhat troublesome method to be used in peatland forests due to greater environmental load to waterbodies and higher releases of greenhouse gases compared to mineral soils (for example, Nieminen et al. 2018. Leppä et al. 2020). Because of this there are arguments for considering continuous cover forestry in peatland forests.

Utilization of sunken wood structures in ditches, streams, and settling pools could be worth consideration at area of the River Koitajoki also, since they have observed to efficiently retain suspended solids, nutrients, and metals from water, when surface growth has been formed after a year or few. More research data on the subject is being developed by project PuuValuVesi, that is directed by Finnish Environment Institute In the future, suspended solid and metal analysis data from moss samples can be used as basis for determining if performed water protection or purification measures, either those that were proposed in this report or others, affect water quality in upper part of the River Koitajoki.

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# Attachments

Analysis result tables of River Koitajoki

21,9,2020		Koitajoki 13	Koitajoki 1 Möhkö
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	7,5	8,6
Turbidity	FNU	2,6 ±0,26	1,7 ±0,17
Solids	mg/l	3,2 ±12	2,3 ±12
Solids	mg/l	4,8 ±0,6	4,4 ±0,5
Solids	mg/l	L 1	L 1
Electrical conductivity	mS/m	2,2 ±0,066	1,9 ±0,057
Alkalinity	mmol/l	0,025 ±0,001	0,016 ±0,001
Acidity (pH)		4,9 ±0,05	4,8 ±0,05
Colour	mg/l Pt	330 ±20	270 ±20
Total nitrogen	µg/l	660 ±53	550 ±44
Nitrite as nitrogen	µg/l	4 ±0,5	3 ±0,5
Nitrite-nitrate as nitrogen	µg/l	6 ±1	L 5
Nitrate as nitrogen	µg/l	L 5	L 5
Ammonium as nitrogen	µg/l	4 ±0,5	5 ±1
Total phosphorus	µg/l	22 ±3	21 ±3
Phosphate as phosphorus	µg/l	5 ±1	3 ±1
PO4-P, filtered	µg/l	2 ±1	2 ±1

Table 7. Water quality in Koltajor
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Iron	µg/l	1800 ±180	1500 ±150
Manganese	μg/l	51 ±5	48 ±5
Sulphate	mg/l	1,2 ±0,1	0,6
Aluminium	μg/l	260 ±39	180 ±27
Arsenic	µg/l	1,4 ±0,1	0,69 ±0,07
Barium	μg/l	13 ±1	9 ±0,9
Mercury	μg/l	0,007 ±0,0011	0,0082 ±0,0012
Phosphorus	μg/l	L 25	L 25
Cadmium	μg/l	0,014 ±0,003	0,013 ±0,003
Potassium	mg/l	0,34 ±0,05	0,26 ±0,05
Calcium	mg/l	2,4 ±0,2	1,5 ±0,2
CODMn	mg/l	48 ±5	40 ±4
Cobalt	μg/l	0,4 ±0,04	0,27 ±0,03
Chrome	μg/l	0,86 ±0,09	0,48 ±0,05
Copper	μg/l	0,88 ±0,09	0,44 ±0,05
Lead	μg/l	0,39 ±0,04	0,42 ±0,04
Magnesium	mg/l	0,66 ±0,07	0,48 ±0,05
Sodium	mg/l	0,93 ±0,09	0,86 ±0,09
Nickel	μg/l	1,6 ±0,2	0,53 ±0,05
Dissolved Organic Carbon	mg/l	34 ±2	27 ±2
Total organic carbon	mg/l	35 ±5	27 ±4
Sulphur	μg/l	L 400	L 400
Selenium	μg/l	L 0,1	L 0,1
Zinc	μg/l	5,1 ±0,5	4,2 ±0,5
Strontium	μg/l	24 ±2	14 ±1
Titanium	μg/l	5,2 ±0,8	3,1 ±0,5
Uranium	μg/l	0,096 ±0,019	0,037 ±0,007
Vanadium	μg/l	1,3 ±0,1	0,84 ±0,08

## Table 8. Water quality in Koitajoki.

4,5,2021		Koitajoki 13	Koitajoki 1 Möhkö
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	4,6	4,9
Turbidity	FNU	1,2 ±0,2	1,2 ±0,2
Solids	mg/l	1,9 ±12	1,4 ±12
Solids	mg/l	2,7 ±0,3	2,6 ±0,3
Solids	mg/l	1,1 ±0,1	L 1
Electrical conductivity	mS/m	1,5 ±0,045	1,3 ±0,039
Alkalinity	mmol/l	0,047 ±0,002	0,027 ±0,001
Acidity (pH)		5,5 ±0,05	5,2 ±0,05
Colour	mg/l Pt	175 ±20	175 ±20
Total nitrogen	µg/l	440 ±44	$400 \pm 40$
Nitrite as nitrogen	µg/l	L 1 ±0,5	L 1 ±0,5
Nitrite-nitrate as	µg/l	20 ±2	22 ±2
Nitrate as nitrogen	µg/l	19 ±2	21 ±3
Ammonium as nitrogen	μg/l	11 ±1	L 2
Total phosphorus	µg/1	15 ±2	15 ±2
Phosphate as phosphorus	µg/l	4 ±1	2 ±1
PO4-P, filtered	µg/l	2 ±1	L 2 ±1

