Monitoring of rain events with a submersible UV/VIS spectrophotometer

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ABSTRACT

A submersible UV/VIS spectrophotometer has been implemented on the pre-treatment unit of a large-scale wastewater treatment plant (350,000 person-equivalent) to monitor the rapid changes in total Suspended Solids and total Chemical Oxygen Demand occurring during rain events as well as injections of reject water from the sludge treatment train or wasted activated sludge. Calibration has been proven to be difficult for fast composition-varying streams but the device is able to monitor qualitatively sudden quality changes, in spite of the noise affecting the signal.

Key words | calibration, noise, on-line monitoring, rain event, UV/VIS spectroscopy

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INTRODUCTION

The sensitivity of wastewater treatment plants for nutrient removal to temporal variability makes the implementation of systems able to inform in real-time the operators of wastewater characteristics an important issue. Furthermore due to the new discharge limits implied by the European Union Water Directive 2000/60/CE a better characterization of the pollution contained in rain and storm water is necessary in order to optimize its handling. UV-visible spectroscopy has been recognized for years as a way to obtain information on the pollution load of water samples due to the vibration properties of unsaturated bonds present in some pollutant molecules (Mrkva 1983). Recently submersible systems have been made available for direct monitoring in rivers, drinking water supply sources (Fleischmann *et al.* 2002) as well as in wastewater treatment works (Rieger *et al.* 2004; Langergraber *et al.* 2004*a*,*b*). In order to help local authorities to fulfil their commitment of improvement of the quality of discharged water in the Meurthe River (classified as a sensitive water body) it has been decided to test the performances of an in-situ spectrometer to monitor rapid changes in the characteristics of wastewater and rain water. For these tests the device has been implemented on the pre-treatment stage of the Nancy-Maxéville wastewater treatment plant (350,000 PE) which receives wastewater from a combined sewer network. In previous work using UV/VIS submersible spectrophotometers on CSOs it has been reported difficulties concerning calibration due to the fast changing composition of the wastewater composition (Stumwöhrer *et al.* 2003; Gruber *et al.* 2005).

MATERIALS AND METHODS

A submersible UV/VIS spectrophotometer (Spectro::lyzer, S::can, Vienna, Austria) fitted on a floating system (pontoon)

doi: 10.2166/wst.2008.144

with a light path length of 5 mm has been used. It has been connected to a Con::stat (PC) on which the Ana::pro operating system was running. The device was always operated according to the manufacturer's indications. The minimum measurement period is 1 min and no smoothing was applied. Only total Chemical Oxygen Demand (COD) and total suspended solids (SS) will be discussed in the present contribution. Air cleaning period was set to 15 min. The system (Figure 1) has been successively positioned in three locations, shown on Figure 2:

- P1: a tank fed by primary settled wastewater and discharging by overflow, located in a laboratory on the WWTP grounds (period 1 – early July 2006)
- P2: in the aerated channel feeding the sand removal units from the grit removal unit (periods 2A, 2B and 2C – late July through October 2006)
- P3: in one of the primary settler units (period 3 – November 2006)

No clogging of the device was observed during the tests, although some fibres or pieces of cloth could get stranded around the steel cables. By precaution the pontoon and the spectrophotometer were cleaned with water once a week.

Reject water from the dewatering unit of the sludge train (anaerobic digestion) was injected in the aerated channel just after the grit removal during period 2A (July 2006) and 2C (October 2006). During period 2B (August-September 2006) excess sludge wasted from the secondary clarifiers was injected together with reject water. During period 3 (November 2006), reject water was not injected anymore in the pre-treatment aerated channel. For the three periods reject water from the sand cleaning unit was injected upstream of P2 in the aerated channel.

Samples were taken manually or with automated samplers (Isco from Teledyne Isco, Wierde, Belgium) and Sigma 9,000 from Hach, Loveland, CO). Aliquots of unfiltrated samples were analyzed for total COD and turdibity (on a Hach DR2400 spectrophotometer, at 450 nm after calibration with a formazine suspension). Suspended solids were measured after filtration on 0.45 μm cellulose nitrate filter (Millipore) of 40 to 100 mL (depending upon the sample concentration) and

