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PRACTITIONER'S REPORT

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Abstract Turbidity is an essential parameter for describing water quality by direct and indirect impacts on fish, invertebrates and aquatic plants. Currently, environmental monitoring measurements are carried out with appropriate quality by accredited testing laboratories, but there is also a need for employing the third sector, i.e. citizens and voluntaries in environmental monitoring. A device called "Secchi3000" was developed as a low-cost and simple-to-operate tool so that water quality measurements can also be carried out by non-experts and citizens. The measurement using the new device is simple: The user fills the container with water and places the measurement structure in the container. The user takes a photograph with the camera on a mobile phone through a hole in the lid. The software sends the photograph to a server, which analyses the photographs automatically. Finally, the results are returned to the user's mobile phone and stored on a database for further analysis. In this study, the measuring system for turbidity measurements in natural waters was validated. Validation included an estimation of the limit of quantification, investigations of the influence of water colour and illumination conditions on turbidity measurement values and the estimation of measurement uncertainty. A comparison of turbidity results obtained with the new device and laboratory instrument in natural water samples was carried out, and turbidity values obtained with different mobile phones were compared. According to the validation results, the new device was appropriate for the measurement of turbidity lower than 7 FNU (Formazine Nephelometric Unit). An algorithm applied for present turbidity calculations is not fully suitable for higher turbidities. For potential routine use, this is not a major problem, since most Finnish natural waters have turbidities lower than 7 FNU. For official monitoring purposes, the limit of the quantification needs to be lower than presently achieved (1.7 FNU). Although the present configuration of the Secchi3000 device is not yet fully suitable for official environmental monitoring, it will already enable the involvement of the third sector in water quality monitoring, and in this way, citizens' observations could then serve at least as supplementary information for reporting and surveys.

Keywords Turbidity · Field measurement · Water quality monitoring · Citizen-based monitoring · Validation

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Introduction

Water resources management carried out under the European Union's (EU) water policy and national legislation on water resource management require knowledge of the chemical and ecological state of waters and measures for achieving good water status [1, 2]. Turbidity is an essential parameter for describing water quality. Turbidity determinations are carried out extensively in Finnish surface waters. In 2012, total of over 30000 turbidity measurements were performed mostly in Finnish lake, pond, river, and brackish waters. Particles and suspended solids in the water cause turbidity. Turbidity is measured as a quantity of water's optical property based on light scattering in sample water. The turbidity value in the sample is dependent on the concentration of particles or suspended solids. In natural waters, turbidity may be caused by clay, silt or organic matter such as algae [3]. There are numerous direct and indirect impacts of silt, suspended sediments and associated turbidity. These include changes in water quality, reduced light penetration, diminished recreational values and aesthetics, as well as direct and indirect impacts on fish, invertebrates and aquatic plants [4–6]. In some cases, e.g. in clayey arable watershed areas, the load of phosphorus and suspended solids can be estimated by turbidity values [7].

According to the current guidelines, only information produced by a standardised method of measurement in an accredited laboratory from samples taken by certified sampling personnel may be used in national and international water status reporting (EU, Helsinki Commission Helcom, Organisation for Economic Cooperation and Development OECD). These requirements ensure the usability of environmental information [8].

On the other hand, in monitoring measurements, there is a global trend away from standard-based requirements and towards performance-based requirements. This means that not only standardised methods (e.g. from International Organization for Standardization) are accepted for monitoring purposes. Performance-based requirements also allow the use of methods that are validated and proved to produce reliable measurement results for a particular purpose [9, 10].

At the same time, pressures to streamline monitoring have increased in the state administration, mainly for economic reasons. The Ministry of the Environment in Finland drew up a monitoring strategy for the period up to 2020 and set a target that included the utilisation of new technologies in the collection of monitoring data. While online measurements, remote sensing and modelling are considered the preferred methods, the role of citizen-based monitoring should also be expanded [10].

