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Uncertainty estimation of online measurement and manual sampling in water quality measurements

Maija Ojanen-Saloranta

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Preface

In this work, measurement uncertainty of several water quality parameters was estimated. The work was carried out in collaboration with EHP-Tekniikka Oy during January 2015 – March 2016.

June 2016
Maija Ojanen-Saloranta

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Abstract
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1. Introduction

In Finland peat production and its monitoring is carried out according to environmental permit, and the Centre for Economic Development, Transport and the Environment (ELY Centre) acts as the supervising authority. Environmental monitoring of peat production consists of different types of monitoring: The discharge monitoring of water and the measurement uncertainties are discussed more detailed in this study.

In this case the operator of peat production would like to partly change the manual water sampling to online monitoring. For this change, the ELY-Centre required a comparison (duration of 1 year) of these methods. The correlation between manual samples and online results should be demonstrated to be statistically valid.

The monitoring wells and sensors were installed, maintained and calibrated by EHP-Tekniikka. In order to estimate the uncertainty of manual sampling combined with laboratory analysis, collaborative sampling and laboratory analysis were carried out. Certified sampling person of EHP-Tekniikka carried out duplicate samples, which were analysed by an accredited laboratory, Metropolilab. Accordingly a certified sampling person of monitoring consulting laboratory carried out sampling at the same time and those samples were analyzed by his own laboratory. The uncertainty of manual sampling has not been thoroughly evaluated earlier. The overall measurement uncertainty in the supply chain shall be taken into account in order to compare online and laboratory results.

The scope of the work was to compare the measurement uncertainty of online environmental measurements to the overall measurement uncertainty of manual sampling and laboratory analysis. The measured parameters were pH, turbidity, suspended solids and COD. The measurement sensors used are given in Appendix A. The laboratory analyses were carried out according to the standards SFS 3021:1979 (pH), SFS-EN ISO 7027:2000 (turbidity), SFS-EN 872:2005 (suspended solids) and SFS 3036:1981 (COD). The measurement results and uncertainty of online measurements were compared with the uncertainties given by Metropolilab and monitoring consulting laboratory, given in Appendix A. Both laboratories have the measured parameters in their accreditation scope. The uncertainty related to sampling for the laboratory analyses was also estimated. The uncertainty estimation for online measurements is carried out according to [1]. The sampling uncertainty is estimated according to [2].

2. Sampling

The sampling was carried out in Iso-Kerusneva according to Figure 1 and sampling schema presented in Appendix A. The test period was carried out 18.3.2015–1.3.2016. The measured parameters were pH, turbidity, suspended solids and COD. Simultaneously to online measurements, laboratory sampling and analysis was carried out. The certified sampling person of EHP-Tekniikka took two samples (A and B) at a time. The analysis was carried out by Metropolilab. Monitoring consultant laboratory took one sample per sampling time and analysed it. The sampling was carried out in monitoring stations located upstreams and downstreams of an overland flow area. There were seven samplings in common for both laboratories. In addition to that, EHP-tekniikka carried out two additional samplings. Monitoring consulting laboratory took samples according to their normal monitoring program, the number of samplings being 26 for the test period. In January sampling could not be carried out due to freezing of monitoring wells during a long period of frost.

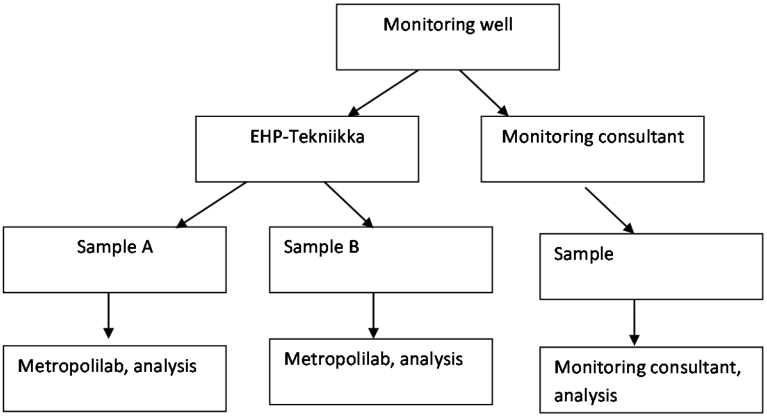

Figure 1. Schema of the sampling

3. Measurement results

Figures 2…5 present the measurement results without uncertainty estimates.

