Self-monitoring of water quality in sewer systems using absorbance of ultraviolet and visible light

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Abstract Continuous pollution measurement is interesting to optimize the operation of sanitary facilities as well as to minimize the stormwater discharges. An experimental study was carried out for the determination of Suspended Solids (SS) and Chemical Oxygen Demand (COD) concentrations in combined sewers using ultraviolet and visible absorbances. The maintenance of the measurement system requires six hours a month for the cleaning of the hydraulic feeding system and adjustment of the optical device. The feeding system developed increased the representativeness and reliability of the pollution measurement, but needs to be validated on other measurement sites. The determination of SS concentrations from visible absorbances requires 2 calibration curves for dry and rainy weather respectively. The corresponding accuracies appear satisfactory when compared with the results of standard sampling/laboratory analysis. The accuracy of COD determination from ultraviolet absorbance is less satisfactory, but could perhaps be improved taking into account another parameter. Then the optical measurement of SS and COD is interesting to determine average or long term pollution loads, for example the yearly impact of urban stormwater discharges. With this kind of continuous and on-line measurement, it is possible to react with short delay to unexpected phenomena which could damage the environment or water treatment efficiency.

Keywords Combined sewer; monitoring; on-line measurement; optical measurement; pollution measurement; stormwater discharges

Introduction

New European and French regulations state that the operators of sewer systems must have a self-monitoring program (Agences de l'Eau, 1996) to control the treatment efficiency of the collected water and to minimize the stormwater discharges.

Besides, real time operation and automatization of sanitary facilities require continuous pollution measurement methods. The use of optical sensors is then interesting as it allows a permanent and instantaneous determination of the water quality, and their signal is tele-transmissible.

An experimental study was then carried out to determine the best use conditions for an optical device measuring ultraviolet and visible absorbances, to reach a reliability and accuracy which comply with the above referenced needs.

This study fits into two research programs: Pollutant flow measurement for urban drainage (Laboratoire Central des Ponts et Chaussées) and Impact of urban stormwater discharges GARIH (Aquatinian Group for Research and Innovation in Hydrology).

Experimental site and measurement equipment

Experimental site characteristics

The experimental site is located at the outlet of a combined sewer system, downstream from an urban and suburban catchment basin (215 ha). Three sewers meet in a flow control chamber (Figure 1), the outlet of which is controlled by hydraulic valves. During dry

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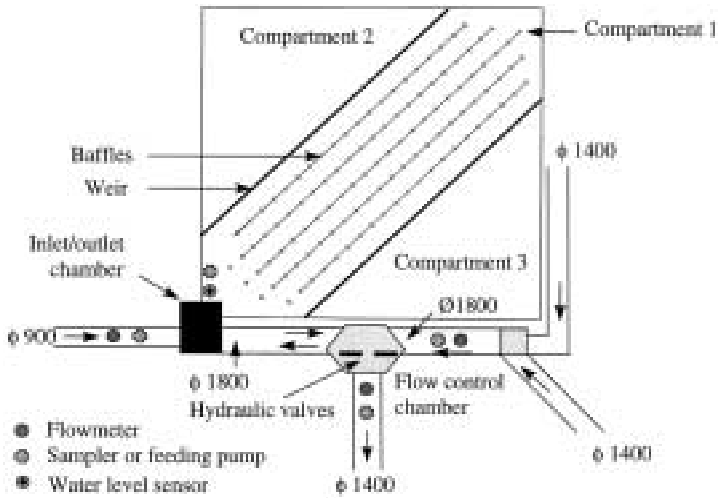

Figure 1 Experimental site equipment

weather the wastewaters flow along in the outlet sewer (1400 mm in diameter). During wet weather the hydraulic valves close gradually, which causes the filling of a three compartment detention basin through an inlet/outlet chamber.