A large number of the testing laboratories worldwide follow the international standard method ISO 7027 in their turbidity measurements [11]. Turbidity is measured nephelometrically using instrument calibrated with formazine standard solutions, and the turbidity of the tested water sample is expressed in formazine nephelometric units (FNU). From the metrological point of view, the accuracy of the turbidity measurements performed by laboratory instruments is presently sufficient for environmental monitoring purposes. However, the possibilities of citizen-based monitoring in the monitoring of the state of surface waters must be identified and utilised. One of the biggest obstacles to that is the expensive equipment that is required for most monitoring tasks. Therefore, the development of low-cost and simple-to-operate monitoring equipment is of great interest.

A device called the Secchi3000 is a low-cost and simple-to-operate tool for water quality measurements, not to replace metrologically appropriate laboratory measurements, but to complement them. In this study, the Secchi3000 measuring system was validated for turbidity measurements in Finnish natural waters.

Measurement principle

The Secchi3000 measurement principle is based on the comparison of intensities of light measured over black, white and grey target areas at two depths. The basic assumption is that the target areas at both depths have the same downwelling irradiance at the surface. This is achieved by placing the transparent side of the container towards the sun or the brightest part of the sky. Thus, the differences in the apparent brightness of the target areas when viewed from above are caused by the optical properties (scattering and absorption by particles and dissolved substances) of the water column between the target levels. By using the black and white targets, it is possible to measure the attenuation caused by water. The grey targets are used for reducing the effects of the difference of exposure properties of different cameras or illumination conditions (sunny or cloudy).

Since digital cameras give values for three bands (red, green, blue), it is possible to measure the attenuation at these three wavelength regions. Using empirical equations, it is possible to calculate from the attenuation values different physical or chemical parameters describing the water quality. The equation for turbidity measurement has been calibrated using results obtained with laboratory measurements. Laboratory measurement for turbidity is based on scattering of light. The set-up of the device and the detection of target positions of white, grey and black areas are described in more detail in Ref. [12].

The Secchi3000 measuring system is composed of three parts (Fig. 1):

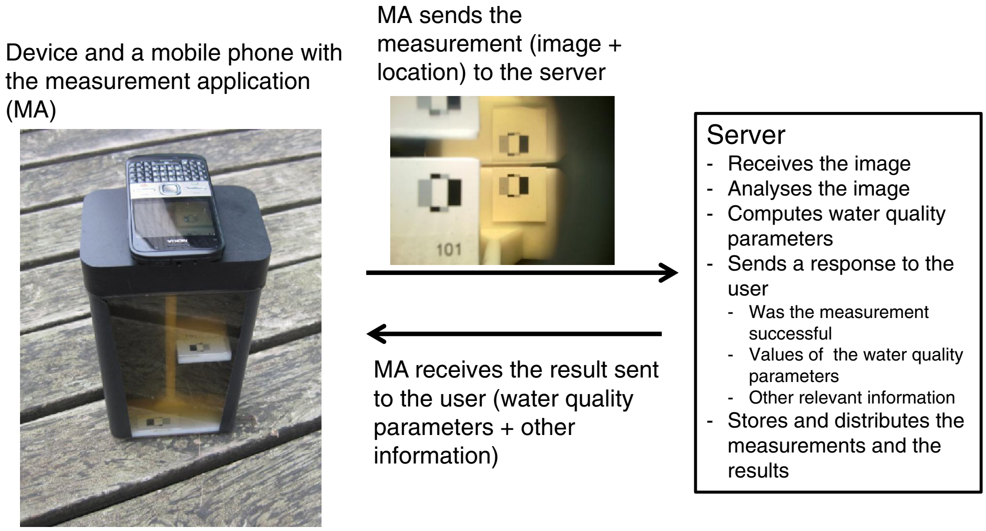

Fig. 1 Secchi3000 measurement system

1. *Device* This includes a plastic container that has one side transparent for light, a measurement structure that goes into the container, and a lid with a hole. The measurement structure has white, black and grey target areas at two depths (10 cm vertical distances between the target areas). The user fills the container with water from a lake, river or sea and places the measurement structure in the container.
2. *Mobile phone with a measurement application (MA)* The software installed on the phone controls the camera and allows the user to take a measurement photograph and input other observations. The software sends the photograph with other information (e.g. GPS position) to the server.
3. *Server* The server receives and analyses the measurement photographs automatically with an algorithm, which finds the target areas from the picture and computes parameters of water quality. Finally, the results are sent back to the user's mobile phone and stored in a database.