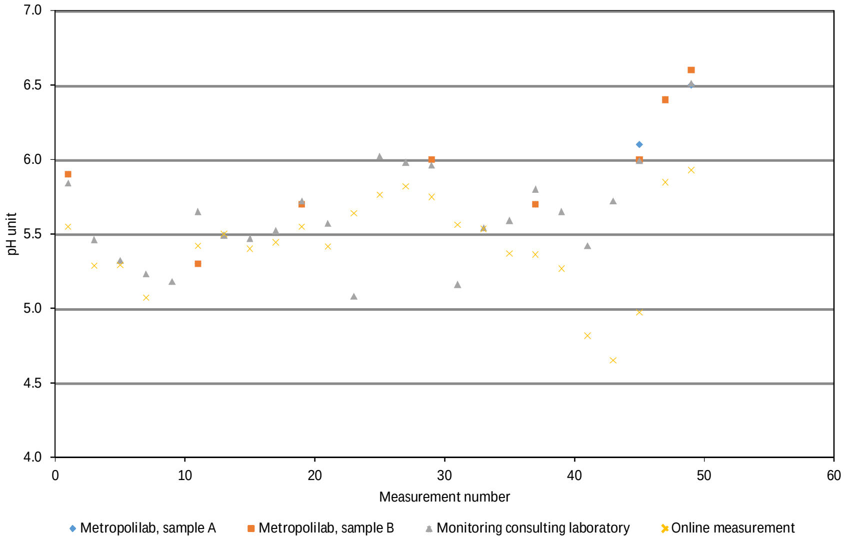

Figure 2a. Results of pH measurement, monitoring station downstreams the overland flow area.

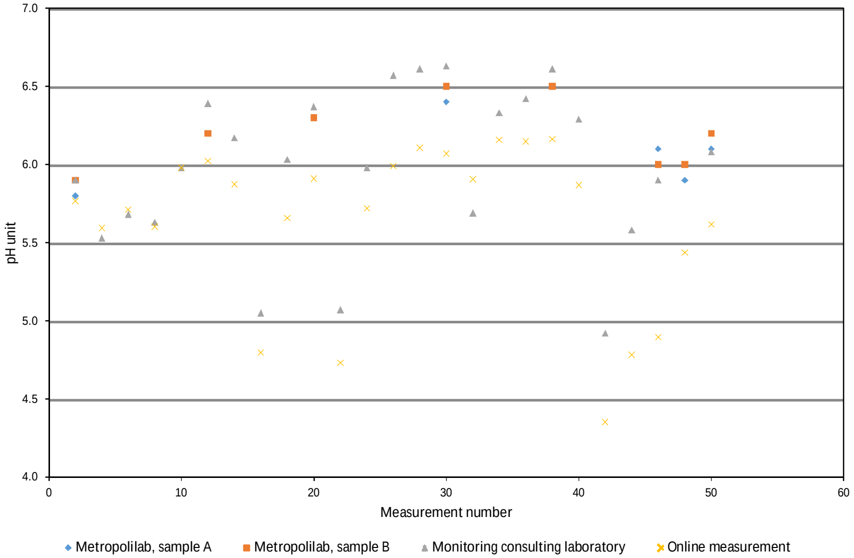

Figure 2b. Results of pH measurement, monitoring station upstreams the overland flow area

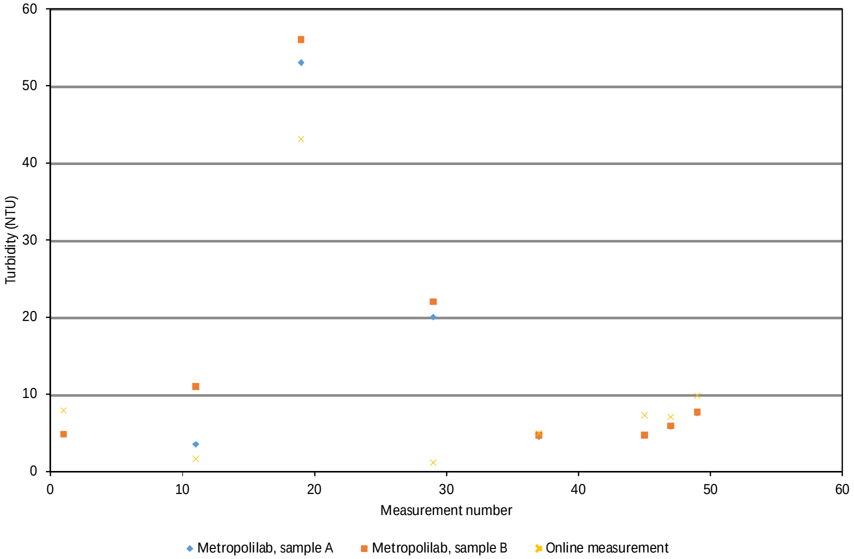

Figure 3a. Results of turbidity measurement, monitoring station downstreams the overland flow area.

