KARELIA CBC // Cross-border cooperation	Project KA5016 «Joint cross-border environmental monitoring system» (ECO-bridge)

Report on the result of intercalibration

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1. Participants

Interlaboratory comparative tests (intercalibrations) were carried out during 24.01-28.02.2019. Participants were analytical laboratories of Savo-Karjala Environment laboratory in Kuopio (Finland) and in Joensuu (Finland), and KarChem laboratory of environmental pollution (the Republic of Karelia, Russia). In sampling Finnish participants were from Finnish Environment Institute SYKE)

2. Primary objective

Primary objective was to compare the analytical methods used by the participating laboratories and how comparable are results of water quality variables. Samples from Tohmajoki river were taken together with same method. Besides, synthetic control samples prepared by both partners were analyzed without knowing the original concentration

3. Sampling, samples and analysed variables

Joint water sampling of natural river water was performed according to the Russian guideline 52.24.309-2016. The grab sampling took place in Russia at a cross-border watercourse Tohmajoki river by representatives of KarChem and SYKE on 23.01.2019.

The river was opened with an ice-drill and the hole was cleaned from the ice with an enamel strainer. The sample was taken with a five-liter, enameled bucket and carried to a car (at a distance of about 50 meters) where the sample was divided into sample bottles (Figure).

Figure. Sampling at Tohmajoki River.

The following variables were measured from the split water sample:

Nutrients

- NH_4-N (ammonium nitrogen)
- PO_4-P (phosphate phosphorus)
- NO_2-N+NO_3-N (nitrate nitrogen and nitrate nitrogen as sum or separately)
- Total P (total phosphorus)
- Total N (total nitrogen)

Metals

- Total Fe (total iron)
- Total Mn (total manganese)

Suspended solids

- Mass concentration of solids in a liquid, normally determined by filtration or centrifuging and then drying all under specified conditions.

Participants used same standard methods that they are using in daily operations (Appendix 1). KarChem used test methods that they have certificate for (Accreditation certificate RA.RU.511024 of 12.08.2015). Savo-Karjala Environment laboratory is accredited (SFS-EN ISO/IEC 17025:2005) and uses SFS-ISO standard methods.

The results of the analyses are presented in Table 1.

4. Control samples

Preparation and exchange of control samples with fixed concentrations of ingredients and schemes for analyses:

- Control samples of KarChem were made from the standard (state-approved) samples corresponding the measured ingredients.
- The lists of control samples with labels (number of sample) and assigned levels of ingredients are presented in tables 2 and 3.
- The participants of intercalibration exchanged control at a work meeting in Sortavala on 23.01.2019.
- The results of qualitative chemical analyses performed by both laboratories participating in intercalibration are presented in tables 4 and 5.

5. Conclusions

The full procedure for intercalibration of the analysis of all control samples was performed by laboratories of KarChem and SAVO-Karjala Environmental Research laboratory in Kuopio.

Separate analyses for NH_4-N and NO_2-N+NO_3-N was performed in SAVO-Karjala Environmental Research laboratories in Kuopio and Joensuu. KarChem analysed NH_4-N and NO_3-N separately.

5.1. Analysis of the split samples of natural river water

Unsatisfactory comparability of measurement was revealed for several ingredients (Table 1).

Significant discrepancies in measurement of the content of manganese, suspended solids, ammonium nitrogen and phosphorus were revealed.

The differences in results are partly linked to the differences of sample preparation and analysis methods. For instance, suspended solids were filtered from water using different types of filters: in KarChem 0.45 µm pore size filter and in Savo-Karjala glass fiber filter was used. The latter allows small particles, with size greater than 0.45 µm, wash away from analysis.

A result of manganese analyzes depends essentially of how much Mn degrades from particles in natural water. There is no difference between results of control samples (Table 5) but results of Mn concentration in river water differ remarkably (Table 1).

5.2. Control samples

Control samples prepared by KarChem for Savo-Karjala were provided with enclosed instructions for preparation of control samples from basic solutions. Nevertheless, this proposed procedure was not implemented by laboratories Kuopio and Joensuu that analyzed basic solutions. The reason for this was that the laboratories did not notice the dilution guidelines. Furthermore, the laboratories did not expect the need to dilute the control samples.

The results of the analysis of the control samples can be considered satisfactory for most parameters taking into account the confidence intervals of margins of error set for the analysis methods used.

Due to the fact, that the laboratory of Kuopio did not dilute the control samples with distilled water according the instructions of KarChem, all the other parameters (except PO_4-P) were on the same level than the non-diluted Russian control samples. Result of PO_4-P was clearly higher than the assigned concentration in the non-diluted sample (Table 4).

Analytical results of synthetic samples prepared by Savo-Karjala are in Table 5. Total P result of KarChem is clearly higher than the original concentration. Total Fe result of KarChem is lower than the original result.