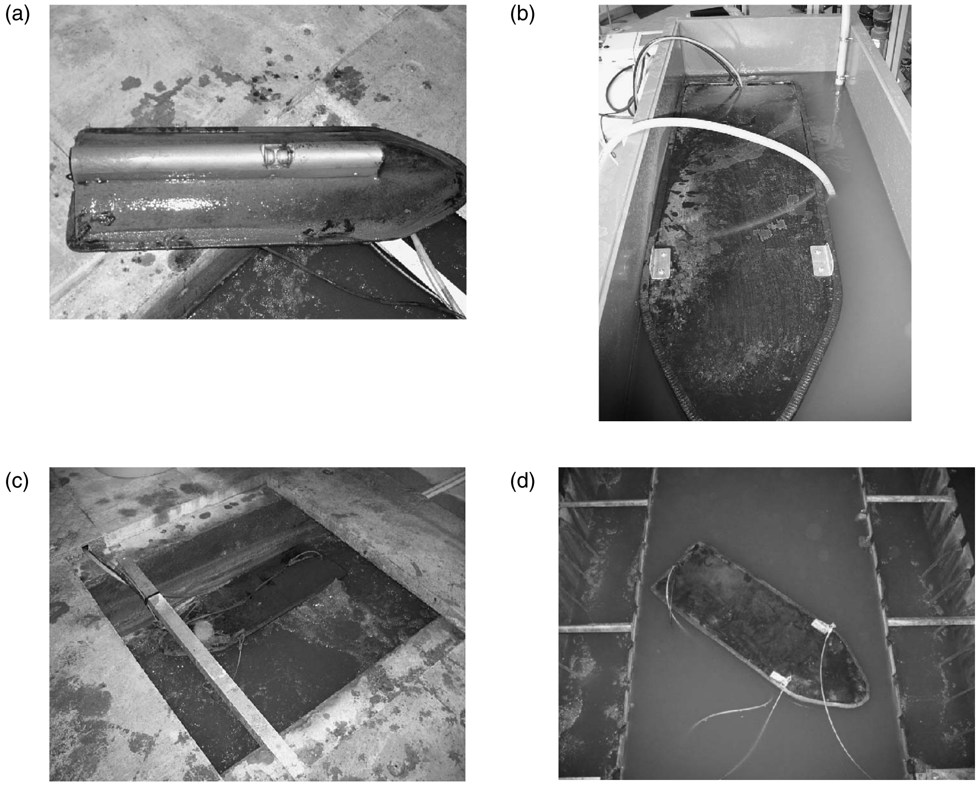

Figure 1 | UV-vis submersible spectrophotometer (a) fixed to its pontoon (photograph taken after 1 week in position P2), in the tank (position P1) (b), in the aerated channel (position P2) (c) and in the primary settler (position P3) (d).

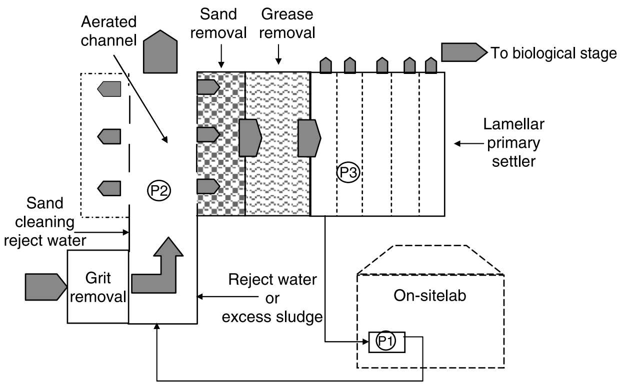

Figure 2 | Location of the three test points.

drying of the filter at 105°C for 24 h (precision 3%). Total COD was analyzed according to Method WAH 8000 (Hach) in the range 20 – 1,500 mg COD/L (precision 2.5%).

Rainfall data were provided by Greater Nancy Water District, which operates a rain gauge network of 21 units. Average daily COD, SS and flow rates values were also obtained from Greater Nancy Water District.

RESULTS

Calibration issues

The primary aim of the tests performed in the at-line tank fed by primary settled wastewater (location P1) was to compare the global calibration provided by the manufacturer and built on a large number of different wastewater samples and the local calibration procedure. In Figure 3a the COD values obtained in the laboratory have been plotted versus the COD values provided by the UV-vis probe using the global correlation. Globally the obtained result is good: the slope is close to 1 but there is some dispersion at high concentrations. In Figure 3b local calibration was performed by taking a sample at the time a UV-visible spectrum was collected by the UV-vis probe. Once the samples have been analyzed in the laboratory, the Ana::lyte software was used to build a local calibration model. A better coefficient of correlation was obtained. The local calibration was verified one week later (Figure 3c). Similar results were obtained for the suspended solids.