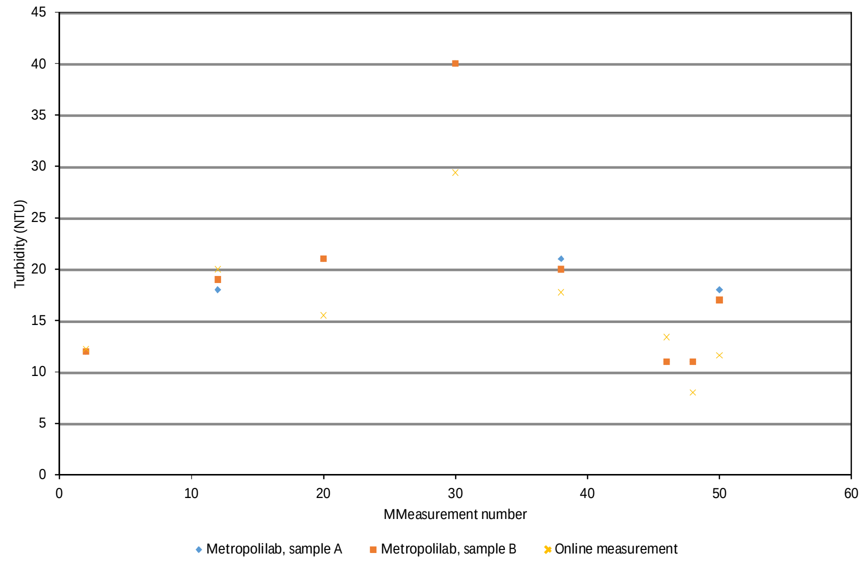

Figure 3b. Results of turbidity measurement, monitoring station upstreams the overland flow area

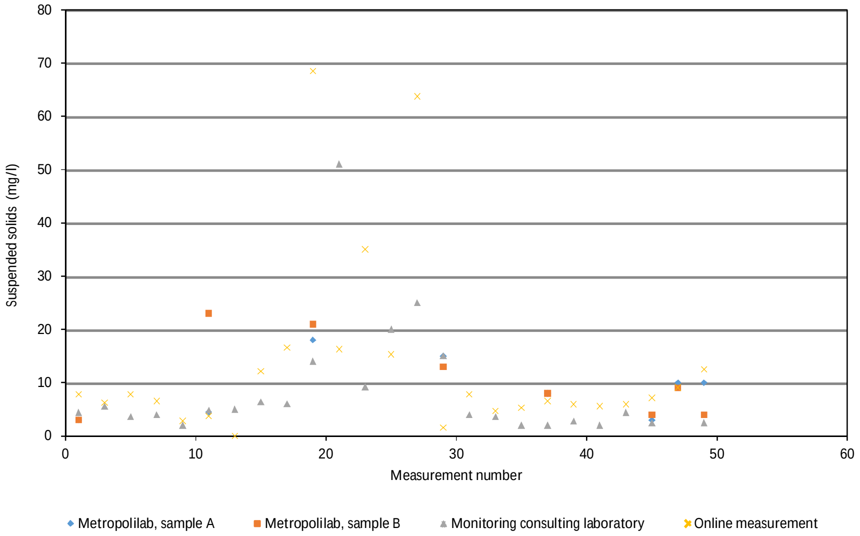

Figure 4a. Results of suspended solids measurement, monitoring station down-streams the overland flow area

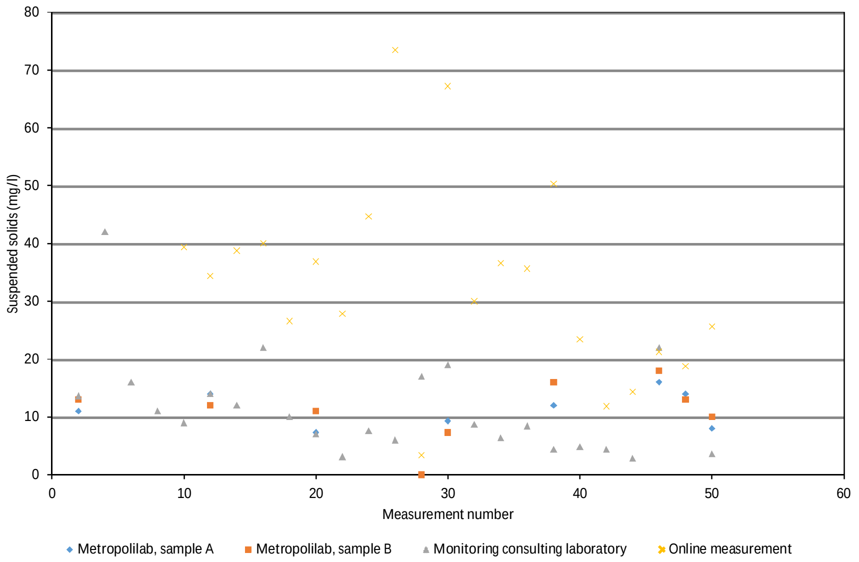

Figure 4b. Results of suspended solids measurement, monitoring station upstreams the overland flow area.