6. Recommendations

It is recommended that KarChem would take apart to Proftest organized by SYKE laboratory. All Finnish laboratories take part to these tests and sometime also laboratories in other countries. Annual schemes of proficiency tests and intercomparison tests are published in SYKE website

Very suitable matrix and variables for KarChem are included to programme in year 2020.

Natural water II		
Lake or river water Coastal water	N_{NH4}, N_{NO2}, N_{NO3}, N_{tot}, P_{PO4}, P_{tot}, $P_{PO4,\ dissolved}$, $P_{tot,\ dissolved}$, alkalinity, pH, conductivity	Every second year 2018, 2020, 2022...
Natural water III		
Lake or river water Coastal water	chlorophyll *a*, oxygen, SiO_2, TOC, TIC, salinity	Every second year 2018, 2020, 2022...

Differences in sample preparation and analytical methods of natural water in Finnish laboratories and KarChem should be studied in more detail.

KarChem has not jet an analytical method for total nitrogen. It is a basic water quality variable and important indicator for nutrient status of natural waters and thus it is very recommended that KarChem would have it.

Table 1. Results of analysis of a split sample of surface water of Tohmajoki river

Variable	Kuopio		Joensuu		KarChem		
	Result µg/l	Margin of error %	Result µg/l	Margin of error %	Result µg/l	Margin of error %	Confidence interval of the result µg/l
NH_4-N	41.7	13	43.4	12	24 ± 10	41	14 - 34
PO_4-P	9.3	12	-	-	13 ± 3	23	10 - 16
NO_2-N+NO_3-N	210	8	213	15	242 ± 64	26	178 - 306
Total P	22.6	15	-	-	34 ± 6	17	28 - 40
Total N	688	15	-	-	-	-	-
Total Fe	1130	10	-	-	1420 ± 150	10	1270 - 1570
Total Mn	27.6	10	-	-	99 ± 13	13	86 - 112
Suspended solids*)	1080	8	-	-	6950 ± 400	57	2950 - 10950

**) Suspended solids: Savo-Karjala used glass fiber filter. It is not possible to give the exact pore size of that filter type. Karelia CHEM used filter with pore size 0.45 µm.*

Table 2. Control (synthetic samples) prepared by KarChem

Elements	Used state standard reference sample (SSRS) or reagent	Range for diluted sample µg/l	Bottle number	Assigned concentration in the non-diluted sample µg/l
NH_4-N	SSRS 7747-99	10 - 20	1	9940
PO_4-P	SSRS 7748-99	3 - 10	2	7990
NO_2-N	SSRS 7753-2000	180 - 230	4	-
NO_3-N	SSRS 820-2000	180 - 230	5	10050
Total P	SSRS 7241-96	10 - 20	3	9800
Total Fe	SSRS 7835-2000	1300 - 1500	6	50000

Table 3. Control (synthetic) samples prepared by SAVO-Karjala Environmental Research

Elements	Range µg/l	Assigned concentration µg/l
NH_4-N	10 - 20	18
PO_4-P	3 - 10	9
NO_2-N+NO_3-N	180 - 230	200
Total P	10 - 20	15
Total N	550 - 650	600
Total Fe	1300 - 1500	1400
Total Mn	100 - 150	130

Table 4. Results of analysis of a control (synthetic sample) prepared by KarChem

Elements	Assigned concentration in the non-diluted sample µg/l	Kuopio		Joensuu		Assigned concentration in the diluted control sample, µg/l	KarChem*	
		Result µg/l	Margin of error %	Result µg/l	Margin of error %		Result µg/l	Margin of error µg/l
NH_4-N	9940	9400	12	9710	10	20	23	± 10
PO_4-P	7990	9490	10	Not analyzed	-	10	10	± 4
NO_2-N+NO_3-N	10050	11300	8	11000	15	200	180	± 50
Total P	9800	9770	12	Not analyzed	-	14.7	13.4	-
Total N	No control sample	Not analyzed		Not analyzed	-	-	-	-
Total Fe	50000	50700	10	Not analyzed	-	1500	1590	± 160
Total Mn	10000	10000	10	Not analyzed	-	150	130	± 17

** Control samples prepared by KarChem for SYKE were provided with enclosed instructions for preparation of control samples from basic solutions. This proposed procedure of diluting the samples was not implemented by laboratories Kuopio and Joensuu that analyzed basic solutions. KarChem followed the instructions when analyzing the samples.*

Table 5. Results of analysis of a control (synthetic sample) prepared by SAVO-Karjala Environmental Research

Elements	Assigned concentrations µg/l	Kuopio		Joensuu		KarChem		
		Result µg/l	Margin of error %	Result µg/l	Margin of error %	Result in µg/l	Margin of error %	Confidence interval of the result µg/l
NH_4-N	18	16.8	13	19.1	26	22	45	12 - 32
PO_4-P	9	7.9	13	Not analyzed	-	10	…	6 - 14
NO_2-N+NO_3-N	200	205	8	202	15	223	26	164 - 282
Total P	15	15.8	15	Not analyzed	-	25	24	19 - 31
Total N	600	625	10	Not analyzed	-	Not analyzed	-	-
Total Fe	1400	1390	10	Not analyzed	-	1260	11	1120 - 1400
Total Mn	130	136	8	Not analyzed	-	127	13	111 - 143

