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► **To cite this version:**

M.N. Pons, A. Néron, B. Loison, P. Battaglia. Spectroscopy-based monitoring of periurban streams during rain events. Novatech 2007 - 6ème Conférence sur les techniques et stratégies durables pour la gestion des eaux urbaines par temps de pluie / Sixth International Conference on Sustainable Techniques and Strategies in Urban Water Management, Jun 2007, Lyon, France. hal-03248875

**HAL Id: hal-03248875**

**<https://hal.science/hal-03248875>**

Submitted on 3 Jun 2021

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## **Spectroscopy-based monitoring of periurban streams during rain events**

Caractérisation par spectroscopie de l'état de ruisseaux périurbains en temps de pluie

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### **RESUME**

La spectroscopie UV-visible et la spectroscopie de fluorescence sont des techniques rapides et sans réactif capables de faire ressortir les principaux traits de qualité d'une masse d'eau : il s'agit notamment de la DCO et des nitrates/nitrites pour la spectroscopie UV-visible, du tryptophane, des acides humiques et fulviques pour la fluorescence. La combinaison des techniques spectroscopiques avec des méthodes chimiométriques a été testée pour suivre la qualité de l'eau en fonction du temps (événements pluvieux) dans des ruisseaux périurbains. En général les deux premières composantes principales sont suffisantes pour tenir compte de plus de 90% de la variabilité totale des données originelles, pour un poids équivalent des deux techniques spectroscopiques.

### **ABSTRACT**

UV-visible and fluorescence spectroscopy are fast and reagent-free techniques able to depict different traits of water quality: COD and nitrates/nitrites for UV-visible spectroscopy, tryptophan-like, humic and fulvic substances for fluorescence in particular. The combination of spectroscopy and chemometrics has been tested to monitor the quality of water surface with respect to time (effect of rain events) and space (effect of industrial and urban discharges and diffused agricultural pollution) in periurban streams. In general the two first principal components are sufficient to account for more than 90% of the total variance contained in the original data sets, built with an equivalent weight of both spectra.

### **KEYWORDS**

Anthropogenic pollution; Synchronous fluorescence spectroscopy; Turbidity;  
UV-visible spectroscopy.

## INTRODUCTION

Periurban streams are assets in the city of tomorrow. These small water bodies usually come from agricultural or natural zones in the outskirts of urbanized areas. In the past they have been diverted to road ditches, covered, canalized, transformed in sewer networks. There has been a growing interest to clean and to restore them in order to enhance the presence of natural water in the city. Intensive sample analyses should be undertaken to assess their quality under dry weather conditions and during rain events.

The assessment of the water quality is based on classical parameters such as COD, BOD, and suspended matter. Optical techniques offer the possibilities to develop in-situ, on-line or portable sensors to assess rapidly the composition of wastewater and the quality of surface waters. They are reagent-free and are more environment-friendly than the analytical techniques based on wet chemistry. For several years UV-visible spectroscopy, which provides information on molecules with unsaturated bonds, has been used as a surrogate method for COD estimation on wastewater, based on the absorbance at 254 nm (Mrkva, 1983). The region of the spectrum around 215 nm is related to nitrates (Ferree and Shannon, 2001). Fluorescence spectroscopy has been suggested to detect pollution related to discharges of untreated sewage in water bodies, based on the tryptophan-like fluorescence ( $\lambda_{exc} \approx 280$  nm and  $\lambda_{em} \approx 340$  nm) (Baker, 2002). Two other fluorescence centres are in general examined to compare water samples: fulvic-like fluorescence (around  $\lambda_{exc} = 320-340$  nm /  $\lambda_{em} = 410-430$  nm) and humic-like fluorescence (around  $\lambda_{exc} = 370-380$  nm /  $\lambda_{em} = 460-480$  nm) (Baker et al., 2003). