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APPLICATION OF ONLINE AND LABORATORY METHODS FOR THE INVESTIGATION OF SURFACE WATERS

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Pollutions in surface waters run down quickly, so the pollution waves cannot be detected by traditional point sampling. Remote controlled online monitoring methods can make the tracking of pollutants possible. These solutions ensure that we can immediately access up-to-date information. The goal of our paper was to compare online monitoring and laboratory measurement techniques. During our work, we investigated the chemical and physical properties of the Séd creek in Veszprém with two different online monitoring systems. Furthermore, we made parallel laboratory measurements of samples taken weekly to evaluate the measurement results of online methods. We discuss the difficulties of installation and operation of online systems and problems arising during emergencies caused by weather.

Keywords: Séd creek, on-line monitoring systems, comparing measurement techniques

Introduction

The 2000/60/EC EU Water Framework Directive (WFD) prescribes that by 2015 all surface water bodies have to reach a good ecological and chemical status. To ensure this, we need to have information about the status of water quality. A desirable feature would be the possibility of continuously track the status of our water bodies with a cost effective monitoring system.

The goal of our work was to introduce online monitoring systems and laboratory methods used to measure the physical-chemical parameters of the Séd creek in Veszprém. In order to continuously monitor water quality, two online monitoring systems were installed, which operate on different principles. The majority of our work was to test the Mobile Monitoring Station (No. 1), which was developed at the Environmental Engineering Institute of the University of Pannonia. In addition, we had the opportunity to follow up the operation of a more complex Mobile Monitoring Station (No. 2), which was manufactured by Combit IT Ltd. The two monitoring stations were placed strategically that the effect of the town of Veszprém on the stream could be measured. With the help of measurements made online and control measurements made in the laboratory, we mapped the loads effecting the Séd creek and to detect pollutant waves travelling down the stream.

Materials and Methods

The investigated water body is the middle section of Séd creek. The water body belongs to the Danube catchment and in it to the Northern-Mezőföld and Eastern-Bakony subunit. The Séd originates in the Bakony, then flows through the city of Veszprém, and joins Nádor Canal at Ősi. The total length of Séd-Sárvíz-mill canal is 71.82 km. Point pollutions are caused on the territory by communal and industrial wastewater inlets. Intensive agriculture and husbandry are characteristic. Because of the side-point sources, we also have to focus on the investigation of diffuse pollutions [4].

Description of Installed Online Monitoring Stations

Two online water quality Mobile Monitoring Stations were installed on the middle section of Séd creek. The evaluated period of continuous measurement was between the August 4, 2013 and October 11, 2013. The two stations were different with respect of place of installation, power source, size, security, sampling, measured physical-chemical parameters, as summarized in *Table 1*. Mobile Monitoring Station 1 *(Fig.1)* was located at the section of Séd creek, where it enters Veszprém, while Mobile Monitoring Station 2 is at the exit point from the city *(Fig.1)*.

Figure 1: Location of installed Mobile Monitoring Stations

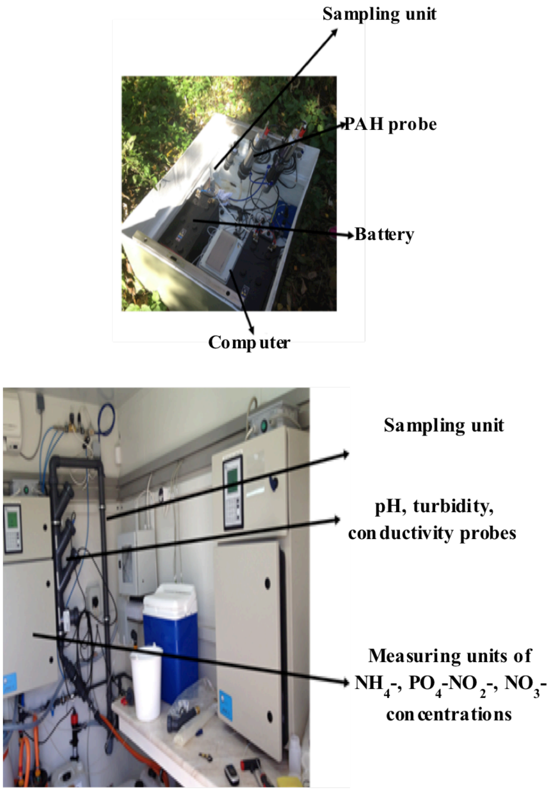

Figure 2: Structure of Mobile Monitoring Station 1 and 2

Results and Discussion

Online Measurements

During the period of August 4, 2013 and October 11, 2013, a tendency was observed for every measured parameter. In *Fig.3*, the pH measured at the examined section of Séd was between 7.3–8.0. The average value of conductivity is 720 µS cm^{-1}, the value of turbidity is 30 NTU. Differences and jumps compared to the baseline indicate pollution, heavy rain or malfunction.

Owing to the placing of the Mobile Monitoring Stations changes could be detected in the pH values between the two sampling points. At Mobile Monitoring Station 1 pH value was in average 0.4–0.5 points higher (7.85) than at Mobile Monitoring Station 2 (7.45) *(Fig.4)*. There are numerous karst water inflows into the Séd as it flows through the city, which causes the lowering of pH. Possible acidic pollutants from roadways, rainwater inlets and industrial areas can also add to the mild acidification of the water body.

In the case of measured ionic concentrations *(Fig.5)* it was observed that all components have a background baseline with a well-defined average concentration. The differences from the baseline appear as peaks that can indicate pollutants or rainy weather. The baseline concentrations are 0.09, 0.03, 0.02, and 4.5 mg dm^{-3} for PO_4^{3-}-P, NH_4^+-N, NO_2^--N, and NO_3^--N, respectively from their average values.

When evaluating the timecourse of all chemical parameters, salient values can be identified and associated with some kind of an event. If we compare *Figs.3* and *5* carefully, we can see that peaks appear at the same time for all components. During the evaluation of data, we identified pollutants, which were washed into the creek due to precipitation.

Table 1: Properties of Mobile Monitoring Stations

	Monitoring Station No.1	Monitoring Station No.2
location of installation	entry point into Veszprém in inner defense area of the waterworks	exit point from Veszprém on an industrial area
size	85×85×85 cm outer size monitoring station made of hardened plastic	2.4×2.4 m base area, 2.5 m height monitoring station
transportation	car	truck with crane
power source	2 pcs of 12 volt lead battery	line power (220V)
measured parameters	pH [11] turbidity [9] conductivity [8] water temperature [11] dissolved oxygen concentration [10] polyaromatic hydrocarbon concentration [17]	pH [12] turbidity [3] conductivity [2] NH_4^+-N concentration [13] PO_4^{3-}-P concentration [16] NO_3^--N concentration [14] NO_2^--N concentration [15]
sampling	every 15 minutes	every hour
maintenance	weekly battery replacement cleaning of the probes	changing reagents and blind reagent calibration (biweekly) supplying distilled water (biweekly) cleaning of sample dispenser vessel sampling tubes

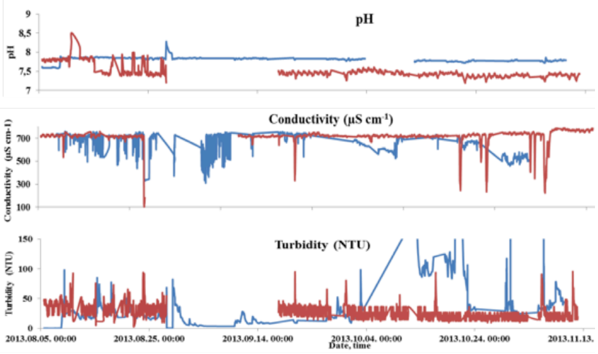

Figure 3: Results of physical parameters measured (blue: Station1, red: Station 2)