The three sewers connected to the flow control chamber and the storm basin are equipped with hydraulic measurement and water sampling devices (a sampler in the storm basin and feeding pumps in the sewers). Those pumps feed water quality sensors (pH, temperature, conductivity) and refrigerated samplers located in a technical building next to the storm basin. An optical device to measure continuously the water quality was installed on the hydraulic feeding line from the main sewer (1800 mm in diameter). The data of the hydraulic and water quality sensors were registered (mean value of 6 min periods for the optical device, every minute when the signal variation is higher than 5%).

Optical device characteristics

The optical device consists in (Figure 2) an optical sensor immersed in a measuring vessel fed by a pump via an overflow tank. The optical sensor consists in 2 rotating cells. The emitting cell provides ultraviolet rays at 254 nm and visible rays at 546 nm. The emitting and receiving cells rotate eccentrically so that the distance between the two is modulated continuously and periodically. This modulation allows us to compensate the deterioration or dirtying of the cells. In addition wipers clean the cells continuously.

The optical sensor is connected to a control unit equipped with 4–20 mA and 0–2 volt signal outputs. The signals were registered on a data logger.

Measurement and calibration methods

Pollution parameters were analyzed according to AFNOR standards: Suspended Solids (SS – NF EN 872) and Chemical Oxygen Demand (COD – NF T 90-101).

For the calibration of the optical device, 1 litre samples were collected directly in the measuring vessel, to have a good representativeness with the optical measurement (same sample characteristics and time synchronization between the sample collection and the optical data registration).

The samples collected were kept at 4°C and analyzed within short delays (maximum 24 hours).

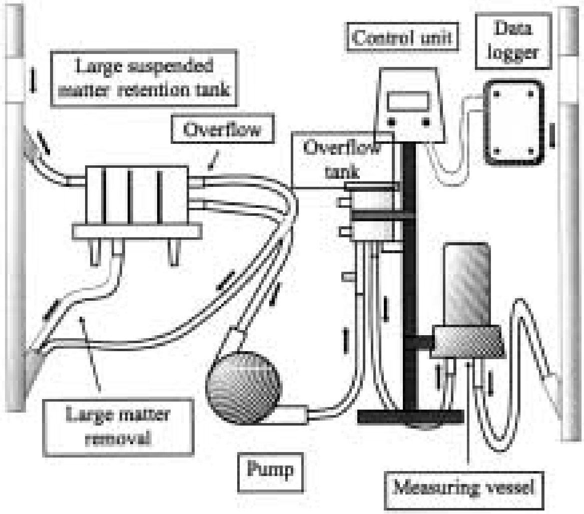

Figure 2 Feeding system and optical device

Measurement periods

16 sets of analysis (153 samples) were carried out between 16/6/98 and 17/7/99, so as to be representative of all situations (night and day, seasons, dry and wet weather).

Results and discussion

Reliability of the hydraulic feeding line

The maintenance of measurement devices is easier when they are installed on a hydraulic line rather than directly in the sewer. Besides, some devices are not submersible. But one of the major problems is the reliability of the hydraulic feeding line because of fouling risks by floating matter or deposits.

Primary feeding line. The primary line (see left of Figure 2) was formerly fed until February 1999 by a pump set on the sewer bottom. Its power is sufficient to guarantee a suction speed greater than 0.5 $m.s^{-1}$ (ISO 5667-10 standard on sampling of wastewaters), but the suction point location is not ideal. It tends to overestimate the pollutant concentrations, and deposits may be collected together with the wastewaters. More especially as a sill was installed to dispose of sufficient water depths for the pump to work. In fact the reliability of this feeding system was unsatisfactory, due to fouling by large suspended matter or deposits.

From February 1999, the feeding system was improved:

- the pump was set on a base 10cm high to prevent the collection of deposits and improve the representativeness;
- the sill was replaced by a new one, with two holes in its lower part to allow the flushing of the deposits, but keeping the water level sufficiently high for the pump to work;
- a baffle was set upstream of the pump to protect it from large suspended matter (hair, paper, plastic, . . .);
- formely the pump working was controlled by the flow, but this was not accurate enough. Then it was controlled by the pressure in the hydraulic line, a pressure too low stopping the pump working.