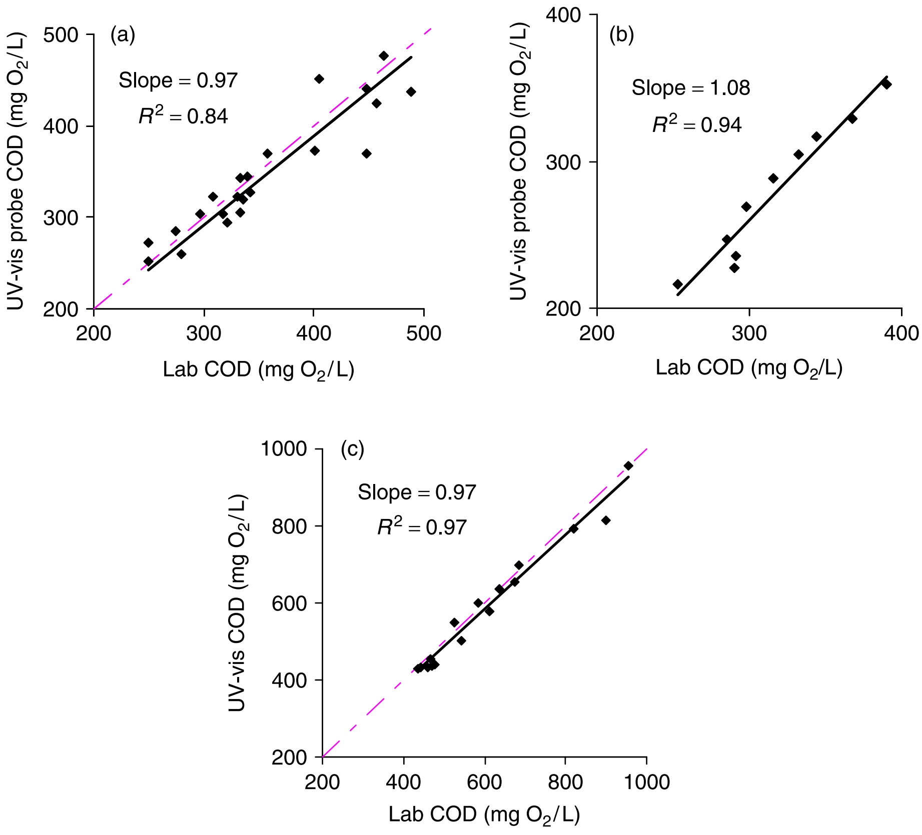

Figure 3 | Total COD calibration in the tank at location P1 (a) Global calibration (b) Local calibration (c) Local calibration validation.

The UV-vis probe was then moved to the aerated channel feeding the primary settler (location P2). Due to flow and aeration, the mixing is much more intense in the channel than in the tank. The local calibration built in the tank was checked (Figure 4a) during period 2A. It was quickly obvious that the calibration worked fine during daytime but discrepancies occurred during night time, when the COD level is the lowest. A new local calibration was performed taking into account night data points. It gave much better results during its validation (Figure 4b). Local calibration was sufficient for our goal, contrarily to what was observed by Rieger *et al.* on Swiss WWTPs (Rieger *et al.* 2006).

The coefficients of correlation obtained at that location were about 0.8, lower than at location P1. Scanning at higher frequency (1 min) was performed and revealed a high noise on the COD and SS data (Figure 5). This noise could not be related to reject water injection, which occurred only during the last hour of the experiment. Reject water from the sand cleaning unit is also injected upstream to the UV-vis probe every 10 minutes approximately. It was noticed that the noise, which could be related to air bubbles or particles, had varying characteristics, being symmetric until midnight and then becoming asymmetric. It was therefore difficult to select a smoothing procedure directly applicable from the Con::stat interface.

During period 2B, discrete injections of excess sludge from the final clarifiers occurred every 35 min and lasted 25 min. These injections modified severely the wastewater matrix. All the attempts to validate the local calibrations for COD and SS or to establish new ones failed during this period. It was indeed not possible to grab a sample exactly at the same time and location the UV-vis probe was collecting its spectra. The UV-vis probe was however able to monitor qualitatively the rapid changes as shown in Figure 6. High COD and SS values were collected during the excess sludge injections. A moving minimum established with a time window of 40 min was calculated to estimate the COD content of the wastewater itself. The estimated COD is in the range of the daily average wastewater COD.