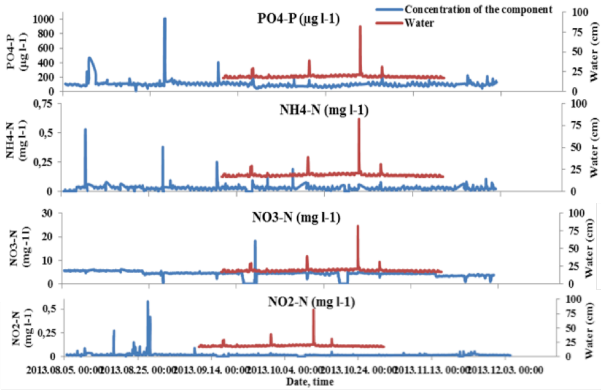

Figure 5: Change of concentration of measured ions

In addition, we detected pollution waves in two occasions. As can be expected, point sampling cannot give detailed information about the status of a water body. The advantage of online methods is clear due to their continuous monitoring, even if they are only operated for a short period of time. Thus, we will get a more holistic picture about the status of a water body toward implementing efficient measures for water quality protection.

Pollutant Leaching from Precipitation

To identify events, we used data from Measurement Station 2. In addition, water level data were downloaded from the water management web page of the Ministry of Interior, Hungary. The water level of Séd is at an average of 20 cm. From the time points in *Figs.3–5*, we select an event occurred on September 30, 2013.

Around the time of the event, the water level started rising, the concentrations of physical-chemical parameters have also started to change. The pollutant downwash was detected between 04:00 and 06:00 according to the results; the concentration peak appeared at 05:00. Viewing physical parameters (*Fig.6*) the value of turbidity has risen, and after reaching the positive peak (14.6 NTU) it started to decrease. Other physical parameters were seen as negative troughs. In the falloff phase all parameters moved back to the average value. Looking at the chemical components *(Fig.6)* as an effect of the rising water level, NH_4^+-N, PO_4^{3-}-N and NO_2^--N concentrations have risen, while NO_3^--N concentration appeared as a negative trough. Outstanding physical-chemical parameters (e.g. PO_4^{3-}-P at 0.15 mg dm^{-3} level) measured as an effect of pollutants washed in during precipitation. Afterwards, the PO_4^{3-}-P level moved back to its near average range of 50 µg dm^{-3}.

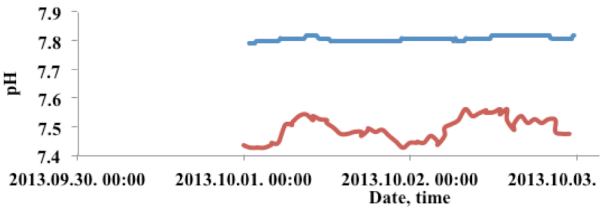

Figure 4: Variation of pH value as a result of discharge from the city (blue: Station1, red: Station 2)

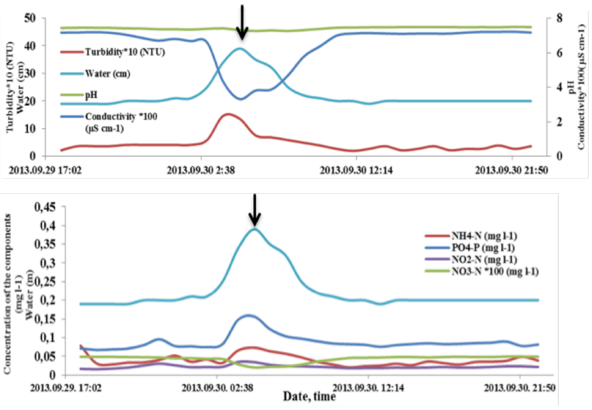

Figure 6: Effect of precipitation on the physico-chemical components

Detecting Pollutants

Pollutant waves were identified as events, when water level rise did not support the deviations of data points from their expected average values. Alternatively, as a result of precipitation, water level of Séd doubled relative to its average value without the presence of in pollutant waves.

As an example, we analyze here the effect of a pollution wave appeared on September 26, 2013. The pollution was detected between 17:00 and 19:00 with reaching its peak at 18:00. Looking at physical parameters *(Fig.7)* turbidity values doubled relative to the average of 60 NTU. Conductivity decreased significantly from 700 µS cm^{-1} to 640 µS cm^{-1}. The pH decreased by 0.1 unit to 7.3. When we look at ion concentrations in *Fig.7*, NH_4^+-N concentration rose fourfold compared to the baseline (0.19 mg dm^{-3}). PO_4^{3-}-P and NO_2^--N concentrations also showed significant rise (30–180 µg dm^{-3}). NO_3^--N displayed a negative trough at 40 µg dm^{-3}, but this component was the least sensitive to the change.