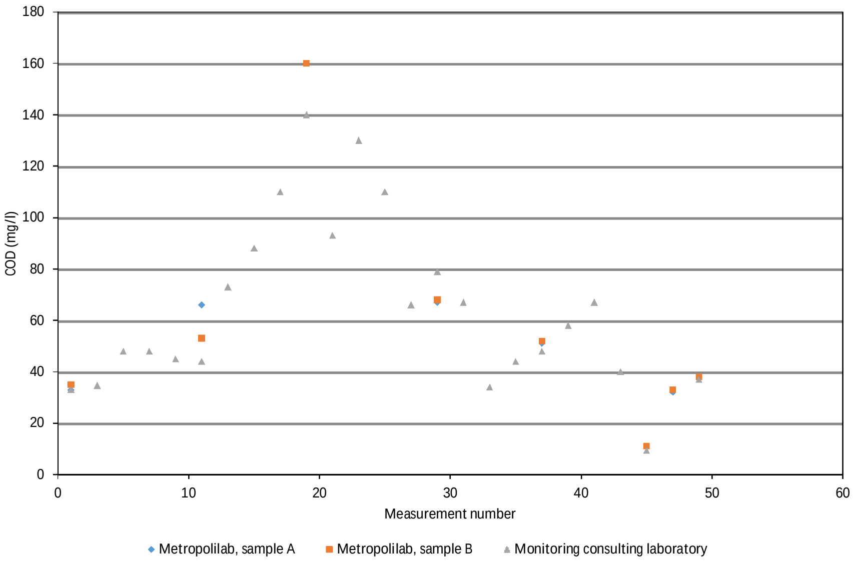

Figure 5a. Results of COD measurement, monitoring station downstreams the overland flow area.

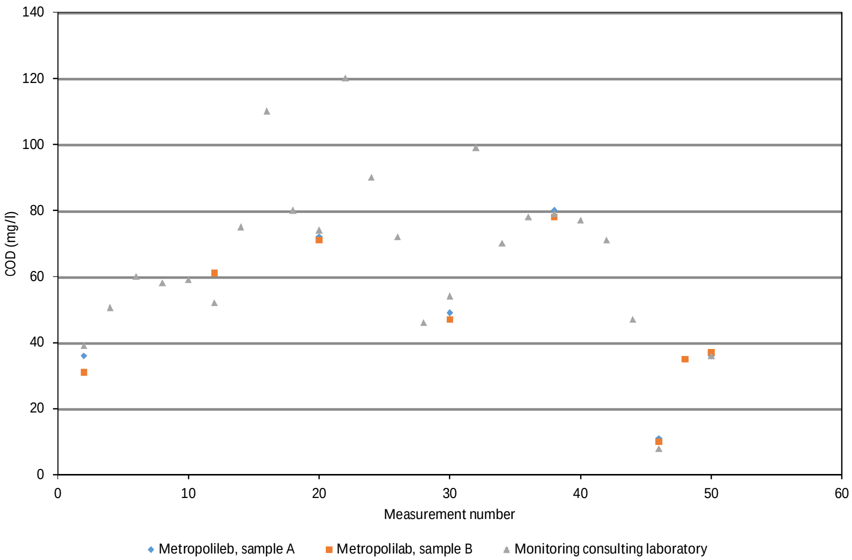

Figure 5b. Results of COD measurement, monitoring station upstreams the overland flow area

4. Estimation of measurement uncertainty

4.1 Online measurements

For online sensors, the following uncertainty contributions are included in the uncertainty estimation:

- Calibration of the measurement device, which includes:
  - Uncertainty of the calibration reference $u(\delta c_{calref})$
  - Uncertainty of the linear calibration equation $u(\delta c_{caleq})$, if applicable
- Non-ideal repeatability of the measurement $u(\delta c_{rep})$
- Finite resolution of the measurement device $u(\delta c_{res})$
- Long-term stability (i.e. drift) of the measurement device $u(\delta c_{stab})$
- Possible temperature and environmental effects on the reading of the measurement device $u(\delta c_t)$

A single measurement result can be presented as

$$c = c_{meas} + \delta c_{calref} + \delta c_{caleq} + \delta c_{rep} + \delta c_{res} + \delta c_{stab} + \delta c_t \ , \qquad (1)$$

where c_{meas} is the reading of the measurement device or measurement value calculated with the calibration equation, and corrections c_{xx} are estimated to be on average zero excluding the correction for the calibration reference. Assuming the terms of Eq (1) non-correlated, the measurement uncertainty can be calculated as:

$$u^2(c) = u^2(\delta c_{calref}) + u^2(\delta c_{caleq}) + u^2(\delta c_{rep}) + u^2(\delta c_{res}) + u^2(\delta c_{stab}) + u^2(\delta c_t) \qquad (2)$$

4.1.1 Accuracy of measurement devices, calibration reference and calibration equation

Manufacturers' specifications were used as estimates for the accuracies of the measurement devices. In this case, the accuracy specified by the manufacturer is estimated to be the standard uncertainty ($k = 1$).

The measurement sensors can also be calibrated using laboratory samples as a reference, or with some other corresponding method. In this case, the uncertainty of laboratory analysis as well as the fitting of the calibration equation must be taken into account in the uncertainty budget, for example applying reference [3].