Feeding system of the optical device (Figure 2). The feeding system consisted in a tank for the retention of large suspended matters fed by the primary line and a 270 $l.h^{-1}$ peristaltic pump. This tank included 3 baffles, an overflow outlet in the upper part and a pipe in the bottom for the removal of the large suspended matter. So it improves the feeding system reliability. A test for the representativeness of the tank in relation with the measurement of the pollution parameters was carried out on samples collected at the inlet of the tank and in the measurement vessel. It showed a mean underestimation of 6% and 4% for the Suspended Solids and Chemical Oxygen Demand concentrations respectively, which is satisfactory.

Feeding system maintenance. The feeding system maintenance requires the following operations:

- the cleaning of the pump in the collector once a month (1 hour)
- the cleaning of the retention tank, overflow tank and measurement vessel takes 1 hour a week on average, but depends on the pollution load. For a continuous working with highly polluted waters (stormy weather), a cleaning every 3 days is necessary.

A monthly maintenance in sewers and a weekly one in treatment works seems satisfactory, but a higher frequency is necessary during stormy weather.

It is difficult to quantify representatively the reliability of the feeding system over the measurement period for the following reasons:

- the conditions of an experimental study are notably different from operational ones. It was not always possible for organizing and security reasons to react quickly to solve technical problems;
- the reliability increased notably after the improvement of the feeding system in February 1999, but it is not easy to carry out pollution measurement at this experimental site as the water levels are too low several hours a day during the dry season. It would have been necessary to modify the works to solve this problem, which could not be considered for this study.

Wastewater quality measurement using ultraviolet and visible absorbance

Terminology. The objective of our study is to determine the concentrations of wastewaters in the pollution parameters Suspended Solids and Chemical Oxygen Demand from calibration relations with ultraviolet and visible absorbances. The use of absorbance standards to keep a stable calibration of the optical device will then be called "adjustment", whereas drawing up relations between pollution and optic parameters will be called "pseudo-calibration" (wastewaters samples cannot be considered as true standards).

Optical device adjustment. The adjustment of the optical device was checked and corrected if necessary every 10 days on average. Adding the corrections between successive adjustments leads to drift values of 1.8 and 3.8% respectively for the zero in the UV and visible range, and of –3.1 and –3.1% respectively for the scale value in the UV and visible range. This is satisfactory for an 8.5 month working period.

Preliminary reflexions on calibration (Ruban G. in Bertrand-Krajewski J.-L. et al., in press). For a suspension of n classes of spherical particles of diameter D_i and volumetric mass ρ_i, the relation between the absorbance A at the wavelength λ and the mass concentration c can be written as follows:

$$A = \log \frac{I_0}{I} = \frac{3}{2}\left(\sum_{i=1}^{n} \frac{Qext(\alpha_i, m_i)\ t_i}{\rho_i D_i}\right) l\ c$$

I_0: light intensity emitted, I: light intensity measured by the receptor, l: path length in the measured medium, t_i: mass percentage of class i particles and $Qext(\alpha_i, m_i)$: extinction coefficient, which depends on the size parameter α_i ($\pi D_i/\lambda$, λ being the measurement wavelength) and on the refractive index of particles in relation with the medium. The extinction coefficient can be calculated using the Mie theory, provided all the particle characteristics are known. This is not the case for wastewater particles, apart from the problem of classing those particles as spherical ones.

We see that the theoritically linear relation between absorbance and concentration may vary with particle characteristics: particle size distribution, volumetric mass and particle composition (expressed by the refractive index). Moreover for COD the relation takes into account the dissolved and particulate kinds, and depends on the ratio oxidizing capacity/mass concentration of the constituents (ratio COD/Dry Matters).

The ratio SS/COD is also an indicator of variability for the physico-chemical characteristics of the particles (Figure 3). During dry weather, the daily evolution of the SS/COD ratio appears reproducible on the whole measurement period, except for some points which belong to the same period. On the contrary this ratio is notably higher during wet weather, which can be logically interpreted as a smaller organic content in the particles. Then separate calibrations for dry and wet weather can be expected.