Measurement of Polyaromatic Hydrocarbons

Based on the data points taken every 15 minutes by the polyaromatic hydrocarbon (PAH) probe (TRIOS) at Measuring Station 1 *(Fig.8)* a PAH pollutant wave was not detected during the investigated period. The baseline of PAH compounds was measured to be 6–7 µg dm^{-3} and 13–15 µg dm^{-3}. Values significantly differing from

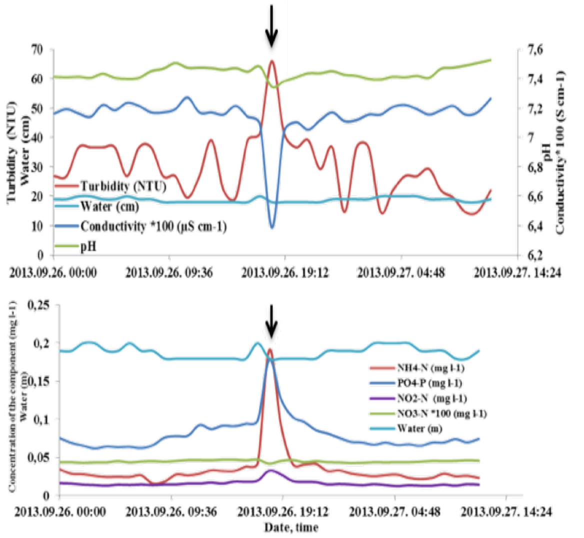

Figure 7: Effects of a pollutant wave on the physical-chemical parameters components

the baseline (35 µg dm^{-3}) can be counted as measurement errors.

Evaluation of Laboratory Measurement Results

In the duration of the investigation, we have taken point samples at the two measurement sites 13 times. The samples were always taken according to standard MSZ ISO 5667–1:2007 [6] in the same time when the monitoring stations recorded data. The samples were transported in a cooler according to standard MSZ EN ISO 5667–3:2004 [7], and were analyzed on the day of sampling. *Table 2* summarized the type of instruments used for measurements.

We compared the data obtained at Measurement Station 2 with the results of laboratory measurements *(Fig.9)*. Correlation can be found for the outliers measured at the monitoring station (250 µg dm^{-3} PO_4^{3-}-P) and in the laboratory (310 µg dm^{-3} PO_4^{3-}-P). However, difference was found in the NO_3^--N concentrations between the laboratory and measurement station results showing around half values for the laboratory measurements than those from the measurement stations. Based on these observations we proposed that the analyzer at the Mobile Monitoring Station measures higher concentration than the real concentration.