4.1.2 Linearity of the device and calibration equation

The pH reading of the measurement device is calibrated at the field using buffer solutions with pH values (3.998 ± 0.013) and (7.000 ± 0.013) at the temperature of 20 °C. The calibration equation is constructed by fitting a first order polynomial between the measured points. Because only two measurement points are used in the fitting, the uncertainty of the calibration equation was estimated with help on repeatability of the measurements. The uncertainty of the calibration equation is calculated as the square sum of the uncertainty of the pH of the buffer solution and the short-term repeatability of the measurements. The linearity of turbidity and suspended solid sensors is estimated with help of their manufacturers' specifications. The linearity of the COD sensor is estimated with help of laboratory analysis results by fitting a first order polynomial between the laboratory analysis results and corresponding online measurement raw data. The estimated non-linearity is the average deviation of a single measurement result from the fitted polynomial. The problem of this approach is that the linearity of the sensor is estimated using the laboratory results, which may itself include significant deviation and thus increase the uncertainty estimation of the online measurements.

4.1.3 Repeatability of the measurements

The repeatability of the measurements is estimated with help of ten series of ten online samples. The uncertainty due to repeatability is calculated as the median of the standard deviations of the measurement series. The repeatability was compared with the manufacturers' specifications in order not to give significantly smaller uncertainty than specified for the repeatability.

4.1.4 Resolution of the measurement device

The uncertainty due to finite resolution of the measurement device was estimated according to reference [1] (assuming an even probability distribution):

$$u^2(\delta c_{res}) = \frac{c_{max}-c_{min}}{2\sqrt{3}} \tag{3}$$

4.1.5 Stability of the measurement devices

The stability of the measurement devices has been studied in an earlier TASO project. No drift was observed in the sensor readings during the 21 month test period. Due to this, the uncertainty due to stability was estimated to be equal to the uncertainty due to finite resolution.

4.1.6 Temperature and environmental conditions

The temperature dependency of the standard solutions used in the pH sensor calibration was estimated using the specification given by the manufacturer of the buffer solution. As the sensors are calibrated at the field, we expect here the minimum operational or calibration temperature to be 0 °C. In this case, by extrapolating the manufacturers' specification, the effect of temperature dependence would be at largest 0.09 pH units. The temperature compensation is not carried out in the pH calibration, but it is considered as an uncertainty component.

For the turbidity and suspended solids sensors the uncertainty due to temperature dependency was estimated with the manufacturers' specification, 0.05%/°C, and the deviation of 20 °C in the ambient temperatures during the measurement.

4.1.7 Combined uncertainty for online measurements

The uncertainty estimation for online measurements is presented in Table 1. The expanded uncertainty is obtained by multiplying the standard uncertainty by a coverage factor *k* = 2, which corresponds to approximately 95% confidence level.

Table 1. Uncertainty budget for online measurements. The relative uncertainty due to resolution and stability has been calculated for an average sample with pH = 6.0, turbidity = 14.5 NTU, suspended solids concentration = 10 mg/l and COD concentration = 52 mg/l.

	pH (unit)	Turbidity (%)	Suspended solids (%)	COD (%)
Accuracy (manufacturer's specification)	0.12	1	5	1.5
Linearity and / or calibration equation	0.02	5	5	6.5
Repeatability	0.01	3.1	2	0.01
Resolution	0.01	0.3	0.3	0.01
Stability	0.01	0.3	0.3	0.01
Temperature / environmental conditions	0.09	0.01	0.01	
Combined standard uncertainty	0.15	6	7.5	7
Expanded uncertainty (*k*=2)	0.30	12	15	14

4.2 Laboratory samples

The uncertainties of the laboratory analyses (given by the laboratories) are given in Appendix A and Table 2. According to reference [4], the uncertainty given for a chemical analysis of an environmental sample should include a) repeatability within laboratory analyses b) laboratory bias or reproducibility between laboratories and c) uncertainty of the analysis method.

To estimate the uncertainty of the analysis, Metropolilab applies validation material for random and systematic errors, certified reference materials and own control samples. The laboratory participates in proficiency tests and monitors the deviation of duplicate samples.

In the monitoring consultant laboratory, the within-laboratory reproducibility is estimated with control samples (X cards) and by carrying out duplicate analysis with real samples. Laboratory bias is estimated with help of proficiency tests, certified reference materials, and in some cases recovery tests.

Both laboratories give their expanded uncertainty with a coverage factor *k* = 2.

Uncertainty due to sampling was estimated based on the deviation between samples [2]. The standard deviation of the measurement results is assumed to be composed of the deviation caused by the analysis and the sampling,

$$s_{measurement} = \sqrt{s_{analysis}^2 + s_{sampling}^2} \tag{4}$$

from which the deviation due to sampling can be calculated as

$$s_{sampling} = \sqrt{s^2_{measurement} - s^2_{analysis}} \quad (5)$$

In the estimation of the deviations, the double split design method presented in [2] was applied. The deviation in analysis, $s_{analysis}$ is estimated using average deviation of the duplicate samples taken by EHP and analyzed by Metropolilab. The deviation in measurements, $s_{measurement}$ is estimated by comparing the mean of the Metropolilab results to the result of the monitoring consulting laboratory, and by calculating their average deviation. The uncertainty estimation for turbidity is calculated based on the duplicate samples of EHP only, as the monitoring consulting laboratory did not carry out turbidity analyses. Collaborative sampling and analysis was carried out seven times, in addition EHP carried out two additional samplings.