Annex 1. List of water quality variables and their analytical methods used by laboratories participated in intercalibration

Indicated elements	Laboratory	Methods	Method range/detection limit [1)]	Sampling, preservation and storage of samples			
				Sample bottle	Preservation and storage	Analysis done in	Analysis done within
Ammonium nitrogen $(NH4)+$	KarChem	РД 52.24.383-2005	0.02-1.0 mg/dm^3	Polymeric material or glass	1. No preservation 2. Preserving at pH <2 3. Freezing down to -20 – -40°C	Laboratory	1. 6 h 2. 3-4 days 3. Continuous
	Savo-Karjala	In-house method, fluorometric, CFA analyser (based on Skalar analytical method no. A157/158)	5 µg/l	Polymeric material	No preservation	Laboratory	24 h
Phosphate phosphorus (PO_4^{3-})	KarChem	РД 52.24.382-2006, paragraph 11	0.010-0.2 mg/dm^3	1.-2. Glass 3. Polymeric material	1. No preservation 2. Storage at 3-6° C with addition of chloroform 3. Freezing down to -20 – -40°C	Laboratory	1. 4 h 2. 3 days 3. Continuous
	Savo-Karjala	In-house method, colorimetric, FIA analyser (based on SFS-EN ISO 15681-1:2005, Part 1.)	2 µg/l	Polymeric material	No preservation		24 h
Nitrite nitrogen (NO_2)	KarChem	РД 52.24.381-2006	0.01-0.25 mg/dm^3	Polymeric material or glass	1. No preservation 2. Storage at 3-6° C 3. Freezing down to -20 – -40°C	Laboratory	1. 2 h 2. 24 h 3. Continuous
	Savo-Karjala	SFS-EN ISO 13395:1997	2 µg/l	Polymeric material	No preservation	Laboratory	24 h

Nitrate nitrogen (NO_3)	KarChem	M-02-1805	0.080-4.0 mg/dm^3	Polymeric material or glass	No preservation	Laboratory	8 h
	Savo-Karjala	SFS-EN ISO 13395:1997	2 µg/l	Polymeric material	No preservation	Laboratory	24 h
Total phosphorus (mineral and organic)	KarChem	РД 52.24.387-2006	0.02-0.4 mg/dm^3	1.-2. Glass 3. Polymeric material	1. No preservation 2. Freezing down to -20 – -40°C 3. Freezing down to -20 – -40°C	Laboratory	1. 4 h 2. 3 days 3. Continuous
	Savo-Karjala	SFS-EN ISO 15681-2:2003	5 µg/l	Polymeric material	1. No preservation 2. Preservation with H_2SO_4	Laboratory	1. 24 h 2. 7 days
Total nitrogen	Savo-Karjala	SFS-EN ISO 11905-1:1998	50 µg/l	Polymeric material	1. No preservation 2. Freezing down to -20 – -40°C	Laboratory	1. 24 h 2. 1 month
Total Fe	KarChem	M-02-1109	0,0020-1,0 mg/dm^3	Polymeric material	Preservation with HNO3 at pH < 2	Laboratory	1 month
	Savo-Karjala	SFS-EN ISO 17294-1 (2006) and 17294-2 (2016) ICP-MS (low concentrations) 2)	1 µg/l	Polymeric material	Preservation with H_2SO_4	Laboratory	6 months
Total Mn	KarChem	M-02-1109	0,0050-50 mg/dm^3	Polymeric material	Preservation with HNO3 at pH < 2	Laboratory	1 month
	Savo-Karjala	SFS-EN ISO 17294-1 (2006) and 17294-2 (2016) ICP-MS (low concentrations)2)	0.5 µg/l	Polymeric material	Preservation with H_2SO_4	Laboratory	6 months
Suspended solids	KarChem	РД 52.24.468-2005. paragraph 10.1, filter size 0.45 µm	5.0-100 mg/dm^3	Polymeric material or glass	Cool down to 3-6°C	Laboratory, right after sampling	7 days
	Savo-Karjala	SFS-EN 872:2005, glass fibre filter was used.	1 mg/l	Polymeric material	Cool down to 2-8°C	Laboratory	2 days

1) Accredited method range in KarChem lab, the limit of determination in Savo-Karjala lab

2) SFS-EN ISO 11885 (2009) ICP-OES for high concentrations

Guidelines in Russia: International standard GOST-31861-2012, P 52.24.353-2012

Guidelines in Finland: Reports of the Finnish Environment Institute 22/2016. Quality recommendations for data entered into the environmental administration's water quality registers: Quantification limits, measurement uncertainties, storage times and methods associated with analytes determined from waters. Teemu Näykki and Tero Väisänen (eds.).

In Finland: transportation cool down to 2-8°C, storage in laboratory -1 - 5°C [SFS-EN ISO 5667-3]