Materials, methods and validation tests

Secchi3000 was validated for turbidity measurements in Finnish natural waters. Validation included an estimation of the limit of quantification (LOQ), investigations of the influence of water colour and illumination conditions on turbidity values, and the estimation of measurement uncertainty. In addition, turbidity values obtained with different mobile phones were compared. A comparison of turbidity results obtained with the Secchi3000 and the laboratory instrument (2100 AN IS, HACH, Loveland, CO, USA) based on nephelometric measurement in natural water samples was carried out. The laboratory instrument measures the scattered light using the angle of the detector of 90 degrees from incident light. The instrument was calibrated with StabCal® formazine turbidity standards (HACH, Loveland, CO, USA), and the turbidity is expressed in FNU [11, 13]. Laboratory instrument was regarded as reference in these experiments.

The samples used for validation were natural water (river, lake, pond and brackish waters). In addition, turbidity reference samples were prepared and analysed. The formazine turbidity standard with certified value of 4000 FNU was used for the preparation of diluted reference suspensions. The colour of the water samples was determined based on the hexachloroplatinate scale according to the standard method EN ISO 7887 [14]. Measurement uncertainty was estimated according to the Nordtest approach [15].

Analyses were performed in the laboratory of the Finnish Environment Institute (SYKE), which is an accredited testing and calibration laboratory according to the requirements for the standard EN ISO/IEC 17025 [16]. The accredited laboratory method is based on the standard method ISO 7027 [11]. Estimated expanded measurement uncertainty ($k = 2$) for laboratory's reference method is 0.2 FNU at turbidity <1.0 FNU and 20 % at turbidity ≥1.0 FNU. The standard method ISO 7027 Annex A gives interlaboratory collaborative trial results, where reproducibility standard deviation (s_R) of analysis of the formazine suspensions equals to 0.09 FNU and bias 0.025 FNU at a turbidity of 0.8 FNU. At a higher turbidity level (3.2 FNU), the s_R and bias components are 6.5 and 3.2 %, respectively [11].

Validation tests were carried out using Nokia E7 mobile phone with Symbian operating system and a camera with a resolution of 3264 × 2448 pixels. However, in the Symbian version of the measurement application (MA), the camera only operated with VGA resolution (640 × 480 pixels). The measurement application used for validation measurements was Levävahti pro version 1.01.

Validation results

Limit of quantification

Limit of quantification is a concentration below which the analytical method cannot operate with an acceptable precision [17]. Thus, LOQ is the lowest measured value that should be reported to customers. Typically, LOQ is calculated as a multiple of the standard deviation of the measurement at low concentration level. Standard deviation of the turbidity measurement was estimated from the difference of the 21 result pairs of the natural water replicate sample analyses at turbidity values below 1 FNU. For analysis, the sample was poured into the container, and the measurement structure was placed in the container and photographed. For replicate analysis, the measurement structure was removed from the sample and placed again into the container and the second photograph was recorded. The standard deviation was calculated using Eqs. 1–3 [15] and the limit of quantification of turbidity measurement (L_T) using Eq. 4.

Denoting the pairs of turbidity values measured in the natural water samples i with $T_{i,1}$ and $T_{i,2}$, their absolute difference is considered D_i (Eq. 1).

$$D_i = |T_{i,1} - T_{i,2}|. \quad (1)$$

The average difference, D_{mean}, is given in Eq. 2

$$D_{mean} = \frac{\sum D_i}{M} \quad (2)$$

where M denotes the number of sample pairs ($M = 21$). The standard deviation is expressed as

$$s = D_{mean}/1.128 \quad (3)$$

where the factor 1.128 accounts for converting the mean difference to the standard deviation when two replicates are used for D_i determination [18].

$$L_T = 10\,s \quad (4)$$

L_T was estimated to be 1.7 FNU.