The uncertainty estimations for laboratory measurements are presented in Table 2. The uncertainties given in the result reports of the laboratories may be larger than the values given in Table 2, for example due to challenging sample matrix.

Table 2. Uncertainty of laboratory measurements. The pH sampling uncertainty is estimated for an average sample with pH = 6.0.

	pH (unit) Metropolilab/mon. cons. Lab	Turbidity (%) Metropolilab	Suspended solids(%) Metropolilab/ mon. cons. lab	COD (%) Metropolilab/ mon. cons. Lab
Laboratory analysis	0,1 / 0,125	5	5 / 11,5	5 /10
Sampling	0,07	7,9	41,5	9
Combined standard uncertainty	0,12/0,14	9,3	41,8/43,0	11,0/14,0
Expanded uncertainty (k=2)	0,24/0,28	19	84/86	22/28

As the turbidity analyses were carried out only at Metropolilab, the uncertainty estimation for turbidity sampling may include also contributions from the internal repeatability within the laboratory. The uncertainty estimate may thus be somewhat overestimated.

It can be seen in Table 2 that in this study the sampling is more significant uncertainty contribution for the suspended solids measurement than the laboratory analysis. For turbidity and COD measurements, the uncertainties due to sampling and laboratory analyses are of the same order of magnitude. For pH measurement, sampling contributes to the combined uncertainty, but the analysis is the most important contribution.

5. Comparison of measurement uncertainties of online and laboratory measurements

The reality of the uncertainty estimations above is estimated by comparing the online measurement results with the laboratory results, and taking into account the measurement uncertainties of both measurement methods. The comparisons are presented in Figures 6…8. As the laboratory measurement uncertainties, we have used the square sum of analysis uncertainties given by Metropolilab and the estimated sampling uncertainties given in Table 2. The uncertainty presented in the figures is the expanded uncertainty (*k*=2), which corresponds to approximately 95% confidence interval in Gaussian distribution. The figure for COD measurement was not included, because only raw data was available from the COD measurement.

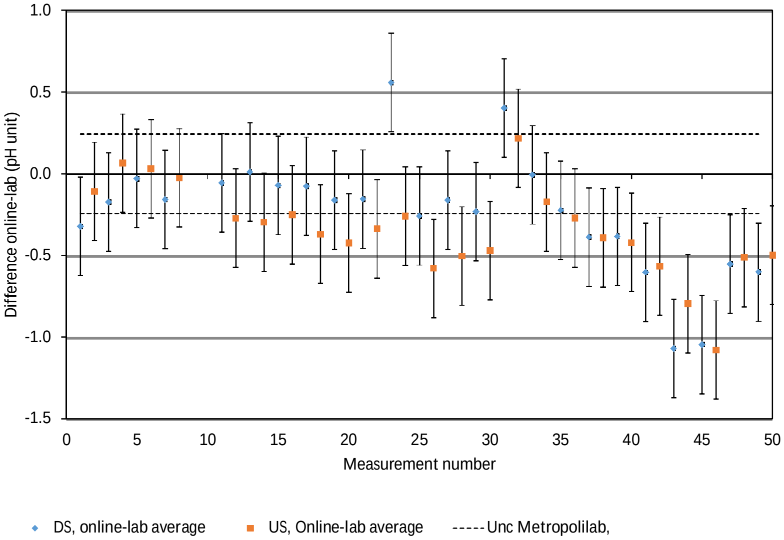

Figure 6. pH measurement. The vertical axis corresponds to the difference between online and laboratory measurements. The uncertainty bars represent the expanded uncertainty of the online measurement (*k*=2), and the dashed lines the expanded uncertainty of Metropolilab analysis and uncertainty due to sampling.