UV absorbance corresponds to both dissolved and particulate organic matters: depending on their molecular structure, numerous dissolved organic substances absorb light in the UV range, according to Beer-Lambert's law (absorbance proportional to substance concentration). Besides, there is a light extinction by particulate matter according to the turbidimetry τ principle ($\tau(\lambda)$ = A/l: see above). UV absorbance is then well adapted for the determination of organic matter concentrations (expressed in our case by the oxidizing capacity parameter COD). Nevertheless the ratio absorbance/COD as well as the global absorbance is larger for dissolved matter than for particulate ones in raw wastewaters.

As for visible absorbance, the spectrum of raw wastewaters shows that the absorbance of dissolved matters is negligible at 546 nm. Visible absorbance is then well adapted for the determination of particulate matters, for the conditions of characteristic changes mentioned above.

The ratio visible/UV absorbance is an indicator of the optical characteristics of the wastewater contituents. Figure 4 shows the daily evolution of this ratio. The dry weather evolution exhibits two analog parallel patterns, corresponding to a change in the optical device adjustment in March 1999. Then the two data series must be processed seperately. The wet weather evolution shows a notable increase of the ratio, which is homogenous with the SS/COD ratio.

Global calibration and accuracy expression. As pollution parameter values are theoretically proportional to optical parameter ones, linear regression is a good method to set up

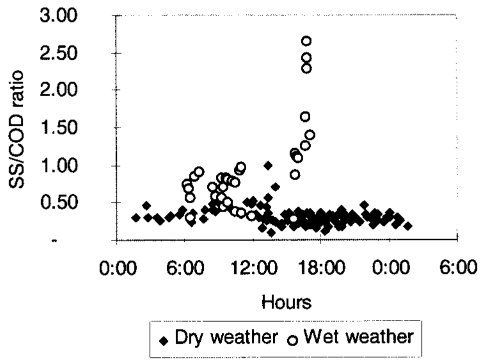

Figure 3 Daily evolution of SS/COD ratio

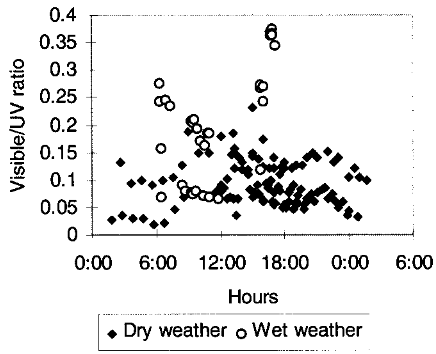

Figure 4 Daily evolution of Visible/UV ratio

calibration relations. But the correlation coefficient (r) is not a relevant accuracy indicator as it depends on the range of the values: for the same value of standard deviation, the correlation coefficient will be low if the experimental points are near, and high if they are far away from each other. The standard deviation (SD) is a better indicator, but as it depends also on the range of the values, we shall use the ratio standard deviation on mean value called the Coefficient of Residual Variation (CRV). Twice this ratio corresponds to a 95% confidence interval for the value distribution, assuming a normal distribution, which is generally the case. Table 1 reports the accuracy values for different sets of samples.

A global correlation (mixed dry and wet weather samples) leads to 2CRV values of ±79% and ±45% for SS and COD respectively. The Guide for the self-monitoring of sanitary systems (Agences de l'Eau, 1996) prescribes ±10% for both parameters. A report of the Working Group "Méthodes d'analyses alternatives" of the French professional association AGHTM (Association Générale des Hygiénistes et Techniciens Municipaux, Paris) specifies values in relation with a concentration threshold : ±15% above 100 mg. l^{-1} and ±40% below for SS, ±10% above 80 mg. l^{-1} and also ±40% below for COD. As the mean values in this case are respectively 174 and 372 mg. l^{-1} for SS and COD, the correlation results are not very satisfactory. Though one must keep in mind that those results hold for individual measurements, to know for example whether a discharge concentration complies with the prescriptions. In the case of a set of n measurements, for instance to determine pollution quantities discharged, the mean variation is divided by $\sqrt{n}$.