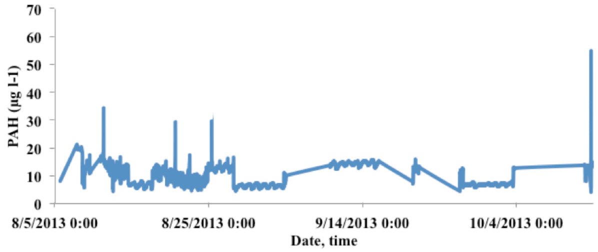

Figure 8: Change in PAH concentration in the investigated timeframe

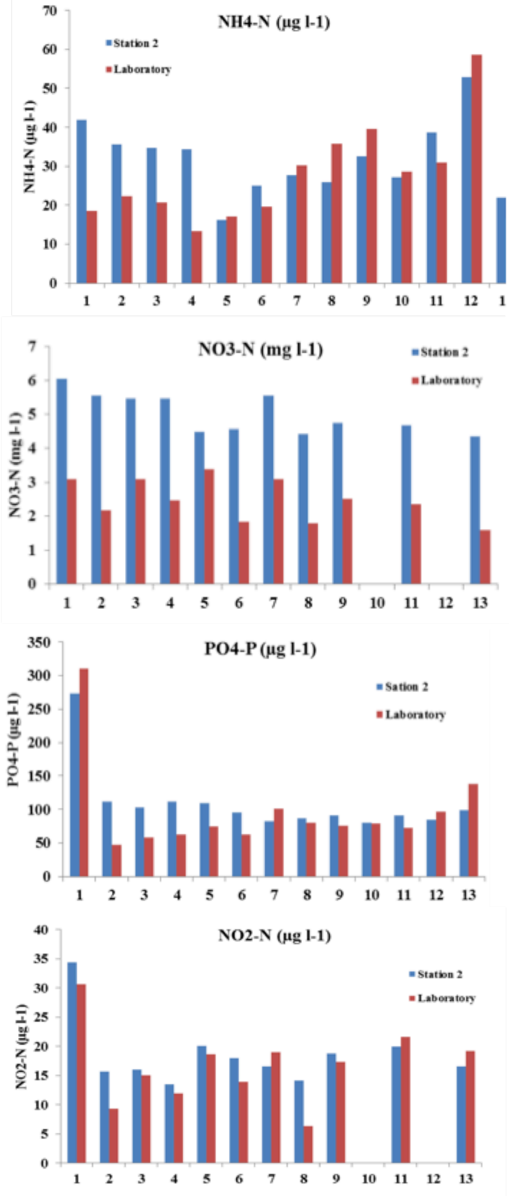

Figure 9: Comparing mobile Monitoring Station 2 and laboratory results

The Effect of the City of Veszprém on Séd

Using laboratory measurements, the effect of the city of Veszprém on the creek's water quality was measured. The results obtained for averages of 13 samples are shown in *Fig.10*. It can be seen that there was no significant change in the concentration of NH_4^+-N (26.4–27.3 mg dm^{-3}) between the entry and exit points of the creek with respect of the city. Jumps in the concentration of NH_4^+-N are characteristic during pollutant waves and precipitation. Decrease in concentration of PO_4^{3-}-P is notable (131–100 µg dm^{-3}) at the exit section. At the entry section, Séd flows near to agricultural areas, backyard gardens. We correlate the decrease of phosphate concentration within city limits with the presence of pure karst water inflows resulting in significant dilution effect.

In the case of NO_3^--N and NO_2^--N concentrations *(Fig.10)* an obvious increase can be seen (1.3–2.6 mg dm^{-3}; 4.3–5.6 mg dm^{-3}), which is related to the high nitrate content of the incoming karst water. The discharges from rainwater drains, backyard gardens, the canal of the zoo, and inflow from roads add to the increase of these concentrations.

Table 2: Devices used to measure physical and chemical properties of water samples

	Mobile Monitoring Station 1	Mobile Monitoring Station 2	Laboratory
pH	NEOTEK-PONSEL, PHEHT	SENTEK PI11	Consort C902
conductivity	NEOTEK-PONSEL, C4E	Endress+Hauser InduMaxP CLS 50	Consort C902
turbidity	NEOTEK-PONSEL, NTU sensor	Endress+Hauser TurbiMax W CUS41/CUS41-W	-
PO_4^{3-}-P NH_4^+-N NO_3^--N NO_2^--N	-	µMAC C	Lovibond PC Spectro
PAH	Trios, eviroFlu-HC	-	-

Table 3: Comparison of laboratory and online measurement results

	EnviroFlu (µg dm^{-3})	Laboratory (µg dm^{-3})
sample form Séd	13.01	0.13
Séd + 20 µg dm^{-3} PAH mix	25.27	13.7
Séd +100 µg dm^{-3} naphtaline-disulphonate	21.03	0.15

Table 4: Monthly average values for water quality parameters

	August	September	October
pH	7.64	7.45	7.43
Conductivity, µS cm^{-1}	711.22	707.16	720.74
Oxygen saturation, %	84.15	93.4	77.32
Dissolved oxygen, mg dm^{-3}	9.39	10.28	8.73
NH_4^+-N, µg dm^{-3}	33	31	26
NO_2^--N, µg dm^{-3}	31	17	15
NO_3^--N, mg dm^{-3}	5.12	4.02	4.14
PO_4^{3-}-P, µg dm^{-3}	113.79	96.58	92.04

Measurement of Polyaromatic Hydrocarbon Concentrations

The two goals of the measurements were the testing the reliability of the results by EnviroFlu and evaluating whether the probe can detect other PAH compounds that are not fluorescent. To check reliability, we used the addition method with EPA TCL Polynuclear Hydrocarbons Mix chemical from Sigma-Aldrich. Furthermore, we also used naphtaline-disulphonate compound for inducing disturbing effect. We measured three solutions as shown in *Table 3* with probe and we have taken emission spectra. Laboratory control measurements (MSZ 1484-6) [5] were done by ELGOSCAR 2000.