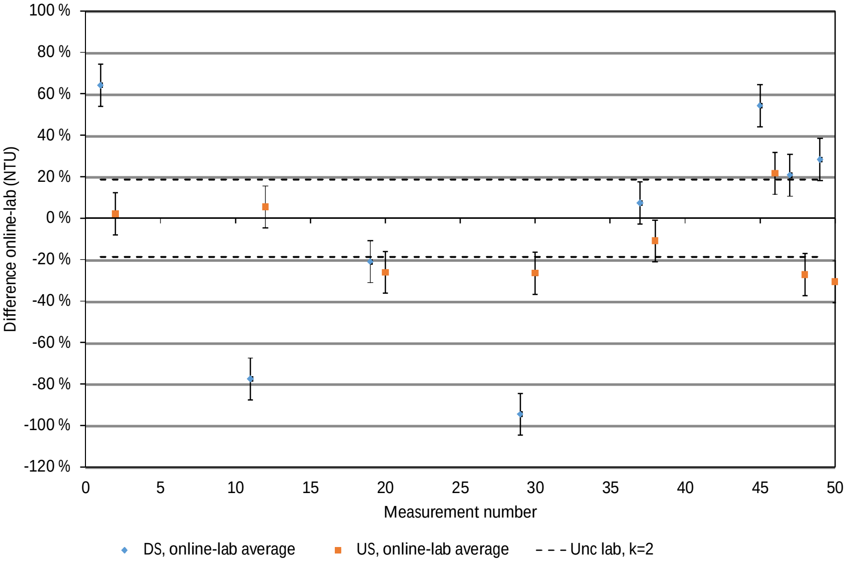

Figure 7. Turbidity measurement. The vertical axis corresponds to the difference between online and laboratory measurements.

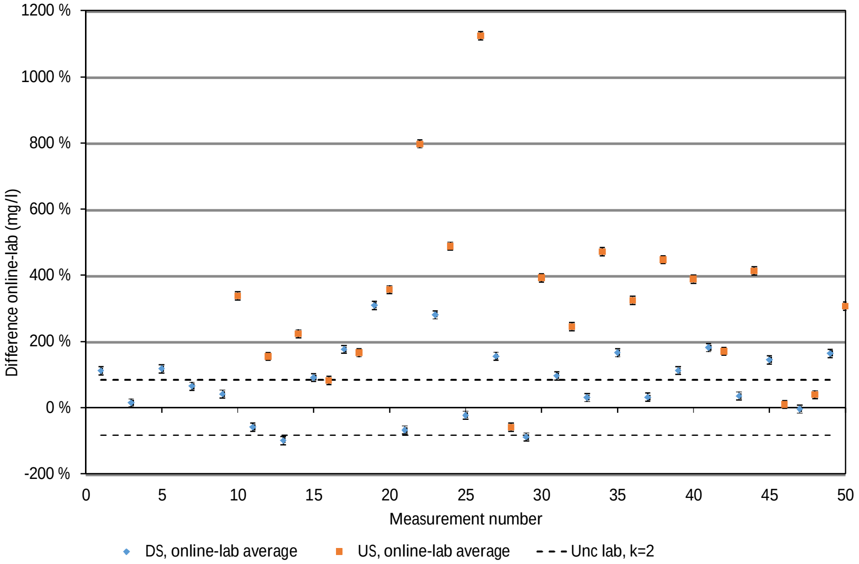

Figure 8. Suspended solids measurement. The vertical axis corresponds to the difference between online and laboratory measurements. The uncertainty bars represent the expanded uncertainty of the online measurement (*k*=2), and the dashed lines the expanded uncertainty of Metropolilab analysis and uncertainty due to sampling.

It can be seen from the comparison that the online and laboratory measurement results mostly agree within their estimated uncertainties in pH and turbidity measurements. This indicates that all the relevant uncertainty components seem to be taken into account in a correct magnitude. All results are not in agreement, and one should thus find out whether the discrepancy is due to erroneous measurements, is the measurement uncertainty underestimated, or whether there is an additional factor in the particular measurement situation that increases the measurement uncertainty. In suspended solids measurement, there is more deviation. It would be preferably to calibrate the turbidity and suspended solids sensors in the field or for the particular measurement, in order to better take into account the measurement situation, such as the particle size and shape of the solids [5]. The manufacturer also recommends an adapted calibration for suspended solids sensor.

6. Conclusions

In this report the uncertainty of online pH, turbidity, suspended solids and COD measurements was estimated, as well as the uncertainty of laboratory sampling based on samples taken by two laboratories. The uncertainty estimation for online sensors is based in the manufacturers' specifications, if available, and experimental results. The uncertainty estimates for online measurements are slightly larger than those for laboratory analyses (analysis part only), but in the laboratory sampling significant deviation may exist, which in turn increases the overall measurement uncertainty larger than in online measurements. It should also be noted that one can repeat online measurements more frequently than laboratory sampling and analysis.

In this study, the uncertainty due to laboratory sampling is the most significant uncertainty contribution for suspended solids. For turbidity and COD, the sampling uncertainty is of the same order of magnitude than the uncertainty of analysis. In pH measurement the uncertainty of analysis was estimated larger than the sampling uncertainty, but the sampling increases the overall uncertainty. The obtained measurement results indicate also that all significant uncertainty components are not known – especially for suspended solids and turbidity measurements, because the deviation between the measurement methods is significantly larger than the estimated uncertainty. In the case of suspended solids, it may be impossible to carry out sampling in flowing water, as the water matrix is changing all the time.

References

[1] Evaluation of measurement data – Guide to the expression of uncertainty in measurement (JCGM 100:2008, GUM 1995 with minor corrections).