Nevertheless it seems necessary to see if those results can be improved by seperate processing of dry and wet weather data. Figure 5 shows SS concentrations versus visible absorbance. The global slope of the experimental points during wet weather stands above the dry weather one. It is less obvious for COD concentrations versus UV absorbance (Figure 6): both slopes are nearer, though some wet weather points belonging to the same rainfall event drift upwards from the group. Table 1 confirms those remarks. Starting from the 2CRV values for the total measurement period of respectively 79 and 45% for SS and COD, the change is larger for SS (99% for dry and 50% for wet weather) than for COD (38% for dry and 52% for wet weather period). Those results will be examined in detail below, especially the rather surprisingly unsatisfactory result for SS during dry weather (99%).

SS pseudo-calibration during dry and wet weather. As already mentioned above, VIS absorbance is theoretically better adapted for SS measurement than UV absorbance. Then the better accuracy 75% with UV during dry weather is surprising. But when taking into account the adjustment change of the optical device in March 1999, the unsatisfactory 99%

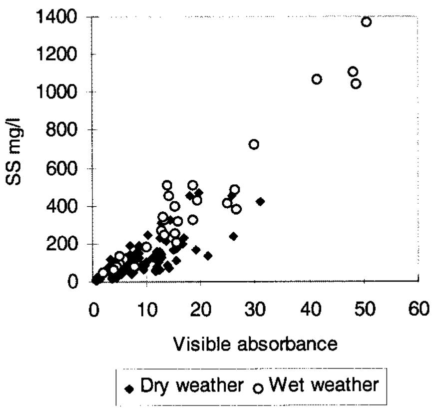

Figure 5 SS versus Visible absorbance

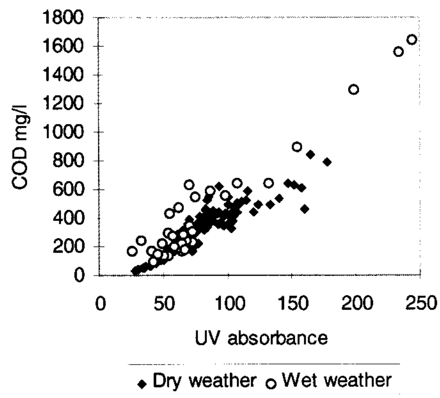

Figure 6 COD versus UV absorbance

accuracy versus VIS absorbance improves to 92% before and 65% after this date. This improvement for both sets of data may be statistically interpreted as characteristic of two different populations. For UV on the contrary, the accuracies before and after March 1999 (68 and 90%) stand above and below the global accuracy, which happens for two sets of the same population. Then the adjustment change seems to influence VIS absorbance rather than UV one. As the accuracy with VIS absorbance remained low before March 1999, we considered the improvement of the primary feeding line in February 1999. The accuracy remains almost the same before (91%), but it improves after (30%). It is possible that large suspended matter and deposits influenced the samples before the feeding improvement. This could induce large changes in effluent characteristics, resulting in a bad correlation. The correlation with UV shows no particular influence (53 before and 50% after).

As for dry weather results, the wet weather accuracy of 50% is notably improved when considering data sets before and after adjustment change (31% for both sets). Though the number of samples is not very large, respectively 22 and 11, UV absorbance gives less good results (68 and 70%).

COD pseudo-calibration during dry and wet weather. We saw above that considering separately dry and wet weather periods does not improve notably the accuracy of COD determination versus UV absorbance. It is the same for dry periods when considering the adjustment change: the global 2CRV value 38% gives respectively 32 before and 45% and after it. As well as for the primary feeding line improvement: 32% gives respectively 23 before and 40% and after it. The accuracies of the sets of data before and after stand above and below the global accuracy value and are not very different from it, which could simply mean they belong to the same stastical population.