Due to the rapid changes of composition related to the injection of various reject waters in the channel, this location is not suitable to monitor the wastewater quality entering biological reactors downstream of the primary settler. Therefore the device was installed for a final test on the primary settler, at the top of the clarifying zone (location P3). The composition of the wastewater is similar to the one observed at location P1, except that the tests were not run under the same seasonal conditions. A secondary calibration procedure was tested at that occasion, by simply correlating the basic COD and SS values given by the UV-vis probe with laboratory values obtained on samples collected by an autosampler at fixed time. This procedure enables to investigate the whole matrix cycle without the requirement of staff presence. This is certainly less accurate than the exact

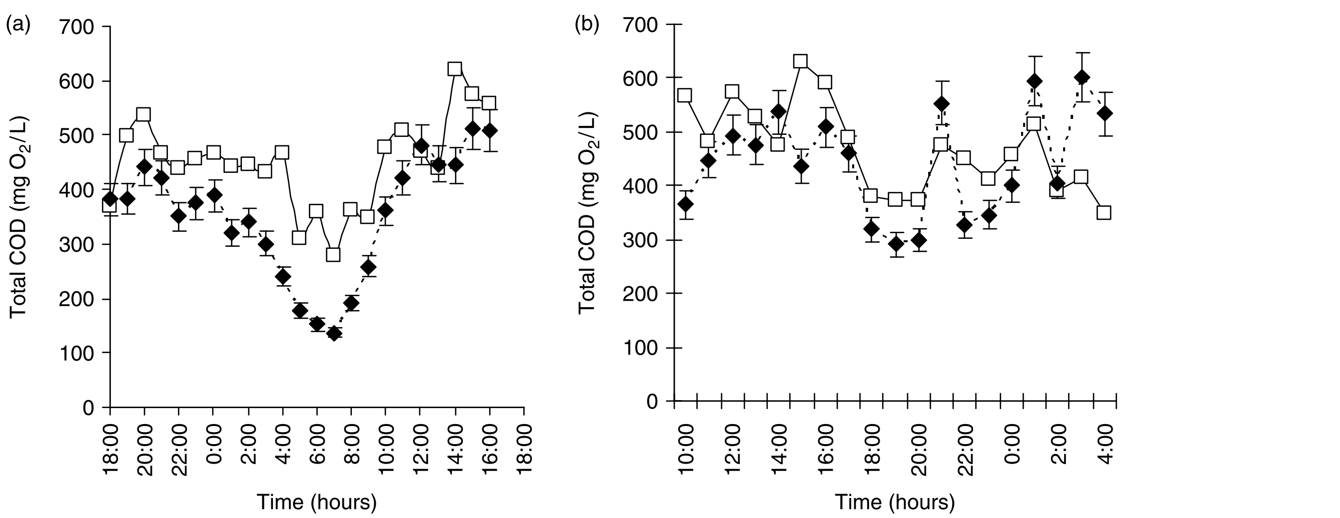

Figure 4 | Local calibration validation at location P2 for total COD: ◆UV-vis probe data □ laboratory data (a) based on previous local calibration in P1 (b) after new local calibration in P2.

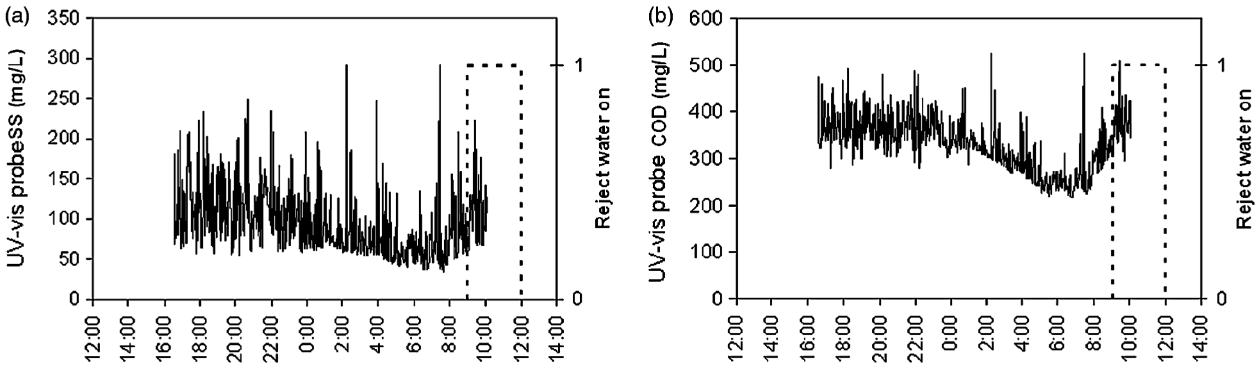

Figure 5 | Monitoring of suspended solids (a) and COD (b) by the UV-vis probe in the aerated channel under dry weather conditions at high sampling frequency (1 min).

calibration procedure indicated by the manufacturer. Figure 7 compares, in a validation step, the final UV-vis probe COD values with values obtained on samples analyzed in the laboratory (2-hours mixed samples) and with the average daily COD measured at the exit of the pre-treatment step. The agreement was found satisfactory considering the constant matrix changes in response to rain events.

Monitoring of rain events

One of the foreseen applications of the UV-vis probe is to monitor COD at the inlet of a combined sewage-rainwater treatment unit. It is therefore important to test the reactivity of the UV-vis probe to rain events, at least qualitatively. In order to evaluate the amount of rainwater produced by each rain event, the rain gauge data were transformed into rain volume by multiplication with the impervious surface that can be affected to each rain gauge. Due to the size of Greater Nancy sewer network (750 km), the presence of several combined sewer overflows and the fact that rain events (especially summer storm) can affect more or less severely different geographical areas, it is difficult to calculate how much rainwater effectively reaches the wastewater treatment plant. To have an idea of the amount of water generated as well as of the duration of the events, the rain volumes have been plotted per rain gauge.

In Figure 8 the monitoring of a summer evening storm is presented. Samples were collected by an autosampler every 30 min during that event. This event caused the amount of wastewater treated in the plant to increase from 63,000 m^3/d to 75,000 m^3/d. Two sub-events can be detected through the raingauge network, the first one at 6 pm and the second one occurring 40 min later. Both sub-events were detected by the UV-vis probe at location P2, in spite of the noise affecting the device at that location. The UV-vis probe COD values are in agreement with the measurements obtained on the samples

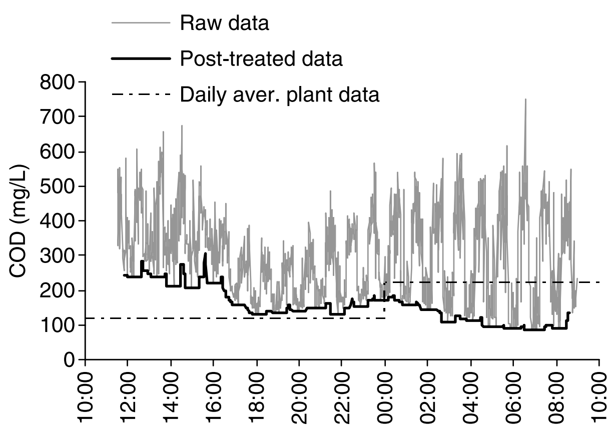

Figure 6 | UV-vis probe raw data and post-treated data (moving minimum), daily average wastewater COD in the aerated channel during the excess sludge injection period. Sampling period = 1 min.

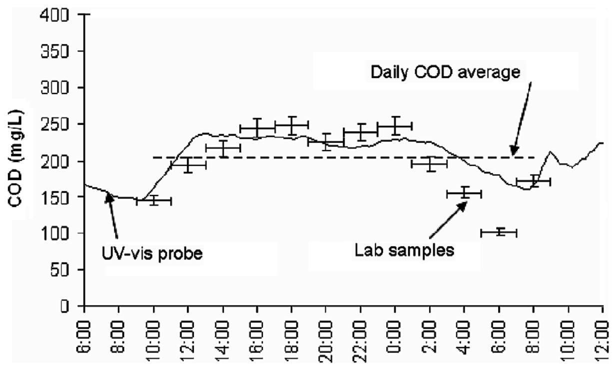

Figure 7 | Validation of the secondary calibration for COD on the primary settler: UV-vis probe sampling period = 15 min.