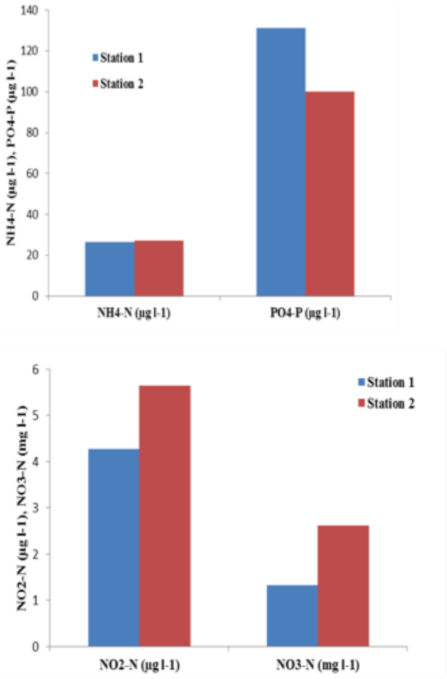

Figure 10: The effect of the city of Veszprém on the investigated section of Séd creek

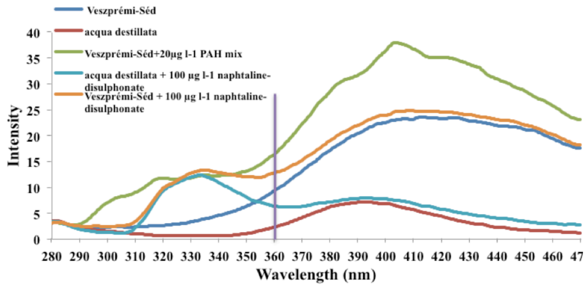

Figure 11: Emission spectra taken with fluorimeter

Comparison of the laboratory and probe results showed significant difference *(Table 3)*. If we deduct the values obtained for the sample from Séd creek as base values, we get similar results. The reliability of results obtained this way was confirmed by spectra taken by a Perkin Elmer LS50B type fluorimeter *(Fig.11)* [1]. The EnviroFlu probe detects fluorescent light at 360 nm. When looking at the curves at 360 nm, we can see that the proportions of intensity differences between the spectra of a sample from Séd and artificially polluted samples correspond to the concentration differences. The significant difference between the laboratory and probe results comes from the fact that the probe senses all compounds giving fluorescence at a given wavelength. This was further elaborated by the significant concentration difference when the sample contained naphtaline-disulphonate.

Water Quality According to Water Framework Directive

The middle section of Séd belongs to Type 3, or alpine, calcic-rough bed material, medium catchment water flow according to Water Management Plan [18] on the basis of Water Framework Plan [19.] We have prepared water qualification in the observed timeframe in monthly divisions. For dissolved oxygen and oxygen saturation values we used the results of Mobile Monitoring Station 1 and for other components the results of Mobile Monitoring Station 2.

We have calculated monthly average values of water quality parameters *(Table 4)*. In addition, we classified each component on a five-level scale and then made class averages. The class minimums provided classifications for each month. The minimum of class average for August, September, and October were 2.5, 3, and 3, respectively; which resulted in water quality that did not reach a good status.

Conclusions

The advantage of online measurement methods was demonstrated due to the possibility of continuously monitoring the quality of the examined creek. With online devices events can be detected that can be missed by point sampling, such as daily fluctuations, pollution waves in extreme time points.

Another advantage of online methods is the remote controllability, which does not require personnel except for maintenance. A drawback of the larger and more complex Mobile Monitoring Station 2 compared to more portable Mobile Monitoring Station 1 is the need for significant chemical, distilled water and maintenance time.