Iron	µg/l	920 ±92	850 ±85
Manganese	µg/l	32 ±3	35 ±4
Sulphate	mg/l	1,1 ±0,1	1,6 ±0,1
Aluminium	µg/l	140 ±21	130 ±20
Arsenic	µg/l	0,72 ±0,07	0,63 ±0,06
Barium	µg/l	6 ±0,6	4,7 ±0,5
Mercury	µg/l	$0,0042 \pm 0,0006$	0,0045 ±0,0007
Phosphorus	µg/l	L 25	L 25
Cadmium	µg/l	0,009 ±0,003	0,009 ±0,003
Potassium	mg/l	0,35 ±0,05	0,28 ±0,05
Calcium	mg/l	1,4 ±0,1	1 ±0,1
CODMn	mg/l	26 ±3	23 ±2
Cobalt	µg/l	0,27 ±0,03	0,2 ±0,02
Chrome	μg/1	0,59 ±0,06	0,36 ±0,04
Copper	μg/1	0,43 ±0,05	0,3 ±0,05
Lead	µg/l	0,21 ±0,02	0,28 ±0,03
Magnesium	mg/l	0,4 ±0,05	0,32 ±0,05
Sodium	mg/l	$0,8 \pm 0,08$	$0,8\pm 0,08$
Nickel	µg/l	0,63 ±0,06	0,4 ±0,04
Dissolved Organic	mg/l	16 ±1	15 ±1
Carbon Total anomia conhan	/I	17.2	
Sulphur	<u>IIIg/1</u>	$1/\pm 3$	$1/\pm 3$
Sulphur	$\mu g/I$	L 400	
Selemum	μg/1	L 0,1	L 0,1
	μg/Ι	$1,5\pm0,5$	$1,6\pm0,5$
Strontium	μg/1	$13 \pm 1$	8 ±0,8
I itanium	μg/1	$2,5\pm0,4$	$2,2\pm0,3$
Uranium	μg/l	0,067 ±0,013	$0.027 \pm 0.005$
Vanadium	μg/l	0,94 ±0,09	$0,65 \pm 0,07$

Table 9. Water quality in Koitajoki.

16,6,2021		Koitajoki13	Koitajoki 1 Möhkö
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	15,3	18
Turbidity	FNU	4 ±0,8	2 ±0,4
Solids	mg/l	3,6 ±12	3,1 ±12
Solids	mg/l	6,4 ±0,8	4 ±0,5
Solids	mg/l	1,2 ±0,1	1,4 ±0,2
Electrical conductivity	mS/m	1,8 ±0,054	1,3 ±0,039
Alkalinity	mmol/l	0,1 ±0,005	0,046 ±0,002
Acidity (pH)		6,3 ±0,05	$5,8 \pm 0,05$
Colour	mg/l Pt	$200 \pm 20$	$180 \pm 20$
Total nitrogen	μg/l	420 ±42	390 ±39
Nitrite as nitrogen	μg/l	2 ±0,5	L 1 ±0,5
Nitrite-nitrate as nitrogen	µg/l	8 ±1	10 ±1
Nitrate as nitrogen	μg/l	6 ±1	9 ±1
Ammonium as nitrogen	µg/l	15 ±2	3 ±0,5
Total phosphorus	μg/l	22 ±3	17 ±3
Phosphate as	μg/l	7 ±1	4 ±1