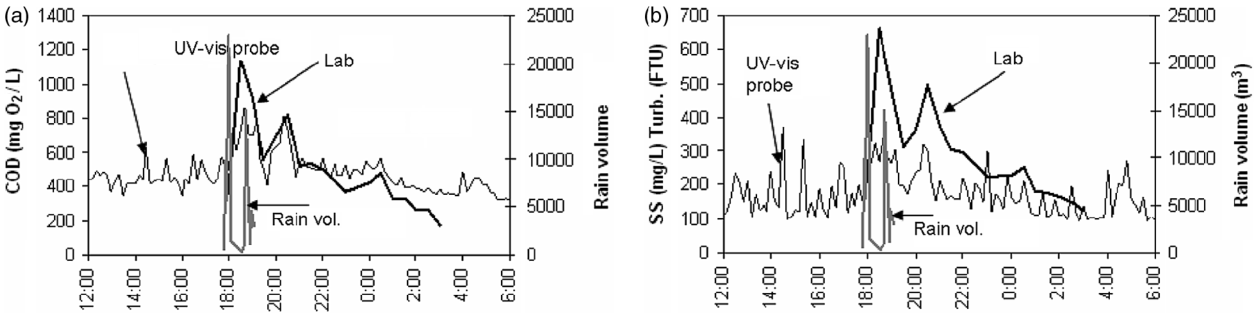

Figure 8 | Monitoring of a summer storm (July 20th, 2006) by the S:can located at P2. (a) COD (b) SS. S::can probe sampling period = 15 min.

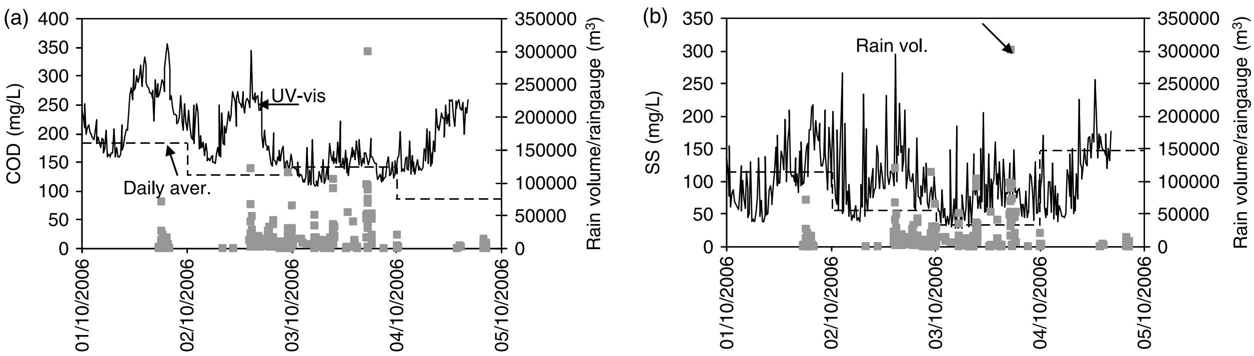

Figure 9 | Monitoring of a large fall rain event by the UV-vis probe located at P2. (a) COD (b) SS. UV-vis probe sampling period = 15 min.

in the laboratory. The agreement is less satisfactory for the suspended solids: this could reflect the change in the nature of particulate pollution transported during rain events.

Figure 9 presents the variations of COD and SS during a large rain event occurring during the fall. The estimated rain volume generated during this event between Oct 2, 2006 (2 pm) and Oct 3, 2006 (12 pm) is about $3.8 \times 10^6\,m^3$. By comparison the July 20th, 2006 storm generated a volume of $96 \times 10^3\,m^3$. The maximal wastewater flow rate that the plant is able to handle ($112{,}000\,m^3/d$) was reached. A small increase of the COD could be observed during the small rain event on Oct 1st (first flush effect). Such an increase was not observed during the subsequent 22 hrs long rain event. A large dilution effect could be seen instead. The SS data are very noisy and difficult to interpret without further processing. For both parameters there is a satisfactory agreement with the average daily values measured at the plant inlet.