The measurement stations can reveal trends, the results provided by them are in the same magnitude, but it cannot compete with the accuracy of an accredited laboratory. The goal of online measurements is to detect pollutant waves and extreme values. In order to enhance the accuracy of online measurements follow up laboratory control measurements is needed.

In addition to the entry and the exit sections of the Séd creek, the Catchment Management Plan requires monitoring the physical and chemical parameters of the middle section of Séd that are missing. The results presented in the given paper may help in the drafting of the measurement plans.

Acknowledgements

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REFERENCES

[1] KRISTÓF J.: Chemical Analysis II. (Instrumental Analysis), VE 13/2000. Veszprém, Pannon Egyetemi Kiadó, *2000* (in Hungarian)

[2] Endress+Hauser Conductivity Sensor InduMaxP CLS 50: Technical Information (TI 182C/07,en, No 51517565), Endress+Hauser in Germany, *2007*

[3] Endress+Hauser Solids Content Sensor Turbimax W CUS 41/CUS 41-W: Technical Information (TI 177C/07,en, No 51517577), Endress+Hauser in Germany, *2007*

[4] Water Management of Central Transdanubia: Significant Water Management Issues 1–13; Northern and Eastern Bakony field land planning sub-unit, Székesfehérvár, *2007* (in Hungarian)

[5] MSZ 1484-6:2003: Testing of waters. Determination of policyclic aromatic hydrocarbons (PAH) content gas chromatographic-mass spectrometry, Hungarian Standards Institution Standards Bulletin, *2003* (in Hungarian)

[6] MSZ ISO 5667-1:2007: Water Quality. Sampling; Part 1: Guidance on the design of sampling programmes and sampling techniques, Hungarian Standards Institution Standards Bulletin, *2007* (in Hungarian)

[7] MSZ EN ISO 5667-3:2004: Water Quality. Sampling; Part 3: Guidance on preservation and handling of water samples, Hungarian Standards Institution Standards Bulletin, *2004* (in Hungarian)

[8] NEOTEK-PONSEL Digital sensorC4E: Conductivity/Salinity Datasheet, NEOTEK-PONSEL in France, *2009*

[9] NEOTEK-PONSEL Digital sensor Nephelometric Turbidity Datasheet, NEOTEK-PONSEL in France, *2009*

[10] NEOTEK-PONSEL Digital sensor ODOT: Optical Dissolved Oxygen Datasheet, NEOTEK-PONSEL in France, *2009*

[11] NEOTEK-PONSEL Digital sensor PHEHT: pH, Redox, Temperature Datasheet, NEOTEK-PONSEL in France, *2009*

[12] SENTEK Electrochemical Sensor Specialists PI 11 pH elektrode manual, SENTEK in UK, *2008*

[13] SYSTEA S.p.A: Ammonia in water 0–0.4 ppm N-NH_3 (LFA-NH3-05 rev.1 common.609) , Systea S.p.A., Italy, *2000*

[14] SYSTEA S.p.A: Nitrate in water DTPA UV reduction 0–100 mg dm^{-3} N-NO_3^-+N-NO_2^- (LFA-NO3DTPA-02 rev.1 comm. 896) Systea S.p.A., Italy, *2000*

[15] SYSTEA S.p.A: Nitrite in water and seawater 0–5 ppm N-NO_2^- (LFA-NO2-01 rev2.comm. 896) Systea S.p.A., Italy, *2000*

[16] SYSTEA S.p.A: Orthophosphate in water and seawater 0–20 ppm (LFA-PO4-02 rev.1 comm.896) Systea S.p.A., Italy, *2000*

[17] TriOS GmbH: Trios Optical Sensors enviroFlu-HC manual submersible fluorimeter for the detection of polycyclic aromatic hydrocarbons (PAHs) in water, TriOS GmbH in Germany, 2004

[18] Directorate for Water and Environmental Protection: Water Management Plan for the Danube River Basin in Hungary, *2009* (in Hungarian)

[19] EU Water Framework Directive: The European Parliament and of the Council, Water Framework Directive (2000/60/EC), OJL 327, 22 December *2000*, 1–73