phosphorus			
PO4-P, filtered	μg/l	3 ±1	4 ±1
Iron	µg/l	1600 ±160	920 ±92
Manganese	µg/l	37 ±4	34 ±3
Sulphate	mg/l	0,8 ±0,1	0,8 ±0,1
Aluminium	μg/l	130 ±20	130 ±20
Arsenic	μg/l	0,85 ±0,09	0,68 ±0,07
Barium	μg/l	6,7 ±0,7	5,4 ±0,5
Mercury	μg/l	0,0031 ±0,0005	0,0026 ±0,0005
Phosphorus	μg/l	L 25	L 25
Cadmium	μg/l	0,006 ±0,003	0,01 ±0,003
Potassium	mg/l	0,37 ±0,05	0,34 ±0,05
Calcium	mg/l	1,8 ±0,2	1,3 ±0,1
CODMn	mg/l	19 ±2	18 ±2
Cobalt	μg/l	0,24 ±0,02	0,16 ±0,02
Chrome	μg/l	0,69 ±0,07	0,39 ±0,04
Copper	µg/l	0,33 ±0,05	0,28 ±0,05
Lead	µg/l	0,28 ±0,03	0,31 ±0,03
Magnesium	mg/l	0,59 ±0,06	0,38 ±0,05
Sodium	mg/l	1,21 ±0,12	0,97 ±0,1
Nickel	µg/l	0,6 ±0,06	0,35 ±0,04
Dissolved Organic	mg/l	$14 \pm 1$	$14 \pm 1$
Carbon			
Total organic carbon	mg/l	15 ±2	15 ±2
Sulphur	µg/l	L 400	L 400
Selenium	µg/l	L 0,1	L 0,1
Zinc	μg/l	1,3 ±0,5	1,8 ±0,5
Strontium	μg/l	16 ±2	9,6 ±1
Titanium	µg/l	2,7 ±0,4	2,2 ±0,3
Uranium	µg/l	0,05 ±0,01	0,031 ±0,006
Vanadium	μg/l	1,3 ±0,1	0,7 ±0,07

Table 10. Water quality in Koitajoki.

6,10,2021		Koitajoki 13	Koitajoki 1 Möhkö
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	6,5	7,6
Turbidity	FNU	3,9 ±0,8	1,8 ±0,4
Solids	mg/l	2,5 ±12	2,5 ±12
Solids	mg/l	5 ±0,6	3,3 ±0,4
Solids	mg/l	L 1	L 1
Electrical conductivity	mS/m	2,3 ±0,069	1,7 ±0,051
Alkalinity	mmol/l	0,137 ±0,007	0,07 ±0,004
Acidity (pH)		$6,4\pm 0,05$	6,1 ±0,05
Colour	mg/l Pt	$160 \pm 20$	140 ±20
Total nitrogen	μg/l	390 ±39	350 ±35
Nitrite as nitrogen	μg/l	1 ±0,5	L 1
Nitrite-nitrate as	μg/l	13 ±1	8 ±1
nitrogen			

Nitrate as nitrogen	μg/l	12 ±2	8 ±1
Ammonium as	µg/l	24 ±2	2 ±0,5
nitrogen			
Total phosphorus	μg/l	17 ±3	18 ±3
Phosphate as	µg/l	8 ±1	5 ±1
phosphorus			
PO4-P, filtered	µg/l	5 ±1	4 ±1
Iron	μg/l	$1700 \pm 170$	$1200 \pm 120$
Manganese	μg/l	37 ±4	19 ±2
Sulphate	mg/l	1,2 ±0,1	1 ±0,1
Aluminium	μg/l	$120 \pm 18$	$120 \pm 18$
Arsenic	μg/l	0,73 ±0,07	0,73 ±0,07
Barium	μg/l	8,8 ±0,9	5,7 ±0,6
Mercury	μg/l	$0,0019 \pm 0,0005$	0,0021 ±0,0005
Phosphorus	μg/l	L 25	L 25
Cadmium	μg/l	0,006 ±0,003	0,006 ±0,003
Potassium	mg/l	0,52 ±0,05	0,38 ±0,05
Calcium	mg/l	2,1 ±0,2	1,5 ±0,2
CODMn	mg/l	21 ±2	19 ±2
Cobalt	μg/l	0,29 ±0,03	0,09 ±0,01
Chrome	μg/l	0,81 ±0,08	0,43 ±0,04
Copper	μg/l	0,28 ±0,05	$0,25 \pm 0,05$
Lead	μg/l	0,21 ±0,02	$0,4 \pm 0,04$
Magnesium	mg/l	$0,76 \pm 0,08$	$0,5 \pm 0,05$
Sodium	mg/l	1,54 ±0,15	1,24 ±0,12
Nickel	μg/l	0,63 ±0,06	0,29 ±0,03
Dissolved Organic	mg/l	15 ±1	13 ±1
Carbon			
Total organic carbon	mg/l	16 ±2	14 ±2
Sulphur	μg/l	490 ±400	$470 \pm 400$
Selenium	μg/l	L 0,1	L 0,1
Zinc	μg/l	1,2 ±0,5	1,3 ±0,5
Strontium	µg/l	18 ±2	12 ±1
Titanium	μg/l	3,1 ±0,5	2,5 ±0,4
Uranium	μg/l	0,045 ±0,009	0,034 ±0,007
Vanadium	μg/l	1,4 ±0,1	0,9 ±0,09