Comparison of results of Secchi3000 and HACH 2100 AN IS laboratory instrument

A total of 107 natural water samples were analysed using both the Secchi3000 and the laboratory instrument. The Secchi3000 measurements were mainly carried out in the laboratory facilities, performing measurement in an open window, but measurements outside the laboratory facilities were also carried out. Turbidities of the samples were between 0.24 FNU and 67.3 FNU. The results show that

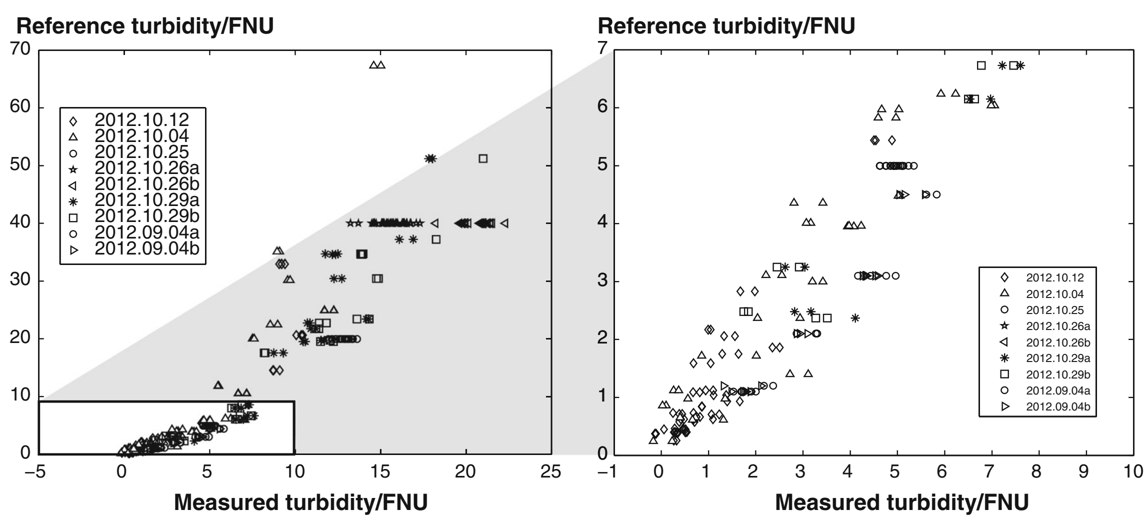

Fig. 2 Comparison of Secchi3000 turbidity results with laboratory reference method (ISO 7027, HACH 2100 AN IS). *x*-axis represents the turbidity obtained by Secchi3000. *y*-axis represents turbidity obtained from same sample by laboratory instrument. In the left figure are all the results, and in the right figure values below 10 FNU are magnified. Correlation coefficient R^2 for full range is 0.86, and slope of regression line is 2.13. For range below 7 FNU, the R^2 and the slope are 0.88 and 0.93, respectively. The measurement date is described as yyyy. mm. dd in the legend

the negative bias of the measurement increases when turbidity exceeds 7 FNU (Fig. 2). Similarly, the correlation of the turbidity values of the Secchi3000 and the laboratory instrument will become nonlinear. The used algorithm applied for turbidity calculations is not fully suitable for turbidity values higher than 7 FNU. In these cases, the attenuation of light in the measured water is strong and small differences in the measured light intensities of the black, white and grey target areas result in large differences between turbidities measured with the Secchi3000 and the laboratory instrument. The measurement with the laboratory instrument is based on light scattering, and this could be one explanation for the difference.

Effect of sample colour

Natural waters are mostly coloured yellowish brown by certain components of iron, clay particles, or by humic matter. This colour can be reproduced by an appropriate solution of hexachloroplatinate. The colour of a given sample is determined according to standard method EN ISO 7887 by visual comparison with a series of such solutions at different concentrations and expressed as the platinum concentration (later "mg/l Pt") of the matching solution [14]. The colour of the natural water samples investigated ($n = 36$) were determined, and only the samples with turbidities below 7 FNU were selected for testing, due to restrictions of the algorithm for higher turbidity values. In the samples tested, the colour was between 5 mg/l and 500 mg/l Pt. The Secchi3000 was observed to be robust for potential interferences caused by water colour, since the colour of the samples did not result in any systematic error in the turbidity results of the Secchi3000.