During wet weather the global accuracy 52% for UV gives 49 and 41% before and after the adjustment change. Given those reduced improvements, it appears not worth considering two different calibration curves, the number of samples being moreover not very large.

The remarks concerning COD correlation versus VIS absorbance are analogous to those concerning SS versus this parameter. The accuracies improve in considering two different calibration curves before and after the adjustment change, for dry and wet weather. But the accuracies during dry weather (between 31 and 36%) are not significantly better than versus UV (38%). During wet weather the results are more heterogeneous : the accuracies are respectively 23 and 88% before and after adjustment change, the global accuracy being

Table 1 Accuracies for the determination of SS and COD versus visible and ultra-violet absorbances in relation with different types of measurement periods

	Samples number	SS = f(VIS) r^2	SS = f(VIS) 2CRV	SS = f(UV) r^2	SS = f(UV) 2CRV	COD = f(UV) r^2	COD = f(UV) 2CRV	COD = f(VIS) r^2	COD = f(VIS) 2CRV
Dry weather total period	114	0.56	99%	0.74	75%	0.80	38%	0.60	54%
Wet weather total period	33	0.93	50%	0.83	75%	0.92	52%	0.69	104%
Dry weather before adjustment change	77	0.64	92%	0.80	68%	0.85	32%	0.61	53%
Dry weather after adjustment change	37	0.78	65%	0.57	90%	0.74	45%	0.84	36%
Dry weather before feeding improvement	51	0.56	91%	0.85	53%	0.78	23%	0.50	35%
Dry weather after feeding improvement	26	0.94	30%	0.84	50%	0.87	40%	0.92	31%
Wet weather before adjustment change	22	0.98	31%	0.89	68%	0.93	49%	0.98	23%
Wet weather after adjustment change	11	0.96	31%	0.79	70%	0.91	41%	0.57	88%

52%. This heterogeneity and the reduced number of samples do not justify consideration of 2 different calibration curves. Finally because of reduced improvements for dry weather and heterogeneous results for wet weather, VIS absorbance appears less interesting than UV absorbance to determine COD.

Conclusion

The use of visible and ultraviolet absorbances for on line determination of the pollution parameters Suspended Solids (SS) and Chemical Oxygen Demand (COD) in combined sewers appears interesting.

The feeding system developed for this study improved the representativeness and reliability of the feeding line of the optical device. But its reliability could not be quantified in operational conditions for organizational and technical reasons. It would be interesting to validate this system for other measurement sites.

The optical parameter theoretically best adapted to the measurement of the corresponding pollution parameter confirms to be the best in practice, i.e. the visible absorbance for SS and the ultraviolet absorbance for COD. But the other optical parameter gives best results on some sets of data, which remains to be explained.

The accuracy of SS measurement (twice the Coefficient of Residual Variation corresponding to a 95% confidence level) using visible absorbance amounts to 65 and 30% respectively during dry weather before and after adjustment change. Given the SS mean 116 mg. l^{-1} for this period, this result compared to the 40% and 15% accuracies reported by the AGHTM Working Group for SS concentrations respectively smaller and larger than 100 mg. l^{-1} appears satisfactory, all the more as these standard method accuracies do not take into account the sampling error. The accuracy 31% during wet weather is also suitable.

The 45% accuracy for the determination of COD using UV absorbance appears less satisfactory when compared with the AGHTM Work Group figures (respectively 40 and 10% for concentrations smaller and larger than 80 mg. l^{-1}), the COD mean being 372 mg. l^{-1}. This less satisfactory result is probably due to the fact that UV absorbance measures both dissolved and particulate COD, the absorbance coefficients of which are different. Research is to be carried out to see whether taking into account another parameter, preferably visible absorbance, could improve this result.

Given the compensation of individual uncertainties, optical measurement of SS and COD is interesting to determine average or long term pollution loads, for example the yearly impact of urban stormwater discharges into receiving waters. With this kind of continuous and on-line measurement, it is possible to react in a short time to unexpected phenomena which could damage the environment or water treatment efficiency.

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