Analysis result tables of River Tohmajoki

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23.6.2020		Tohmajoki 9 upper reach	Tohmajoki lower reach
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	22,4	20,5
Turbidity	FNU	2,8 ±0,28	4,9 ±0,49
Solids	mg/l	3,1 ±12	4,6 ±12
Solids	mg/l	3,9 ±0,5	6,5 ±0,8
Solids	mg/l	1,6 ±0,2	2,7 ±0,3
Electrical conductivity	mS/m	8 ±0,24	8,7 ±0,261
Alkalinity	mmol/l	0,235 ±0,012	0,265 ±0,013
Acidity (pH)		7,1 ±0,05	6,9 ±0,05
Colour	mg/l Pt	90 ±20	100 ±20
Total nitrogen	μg/l	630 ±50	640 ±51
Nitrite as nitrogen	μg/l	2 ±0,5	2 ±0,5
Nitrite-nitrate as nitrogen	µg/l	150 ±9	160 ±10

Nitrate as nitrogen	µg/l	150 ±17	160 ±18
Ammonium as nitrogen	µg/l	L 2	17 ±2
Total phosphorus	µg/l	19 ±3	23 ±3
Phosphate as phosphorus	µg/l	3 ±1	4 ±1
PO4-P, filtered	µg/l	L 2	4 ±1
Iron	µg/l	700 ±70	1300 ±130
Manganese	μg/l	76 ±8	110 ±11
Sulphate	mg/l	17 ±1	17 ±1
Aluminium	µg/l	84 ±13	88 ±13
Arsenic	μg/l	0,28 ±0,03	0,37 ±0,04
Barium	μg/l	17 ±2	17 ±2
Mercury	μg/l	0,0007 ±0,0005	0,0007 ±0,0005
Phosphorus	μg/l	L 25	L 25
Cadmium	μg/l	0,011 ±0,003	0,01 ±0,003
Potassium	mg/l	2,06 ±0,21	2,06 ±0,21
Calcium	mg/l	9 ±0,9	9,3 ±0,9
CODMn	mg/l	12 ±1	$14 \pm 1$
Cobalt	μg/l	0,16 ±0,02	0,32 ±0,03
Chrome	μg/l	0,35 ±0,04	0,44 ±0,04
Copper	μg/l	1,5 ±0,2	1,4 ±0,1
Lead	μg/l	0,12 ±0,02	0,13 ±0,03
Magnesium	mg/l	2,15 ±0,22	2,27 ±0,23
Sodium	mg/l	2,83 ±0,28	2,92 ±0,29
Nickel	µg/l	3,4 ±0,3	3,7 ±0,4
Dissolved Organic Carbon	mg/l	11 ±1	11 ±1
Total organic carbon	mg/l	12 ±2	12 ±2
Sulphur	μg/l	6000 ±900	6200 ±930
Selenium	μg/l	L 0,1	L 0,1
Zinc	μg/l	1,7 ±0,5	2,4 ±0,5
Strontium	μg/l	41 ±4	41 ±4
Titanium	μg/l	2,2 ±0,3	2,8 ±0,4
Uranium	μg/l	0,0 <del>4</del> 7 ±0,009	0,05 ±0,01
Vanadium	μg/l	0,33 ±0,03	0,52 ±0,05
BOD5-ATU	mg/l O2	1,2	1,4

Table 12. Analysis results from Finnish area of the River Tohmajoki.

23.9.2020		Tohmajoki upper reach	Tohmajoki lower reach
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	10,5	9,5
Turbidity	FNU	3,8 ±0,8	4,6 ±0,9
Solids	mg/l	3,5 ±12	1,1 ±12
Solids	mg/l	4,2 ±0,5	5 ±0,6
Solids	mg/l	L 1	L 1
Electrical conductivity	mS/m	8,4 ±0,252	7,7 ±0,231
Alkalinity	mmol/l	0,26 ±0,013	0,218 ±0,011
Acidity (pH)		7,2 ±0,05	6,4 ±0,05