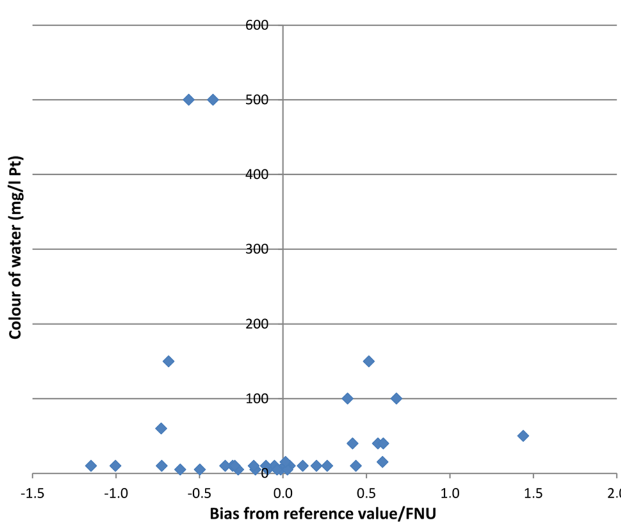

Fig. 3 Bias of the Secchi3000 turbidity from the laboratory measurement (ISO 7027; HACH 2100 AN IS) result as a function of colour of the sample

The differences between Secchi3000 and HACH 2100 AN IS turbidity measurements are distributed evenly between ±1.5 FNU (Fig. 3).

Effect of illumination conditions

First, possible systematic errors due to different illumination conditions were investigated by measuring natural water samples with turbidities between 2.4 FNU and 51 FNU ($n = 18$), both indoors in room lightning and outdoors and additionally using the laboratory's reference method. The results obtained indoors and outdoors by Secchi3000 were consistent with turbidity values lower than 10 FNU, and they were also in accordance with the values given by the laboratory reference method (Fig. 4). For values higher than 10 FNU, a similar trend was observed as for synthetic samples described below: measurement results were systematically higher for the samples measured indoors compared with outdoors. This may be due to the unsuitability of the measurement algorithm to deal with higher turbidities.

In addition to the natural water samples, the measurements were also carried out with standard reference samples (20 FNU; $n = 20$) with the Secchi3000 outdoors in sunlight, indoors in room lighting and indoors, while the sun was shining through the window onto the sample water. Two-tailed F tests (95 % significance level) were applied to each pair of the data set, to evaluate whether the variances of the data sets are equal or not. Variances were found to be equal, and therefore, a two-tailed t test for equal variances (95 % significance level) was applied for testing the difference of the averages of the data sets. According to the t test, a significant difference was found between the average values obtained from the same sample under different illumination conditions. Measured turbidity was higher for the samples analysed indoor in room light than samples analysed outdoors. On the other hand, the difference between the results measured outdoors and indoors in sunlight was only 1 FNU, and the critical t test value was exceeded due to the small variability in replicate measurements within the sample batches. Although the turbidity of the standard reference (20 FNU) is above the linear operation range of the device, this test still indicates that the device is not very sensitive to changes in the illumination.

Comparison of different mobile phones

A field test was carried out for the Secchi3000 in the coastal area of southern Finland near the town of Inkoo consisting of six monitoring stations, where the measurements of water quality were performed. In all locations, four to eight measurements using the Secchi3000 were