[2] Nordtest TR 604 Uncertainty from Sampling – a Nordtest Handbook for Sampling Planners on Sampling Quality Assurance and Uncertainty Estimation, 2007.

[3] Eurachem/Citac, Quantifying Uncertainty in Analytical Measurement, 3rd edition, 2012.

[4] Nordtest TR 537 Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, edition 3.1.2012.

[5] E-mail conversation with Ilkka Dahlström, Risto Hiljanen and Lea Nikupeteri, March 2016.

Appendix A: Sampling schema for Iso-Kerusneva

1. Sampling of monitoring consulting laboratory

Water samples are taken in the period 1.4.–31.12. at two weeks intervals, in the period 1.1.–31.3. at one month interval, in spring flood period (mainly 15.4.–15.5.) at one week interval. Extensive set of analyses is carried out in winter and in spring flood period at every second sampling time, and in summer (15.5.–15.9.) every third sampling time. Otherwise, a concise set of analyses is carried out. On yearly level, samples from both upstreams and downstreams of an overland flow area are taken about 50 times. Extensive analysis set includes: suspended solids, CODMn, total P, total N, pH, NH4-N, PO4-P(filt.), Fe. Concise analysis set includes: suspended solids, CODMn, total P, total N, pH.

Table A1. Uncertainties of laboratory analyses given by monitoring consulting laboratory

	Detection limit	**Range**	**Uncertainty**	**Range**	**Uncertainty**
pH (A)			± 0.25 units		
turbidity (A)	0.05 FTU	<2 FTU	± 30%	>2 FTU	± 20%
suspended solids, GF/C filter (A)	2.0 mg/l	>2 mg/l	± 23%		
CODMn (A)	0.5 mgO2/l	>0.5 mgO2/l	± 20%		

A = accredited method

2. Sampling schema of EHP-Tekniikka, uncertainty of sampling

A one-year test period begins in March–April 2015. The monitoring consulting laboratory carries out sampling according to the sampling plan. If possible, the certified sampler of EHP-Tekniikka takes collaborative samples. The sampler of EHP-Tekniikka takes during the test period in total 8–10 collaborative samples at both measurement stations (if possible, in different content levels and at different seasons, two parallel samples per sampling time), in order to obtain sufficient amount of data for statistical analysis. The samples taken by EHP-Tekniikka are delivered within 24 hours to the contract laboratory (Metropolilab). Appropriate care is taken in the transport and storage. The sampling equipment needed is purchased from the contract laboratory. The samples are analyzed for:

- pH
- suspended solids
- turbidity
- CODMn

Table A2. Uncertainties of laboratory analyses given by Metropolilab

	Detection limit	**Range**	**Uncertainty**
pH (A)			± 0.2 units
turbidity (A)	0.1 FTU	> 0.1 FTU	± 10%
suspended solids, GF/C filter (A)	1 mg/l	> 1 mg/l	± 10%
CODMn (A)	0.5 mgO2/l	> 0.5 mgO2/l	± 10%

A= accredited method

3. Measurement uncertainty of online measurements

The measurement uncertainty of the online sensors will be estimated by setting the measurement interval to one minute for a ten-minute period. It can be assumed that the quality and flow of the water do not change significantly during a such period. The corresponding measurement sequences are repeated 8–10 times at as many different content levels as possible.

Table A3. Sensors used in online measurements

Parameter	Sensor	Range	Resolution	Accuracy
Temperature	Ponsel	0–50 ˚C	0.01 ˚C	± 0.5 ˚C
pH	Ponsel	0–14	0.01 pH	± 0.1 pH
Suspended solids	Hach Lange Solitax	0.001–50 g/l		< 5%
Turbidity	McVan Analite NEP9000	0–100NTU	± 0.2 NTU	± 1%
COD	Trios ProPS	0–5000 mg/l		

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Nimeke	**Veden laadun jatkuvatoimisen mittaamisen ja manuaalisen näytteenoton kokonaisepävarmuudet**
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Tiivistelmä	Tutkimuksessa verrattiin veden laadun mittauksiin liittyvää mittausepävarmuutta jatkuvatoimisissa (online) mittauksissa vastaavan laboratorioanalyysin ja näytteenoton kokonaisepävarmuuteen. Mitattavat suureet olivat pH, sameus, kiintoaine ja COD. Mittaustuloksia ja niiden arvioitua epävarmuutta verrattiin kahden akkreditoidun analyysilaboratorion ilmoittamiin analyysin epävarmuuksiin. Tutkimuksessa arvioitiin myös laboratorioanalyysien näytteenottoon liittyvää epävarmuutta. Jatkuvatoimisten mittausten epävarmuusarvio laadittiin oppaan "Evaluation of measurement data – Guide to the expression of uncertainty in measurement (JCGM 100:2008, GUM 1995 with minor corrections)" mukaisesti. Näytteenoton epävarmuutta arvioitiin oppaan "Nordtest TR 604 Uncertainty from Sampling" mukaisesti.
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