Colour	mg/l Pt	100 ±20	240 ±20
Total nitrogen	µg/l	530 ±53	770 ±77
Nitrite as nitrogen	µg/l	2 ±0,5	3 ±0,5
Nitrite-nitrate as nitrogen	µg/l	21 ±2	53 ±5
Nitrate as nitrogen	µg/l	19 ±2	50 ±7
Ammonium as nitrogen	µg/l	L 2	21 ±2
Total phosphorus	µg/l	22 ±3	25 ±4
Phosphate as phosphorus	µg/l	$4\pm1$	6 ±1
PO4-P, filtered	µg/l	3 ±1	$4\pm 1$
Iron	µg/l	630 ±63	$1800 \pm 180$
Manganese	µg/l	76 ±8	210 ±21
Sulphate	mg/l	16 ±1	16 ±1
Aluminium	µg/l	51 ±8	140 ±21
Arsenic	µg/l	0,35 ±0,04	0,47 ±0,05
Barium	µg/l	16 ±2	18 ±2
Mercury	µg/l	0,0013 ±0,0005	0,0025 ±0,0005
Phosphorus	µg/l	L 25	L 25
Cadmium	µg/l	0,009 ±0,003	0,022 ±0,004
Potassium	mg/l	1,95 ±0,2	1,68 ±0,17
Calcium	mg/l	9,2 ±0,9	8,3 ±0,8
CODMn	mg/l	14 ±1	28 ±3
Cobalt	µg/l	0,18 ±0,02	0,99 ±0,1
Chrome	μg/l	0,25 ±0,03	0,48 ±0,05
Copper	μg/l	1,6 ±0,2	1,5 ±0,2
Lead	µg/l	0,12 ±0,02	0,22 ±0,02
Magnesium	mg/l	2,15 ±0,22	2,11 ±0,21
Sodium	mg/l	2,93 ±0,29	2,62 ±0,26
Nickel	µg/l	3,2 ±0,3	4 ±0,4
Dissolved Organic Carbon	mg/l	12 ±1	20 ±1
Total organic carbon	mg/l	13 ±2	20 ±3
Sulphur	µg/l	5700 ±855	5500 ±825
Selenium	µg/l	L 0,1	L 0,1
Zinc	µg/l	1,8 ±0,5	4,4 ±0,5
Strontium	µg/l	41 ±4	38 ±4
Titanium	µg/l	1,6 ±0,2	2,7 ±0,4
Uranium	µg/l	0,054 ±0,011	0,049 ±0,01
Vanadium	µg/l	0,36 ±0,04	0,63 ±0,06
BOD5-ATU	mg/l O2	1,1	1,4

Table 13. Analysis results from Finnish area of the River Tohmajoki.

28.4.2021		Tohmajoki 9 upper reach	Tohmajoki lower reach
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	4,5	4,4
Turbidity	FNU	3,9 ±0,8	4,2 ±0,8
Solids	mg/l	2,8 ±12	4,1 ±12
Solids	mg/l	3,5 ±0,4	4,9 ±0,6
Solids	mg/l	1,3 ±0,2	2,4 ±0,3

Electrical conductivity	mS/m	7,8 ±0,234	6,9 ±0,207
Alkalinity	mmol/l	0,238 ±0,012	0,193 ±0,01
Acidity (pH)		6,7 ±0,05	6,5 ±0,05
Colour	mg/l Pt	140 ±20	160 ±20
Total nitrogen	µg/l	890 ±89	900 ±90
Nitrite as nitrogen	µg/l	2 ±0,5	2 ±0,5
Nitrite-nitrate as nitrogen	µg/l	380 ±23	330 ±20
Nitrate as nitrogen	µg/l	380 ±42	330 ±36
Ammonium as nitrogen	µg/l	L 2 ±0,5	6 ±1
Total phosphorus	µg/l	21 ±3	20 ±3
Phosphate as phosphorus	µg/l	6 ±1	6 ±1
PO4-P, filtered	µg/l	4 ±1	2 ±1
Iron	µg/l	$1200 \pm 120$	$1200 \pm 120$
Manganese	µg/l	$140 \pm 14$	100 ±10
Sulphate	mg/l	13	12
Aluminium	µg/l	170 ±26	220 ±33
Arsenic	µg/l	0,33 ±0,03	0,36 ±0,04
Barium	μg/l	16 ±2	15 ±2
Mercury	µg/l	$0,002 \pm 0,0005$	0,0025 ±0,0005
Phosphorus	µg/l	L 25	L 25
Cadmium	µg/l	0,017 ±0,003	0,021 ±0,004
Potassium	mg/l	1,94 ±0,19	$1,76 \pm 0,18$
Calcium	mg/l	8,6 ±0,9	7,6 ±0,8
CODMn	mg/l	20 ±2	24 ±2
Cobalt	µg/l	0,53 ±0,05	0,54 ±0,05
Chrome	µg/l	0,39 ±0,04	0,49 ±0,05
Copper	µg/l	1,5 ±0,2	1,6 ±0,2
Lead	µg/l	0,13 ±0,03	0,17 ±0,03
Magnesium	mg/l	2,06 ±0,21	1,85 ±0,19
Sodium	mg/l	2,64 ±0,26	2,37 ±0,24
Nickel	µg/l	3,4 ±0,3	3,5 ±0,4
Dissolved Organic Carbon	mg/l	14 ±1	17 ±1
Total organic carbon	mg/l	16 ±2	18
Sulphur	µg/l	5200 ±780	4800 ±720
Selenium	µg/l	L 0,1	L 0,1
Zinc	µg/l	3 ±0,5	3 ±0,5
Strontium	µg/l	38 ±4	34 ±3
Titanium	µg/l	2,7 ±0,4	4,3 ±0,6
Uranium	µg/l	0,051 ±0,01	0,052 ±0,01
Vanadium	µg/l	0,47 ±0,05	0,64 ±0,06
BOD5-ATU	mg/l O2	1,5	1,9

Table 14. Analysis results from Finnish area of the River Tohmajoki.