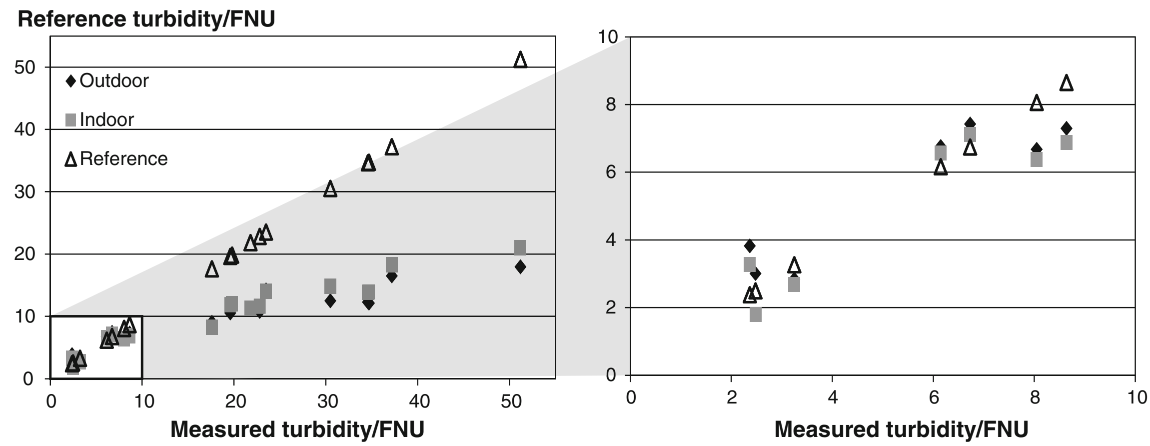

Fig. 4 Effect of lighting conditions on turbidity values obtained by Secchi3000 in natural waters. Laboratory method (ISO 7027; HACH 2100 AN IS) was applied as a reference method. In the left figure are all the results, and in the right figure values below 10 FNU are magnified. Note that the graphs have the different axes

performed using two different mobile phones (Nokia N500 and Nokia E5). Simultaneously certified sampling personnel form Uusimaa ELY Centre (Centre for Economic Development, Transport and the Environment) collected the water samples for laboratory analysis. Samples were transported to the laboratory of the Finnish Environment Institute. The results obtained with two different mobile phones were consistent, but the bias to the measurement results obtained with laboratory instrument was observed (Fig. 5). The reason for this was not further studied, but the laboratory measurements were carried out approximately 24 h later than the Secchi3000 measurements. Water samples are not always stable, which means that the content of suspended solids depends on the storage time, means of transportation, pH value and other circumstances [19]. Standard method ISO 7027 states that analysis should be performed within 24 h [11], but the character of the samples will always change over time due to physical and biological processes that occur during storage. The coastal water samples were not assumed to be particularly unstable, but during the summer time, water usually contains algae that may flocculate or sediment over time and will change the original sample characteristics.

In addition to the field test, the different mobile phones were also tested by analysing 3.0 FNU turbidity standard reference samples using two different mobile phones (Nokia E7 and Nokia Lumia 920). The measurement applications for the E7 (MA version 1.01; operating system Symbian) and the Lumia 920 (MA version 1.0.0.0; operating system Windows 8) were different, but they should process the images similarly. The Nokia E7 uses the video recording feature of the mobile phone and saves one frame as the photograph with a VGA resolution of 480 × 640 pixels. The Lumia phone saves the photograph using its camera with a resolution of 3552 × 2000 pixels.

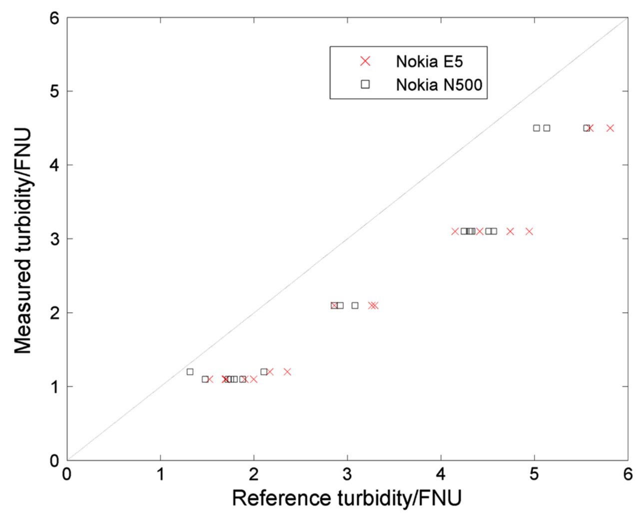

Fig. 5 Turbidities in natural water obtained by Secchi3000 field tests, when photographs were taken using two different mobile phones (Nokia E5 and Nokia N500). Reference turbidities were measured with laboratory instrument (HACH 2100 AN IS)

A total of 20 samples were measured using the Nokia E7 and 32 samples using the Nokia Lumia 920. In addition to that, turbidity was measured using the laboratory instrument ($n = 6$). According to the results, turbidity values obtained with the E7 were closer to the average of the laboratory measurement results and turbidities obtained with the Lumia 920 were systematically lower than values obtained with the E7 (Fig. 6). However, the difference between the turbidity mean values obtained using the different phones was only 0.6 FNU.