Finally a series of rain events of moderate intensity was monitored when the UV-vis probe was installed on the

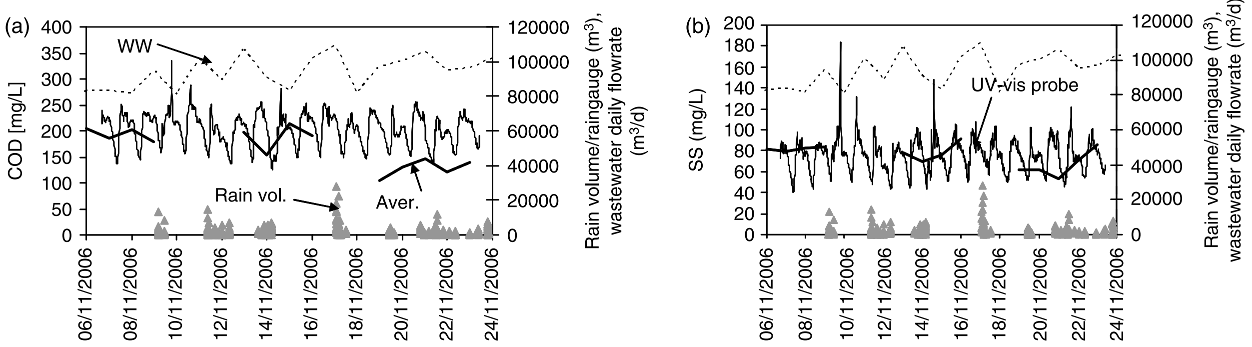

Figure 10 | Monitoring of a series of fall rain events by the UV-vis probe located at P2. (a) COD (b) SS. UV-vis probe sampling period = 15 min.

primary settler (Figure 10). Location P3 is less suitable for rain event monitoring due to the dampening effect of the primary settler. Nevertheless a perturbation of the daily cycles can be seen in the case of long rain events (Nov 11 & 12, 2006; Nov 20 to 22, 2006). The wastewater flow rate was very large for the whole period. A satisfactory agreement was observed with the daily average values, except toward the end of the test.

CONCLUSIONS

A UV/VIS submersible spectrophotometer has been tested at the inlet of a wastewater treatment plant to monitor rapid changes in COD and SS that occur during rain events. Although the device is able to provide very useful qualitative information on the variations in the wastewater composition, two problems were found which affects his performance: large noise (probably due to air bubbles and particles) of varying characteristics and difficult calibration. This problem has previously reported for experiments on a smaller catchment (Gruber *et al.* 2005). As wastewater composition is very dependent upon the type of rain event, calibration should be done for each event, which is certainly not the goal. As stated by Rieger *et al.* (2006) it is not easy to take into account large shifts in the wastewater matrix. One should not forget however that COD and SS are very global parameters that have their own limitations. The focus of our current work is on the treatment of the signal noise problem which should be solved before trying to improve the calibration procedure and direct use of the spectral information.

ACKNOWLEDGEMENTS

The authors wish to thank the Greater Nancy Water District, the staff of the Greater Nancy Wastewater Treatment Plant and Bamo Company for their help.

REFERENCES

Gruber, G., Winkler, S. & Pressl, A. 2005 Continuous monitoring in sewer networks: an approach for quantification of pollution loads from CSOs into surface water bodies. *Water Sci. Technol.* **52**(12), 215–223.

Fleischmann, N., Staubmann, K. & Langergraber, G. 2002 Management of sensible water uses with real-time measurements. *Water Sci. Technol.* **46**(3), 33–40.

Langergraber, G., Fleischmann, N., Hofstaedter, F. & Weingartner, A. 2004*a* Monitoring of a paper mill wastewater treatment plant using UV/VIS spectroscopy. *Water Sci. Technol.* **49**(1), 9–14.

Langergraber, G., Gupta, J. K., Pressl, A., Hofstaedter, F., Lettl, W., Weingartner, A. & Fleischmann, N. 2004*b* On-line monitoring for control of a pilot-scale sequencing batch reactor using a submersible UV/VIS spectrometer. *Water Sci. Technol.* **50**(10), 73–80.

Mrkva, M. 1983 Evaluation of correlations between absorbance at 254 nm and COD of river waters. *Water Res.* **17**, 231–235.

Rieger, L., Langergraber, G., Thomann, M., Fleischmann, N. & Siegrist, H. 2004 Spectral in-situ analysis of NO_2, NO_3, COD, DOC and TSS in the effluent of a WWTP. *Water Sci. Technol.* **50**(11), 143–152.

Rieger, L., Langergraber, G. & Siegrist, H. 2006 Uncertainites of spectral in-situ measurements in wastewater using different calibration approaches. *Water Sci. Technol.* **53**(12), 187–197.

Stumwöhrer, K., Matsché, N. & Winkler, S. 2003 Influence of changes of the wastewater composition on the applicatbility of UV-absorption measurements at combined sewer overflows. *Water Sci. Technol.* **47**(2), 73–78.