22.6.2021		Tohmajoki 9 upper reach	Tohmajoki lower reach
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	23	21,8

Turbidity	FNU	3,5 ±0,7	6,4 ±1,3
Solids	mg/l	4,2 ±12	5,5 ±12
Solids	mg/l	4,8 ±0,6	7,4 ±0,9
Solids	mg/l	1,4 ±0,2	2,4 ±0,3
Electrical conductivity	mS/m	7,7 ±0,231	8,2 ±0,246
Alkalinity	mmol/l	0,239 ±0,012	0,273 ±0,014
Acidity (pH)		7,1 ±0,05	6,7 ±0,05
Colour	mg/l Pt	130 ±20	160 ±20
Total nitrogen	µg/l	770 ±77	760 ±76
Nitrite as nitrogen	µg/l		
Nitrite-nitrate as nitrogen	µg/l	170 ±10	140 ±8
Nitrate as nitrogen	µg/l		
Ammonium as nitrogen	µg/l	2 ±0,5	22 ±2
Total phosphorus	µg/l	20 ±3	30 ±5
Phosphate as phosphorus	µg/l	3 ±1	6 ±1
PO4-P, filtered	µg/l	3 ±1	5 ±1
Iron	µg/l	$780 \pm 78$	1800 ±180
Manganese	µg/l	100 ±10	140 ±14
Sulphate	mg/l	14 ±1	15 ±1
Aluminium	µg/l	97 ±15	110 ±17
Arsenic	µg/l	0,35 ±0,04	0,49 ±0,05
Barium	µg/l	17 ±2	16 ±2
Mercury	µg/l	0,0011 ±0,0005	0,0016 ±0,0005
Phosphorus	µg/l	L 25	L 25
Cadmium	µg/l	0,014 ±0,003	0,014 ±0,003
Potassium	mg/l	1,9 ±0,19	1,95 ±0,2
Calcium	mg/l	8,7 ±0,9	8,6 ±0,9
CODMn	mg/l	16 ±2	17 ±2
Cobalt	µg/l	0,17 ±0,02	0,43 ±0,04
Chrome	µg/l	0,38 ±0,04	0,54 ±0,05
Copper	µg/l	1,6 ±0,2	1,5 ±0,2
Lead	µg/l	0,11 ±0,02	0,21 ±0,02
Magnesium	mg/l	2,03 ±0,2	2,17 ±0,22
Sodium	mg/l	2,58 ±0,26	2,79 ±0,28
Nickel	µg/l	3,5 ±0,4	3,8 ±0,4
Dissolved Organic Carbon	mg/l	13 ±1	14 ±1
Total organic carbon	mg/l	15 ±2	15 ±2
Sulphur	µg/l	4800 ±720	5300 ±795
Selenium	µg/l	L 0,1	L 0,1
Zinc	µg/l	1,3 ±0,5	2 ±0,5
Strontium	µg/l	38 ±4	37 ±4
Titanium	µg/l	1,9 ±0,3	3,5 ±0,5
Uranium	µg/l	0,053 ±0,011	0,056 ±0,011
Vanadium	µg/l	0,37 ±0,04	0,72 ±0,07
BOD5-ATU	mg/l O2	1,6	1,4

Table 15. Analysis results from Finnish area of the River Tohmajoki.

20.9.2021		Tohmajoki 9 upper reach	Tohmajoki lower reach
Variable	Unit	Depth 0,1 m	Depth 0,1 m
Temperature	°C	8,7	8,3
Turbidity	FNU	3,7	3,5
Solids	mg/l	3,8	2,5
Solids	mg/l	4	3,9
Solids	mg/l	2,1	1,4
Electrical conductivity	mS/m	8,2	7,4
Alkalinity	mmol/l	0,280	0,243
Acidity (pH)		7,2	6,7
Colour	mg/l Pt	70	140
Total nitrogen	µg/l	500	550
Nitrite as nitrogen	µg/l	<1	<1
Nitrite-nitrate as nitrogen	µg/l	18	32
Nitrate as nitrogen	µg/l	17	31
Ammonium as nitrogen	µg/l	<2	7
Total phosphorus	µg/l	26	18
Phosphate as phosphorus	µg/l	<2	3
PO4-P, filtered	µg/l	<2	3
Iron	µg/l	570	1000
Manganese	µg/l	85	82
Sulphate	mg/l	14	14
Aluminium	µg/l	72	110
Arsenic	µg/l	0,36	0,39
Barium	µg/l	15	15
Mercury	µg/l	0,0011	0,0017
Phosphorus	µg/l	<25	<25
Cadmium	µg/l	0,008	0,011
Potassium	mg/l	1,97	1,85
Calcium	mg/l	9,1	8,6
CODMn	mg/l	16	21
Cobalt	µg/l	0,21	0,34
Chrome	µg/l	0,25	0,35
Copper	µg/l	1,6	1,4
Lead	µg/l	0,140	0,180
Magnesium	mg/l	2,17	2,09
Sodium	mg/l	2,86	2,70
Nickel	µg/l	2,9	3,1
Dissolved Organic Carbon	mg/l	12	16
Total organic carbon	mg/l	13	17
Sulphur	µg/l	5600	5500
Selenium	µg/l	<0,1	<0,1
Zinc	µg/l	1,2	1,9
Strontium	µg/l	42	40
Titanium	µg/l	2,5	2,6
Uranium	µg/l	0,059	0,054
Vanadium	µg/l	0,38	0,49