Measurement uncertainty

Measurement uncertainty was estimated according to the Nordtest approach, where combined measurement

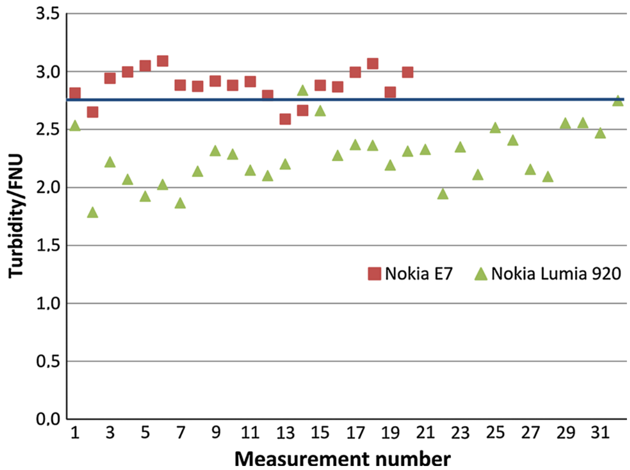

Fig. 6 Turbidity values of the standard reference samples measured with Secchi3000, when photographs were taken using two different mobile phones (Nokia E7 and Nokia Lumia 920). *Thick line* describes the average of the laboratory turbidity measurements

Table 1 Summary of MUkit uncertainty calculations for Secchi3000 turbidity measurement in natural water

Source of uncertainty	Low range (1.7–4.0 FNU)	High range (4.0–7.0 FNU)
Within-laboratory reproducibility		
Standard deviation from control samples	0.14 FNU	3.8 %
Standard deviation from routine sample replicates	0.28 FNU	4.1 %
u_{Rw}	0.31 FNU	5.6 %
Method and laboratory bias		
Bias	−0.12 FNU	−0.8 %
s_b	0.14 FNU	3.8 %
u_{cref}	0.06 FNU	1.2 %
u_b	0.13 FNU	1.6 %
u_c	0.34 FNU	5.8 %
U ($k = 2$)	0.7 FNU	12 %

For high range, uncertainty is expressed as absolute FNU values, while for high range as relative FNU values (%)

s_b = the standard deviation of the turbidity standard analysis results applied for bias estimate

u_{cref} = the uncertainty of the reference value of the turbidity standard

uncertainty is broken down into two main components—the within-laboratory reproducibility u_{Rw} and the uncertainty due to possible bias u_b [15]. The measurement range was divided into two sub-ranges: a low range from 1.7 to <4.0 FNU and a high range from 4.0 to 7.0 FNU. Higher turbidity values were ignored due to restrictions to the present algorithm to measure these values. The MUkit (Measurement Uncertainty Kit) software package was employed for calculations [20, 21], and the equations used for calculation of measurement uncertainty are presented in more detail in Table 1 in [20].

In the low range the u_{Rw} was estimated from replicate analyses of the routine samples (number of sample pairs $M = 20$) with turbidities appropriate for the low level. Additionally, standard deviation of the turbidity standard reference samples (3.0 FNU, $n = 20$) was included in the u_{Rw}. u_b was estimated using the analysis results of turbidity standard reference samples (3.0 FNU). Expanded measurement uncertainty ($k = 2$) was estimated to be 0.7 FNU in the low range.