BOD5-ATU	mg/l O2	1,7	1,6

Sampling time	pН	Solids mg/l	BOD5	Total N mg/l	Ammonia mg/l	Nitrate mg/l	Nitrite mg/l	Phosohate mg/l	Sulphate mg/l	Oil products mg/l	Тι
	7,10 ± 0,20	3,20 ± 0,96	$1,1 \pm 0,3$	0,33	$0,07 \pm 0,03$	$0,26\pm 0,05$	< 0,02	< 0,05	< 10,0	< 0,05	1,
18.06.2020 - 23.06.2020	7,14 ± 0,20	4,0 ± 1,2	1,15 ± 0,30	0,61	$\substack{0,07\pm\\0,03}$	$0,54\pm 0,06$	< 0,02	0,06 ± 0,01	< 10,0	< 0,05	2,
	7,20 ± 0,20	4,0 ± 1,2	1,50 ± 0,39	0,67	0,15 ± 0,05	$0,52\pm 0,09$	< 0,02	$0,08 \pm 0,01$	< 10,0	< 0,05	5,
	6,76 ± 0,20	$3,2 \pm 0,96$	$1,2 \pm 0,3$	0,78	0,48± 0,17	0,3 ± 0,05	< 0,02	$0,05 \pm 0,008$	10,0 ± 2,0	< 0,05	1,
22.09.2020 - 27.09.2020	6,87 ± 0,20	3,2 ± 0,96	1,70 ± 0,44	1,11	0,51 ± 0,18	$0,6\pm 0,1$	< 0,02	0,06 ± 0,01	< 10,0	< 0,05	1,
	6,90 ± 0,20	4,4 ± 1,3	1,90 ± 0,49	1,19	0,59± 0,21	$0,6\pm 0,1$	< 0,02	0,078 ± 0,012	< 10,0	< 0,05	1
28.09.2020 - 03.10.2020	6,85 ± 0,20	9,8 ± 2,9	2,75 ± 0,72	0,65	$_{0,15\pm}^{0,15\pm}$	$_{0,5\pm}^{0,5\pm}$	< 0,02 (0,015)	< 0,05 (0,04)	< 10,0 (4,2)	< 0,05 (АСПАВ 0,026)	1,
	5,96 ± 0,20	5,1 ± 1,5	$2,7 \pm 0,7$	0,8	0,3 ± 0,11	$0,5\pm 0,09$	< 0,02	< 0,05	< 10,0	< 0,05	1,
15.12.2020 - 20.12.2020	6,30 ± 0,20	8,0 ± 2,4	3,0 ± 0,8	1,43	0,43 ± 0,15	1±0,02	< 0,02	$0,050 \pm 0,008$	< 10,0	< 0,05	2,
	6,37 $\pm$ 0,20	10,7 ± 3,2	3,2 ± 0,8	1,27	0,27 ± 0,09	1±0,02	< 0,02	0,056 ± 0,009	< 10,0	< 0,05	2,

Table 16	Laboratory	regulte	from	Karolian	aroa	of the	River	Tohmai	obi
<i>Tuble</i> 10.	Laboratory	resuits	10m	Nurenun	ureu	<i>j</i> ine	niver	ronnaj	υπι.

Table 17. Laboratory results from Karelian area of the River Tohmajoki.

Samp ling time	рН	Soli ds mg/l	BOD 5	T ota 1 N mg /l	Amm onia mg/l	Nitrat e mg/l	Nitrit e mg/l	Phosoh ate mg/l	Sulp hate mg/l	Oil prod ucts mg/l	Turb idity	Colour	Oxida tivity, mg / l	Sam pling site
23.03.	5,96 ± 0,20	8,5 ± 2,6	2,1 ± 0,6	1,7 1	0,9± 0,32	0,81± 0,15	< 0,02	< 0,05	12,2 ± 2,4	< 0,05	2,0 ± 0,4	140,0 ± 14,0	_	Matk asel- kä
2021 	6,30 ± 0,20	9,0 ± 2,7	2,9 ± 0,8	2,0 1	0,81± 0,28	$^{1,2\pm}_{0,2}$	< 0,02	0,06 ± 0,01	13,7 ± 2,7	< 0,05	2,5 ± 0,5	144,5 ± 14,5	_	Rytty
2021	6,37 ± 0,20	16,0 ± 3,2	2,6 ± 0,7	2,1 3	1,03± 0,22	$1,1\pm 0,2$	< 0,02	0,099 ± 0,016	12,2 ± 2,4	< 0,05	3,3 ± 0,7	110,0 ± 20,7		Helyl ä