In the high range the u_{Rw} was estimated from replicate analyses of the routine samples ($M = 21$) with turbidities appropriate for the high level. Additionally, standard deviation of the turbidity standard reference samples (5.0 FNU, $n = 20$) was included in the u_{Rw}. u_b was estimated using the analysis results of turbidity standard reference samples (5.0 FNU). Expanded measurement uncertainty ($k = 2$) was estimated to be 12 % for the high range. A summary of the MUkit uncertainty calculations is presented in Table 1 and the file for full calculations of measurement uncertainty (MU_Secchi3000.muk2) is available from the ENVICAL SYKE website [21]. The file can be viewed and modified using MUkit (Measurement Uncertainty kit) software version 1.9.5.0 or higher, which is also freely available from the ENVICAL SYKE website [21].

u_b contains the term u_{cref} (see Table 1 in [20]), which describes the uncertainty of the reference value of the turbidity standard. This was calculated from the uncertainty given in the certificate of the standard as well as from uncertainties arising from serial dilutions of the standard solution. The calculation of u_{cref} was carried out using the GUM Workbench Pro software [22], where measurement uncertainty estimation is based on the bottom-up principle with the detailed mathematical model described in GUM [23] and QUAM-guide [24], for example. The measurement model for the calculation of the turbidity standard values and associated uncertainties are shown in Electronic Supplementary Material.

Discussion

The new monitoring system was validated for field water turbidity measurements of natural waters, and according to the results, it was appropriate for the measurement of turbidity lower than 7 FNU. The algorithm applied for the current turbidity calculations is not fully suitable for higher turbidities. For potential routine use this is not a major problem, since turbidities in Finnish natural waters are usually low. In May–September 2012, an average of 89 % of the measured surface water turbidity values were below

7 FNU in Finnish lake waters ($n = 2770$) and 57 % in rivers ($n = 4787$). Another problem is that approximately 40 % of the results in lake waters and 20 % in river waters were even below the LOQ (1.7 FNU) of the Secchi3000. Therefore, further development of the Secchi3000 is needed, particularly for achieving a lower limit of quantification. One potential method for this is to increase the path length of the device. With a longer path length the attenuation will increase and samples with lower turbidities can cause enough attenuation for the measurement.

The achieved expanded (at $k = 2$ level) measurement uncertainties may be underestimated due to the low amount of data used in calculations. When routine laboratories estimate the measurement uncertainty based on a quality control data, to achieve a representative basis for the uncertainty calculations and to reflect any such variation, the number of results should ideally be more than 50 and cover a time period of approximately one year, but the need differs from method to method [15]. For measurement of turbidity with the Secchi3000, probably 50–100 measurement results covering a time period of approximately one summer (4 months) would give more reliable uncertainty estimates. During the validation tests the amount of data available is usually restricted. In this validation study, the number of tests was lower and the time scale was much shorter. The measurement uncertainty needs to be re-estimated with more comprehensive data.

SYKE has recently published quality recommendations for laboratories producing and delivering environmental monitoring data for registers of water quality in Finland [25]. The recommended LOQ for water turbidity measurement is 0.5 FNU, while the recommendation for expanded measurement uncertainty ($k = 2$) is 0.2 FNU for the range of 0.5–1.0 FNU and 20 % for the range of >1 FNU.

The present estimate of measurement uncertainty for the Secchi3000 is higher than in the recommended quality criteria for official monitoring methods at turbidity values below 3.5 FNU. With higher turbidities (up to 7.0 FNU), the quality criterion for expanded measurement uncertainty is fulfilled. For official monitoring purposes, the LOQ needs to be less than one-third than presently achieved.

As the global trend is from standard-based towards performance-based requirements, new innovations such as those presented in this article may also achieve the status of an officially approved monitoring method. In addition, the authorities must ensure that such information is accepted for reporting. Before achieving this status, the system has to prove it is able to produce reliable measurement results, particularly to fulfil the set quality criteria for measurement uncertainty and limit of quantification. The method should preferably be accredited, as well as have established internal and external quality assurance protocols, before information for water quality monitoring purposes can be produced. Therefore, the next goal is to lower the limit of quantification and measurement uncertainty to be able to utilise the measuring system for official monitoring purposes.

Although the present configuration of the Secchi3000 system is not yet fully suitable for official monitoring, it will already enable the involvement of the third sector in the monitoring of water quality, and in this way citizens' observations could serve at least as supplementary information for reporting and surveys, which was actually the original purpose of the Secchi3000 from the beginning.

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