28.04.	$5,57 \\ \pm 0,20$	6,50 ± 1,95	2,25 ± 0,59	1,7 4	$0,54 \\ \pm 0,19$	1,2 ± 0,2	< 0,02	< 0,05	< 10,0	< 0,05	2,3 ± 0,5	160,0 ± 16,0	_	Matk asel- kä
2021 - 04.05. 2021	5,90 ± 0,20	7,4 ± 2,2	$1,15 \\ \pm 0,30$	1,5 7	$0,37\pm 0,13$	$^{1,2\pm}_{0,2}$	< 0,02	< 0,05	< 10,0	< 0,05	4,3 ± 0,9	194,5 ± 19,5	_	Rytty
2021	6,00 ± 0,20	14,2 ± 2,8	2,95 ± 0,77	1,4	0,3± 0,11	1,1 ± 0,2	< 0,02	0,080 ± 0,013	< 10,0	< 0,05	17,5 ± 2,5	181,8 ± 18,2		Helyl ä
6,14 ±0,2 0	6,14 ±0,2 0	5,8 ± 1,7	1,15 ±0,3 0	1,6 7	0,72 ±0,2 5	0,92 ±0,1 7	0,03 0± 0,00 6	<0,05	< 10,0	<0, 05	1,6± 0,3	163,6 ± 16,4		Matk asel- kä
23.6.2 021	6,16 ±0,2 0	6,4 ± 1,9	1,20 ±0,3 1	1,7	0,66 ±0,2 3	1,0± 0,2	0,04 0± 0,00 8	0,050± 0,008	< 10,0	<0, 05	2,5	172,7	_	Rytty
	6,30 ±0,2 0	7,2 ± 2,2	1,35 ±0,3 5	1,9 1	0,76 ±0,2 7	1,1± 0,2	0,05 ±0,0 1	0,070± 0,011	< 10,0	<0, 05	3,8± 0,8	160,9 ±16,1	_	Helyl ä
	6,32 ±0,2 0	4,7 ± 1,4	1,4 ±0,4	1,0	0,69 ±0,2 4	0,31 ±0,0 6	<0,0 2	0,065 ±0,010	< 10,0	<0, 05	2,9± 0,6	177,3 ± 17,7	_	Matk asel- kä
27.9.2 021	6,35 ±0,2 0	5,9 ± 1,8	1,3± 0,3	1,3 5	0,72 ±0.2 5	0,63 ±0,1 1	<0,0 2	0,081± 0,013	< 10,0	<0, 05	4,0± 0,8	180,9 ± 18,1	_	Rytty
	6,50 ±0,2 0	6,7 ±2, 0	1,8± 0,5	1,0 2	0,47 ±0,1 6	0,55 ±0,1 0	<0,0 2	0,111± 0,018	< 10,0	<0, 05	5,4± 1,1	188,2 ± 18,8	_	Helyl ä

Table 18. Observed metal levels in water samples from the River Tohmajoki.

					Tohmajoki upper reach 23.6.2020	Tohmajoki lower reach 23.6.2020	Tohmajoki upper reach 22.6.2021	Tohmajoki lower reach 22.6.2021		Point №1	Point №2 (Ruskeala)	Point №3	Point №4
		Variable	Unit	MAC	0.1 m	0.1 m	0.1 m	0.1 m	Karelia				
	Finland	Al	μg/l	<u>~6/ '</u>	84 ±13	88 ±13	97 ±15	110 ±17	c of I	112±15	131±17	128±17	130±17
		Fe	μg/l		700 ±70	1300 ±130	780 ±78	1800 ±180	ublid	679±84	654±81	716±	659±82
		Cd	μg/l	0,6	0,011 ±0,003	0,01 ±0,003	0,014 ±0,003	0,014 ±0,003	e Repi	-	-	-	-
		Mn	µg/l		76 ±8	110 ±11	100 ±10	140 ±14	L L	42±5	69±9	71±9	67±9
		Ni	μg/l	34	3,4 ±0,3	3,7 ±0,4	3,5 ±0,4	3,8 ±0,4		-	-	-	-
		Hg	μg/l	0,07	0,0007 ±0,0005	0,0007 ±0,0005				-	-	-	-
		Pb	μg/l	14	0,12 ±0,02	0,13 ±0,03	0,11 ±0,02	0,21 ±0,02		-	-	-	-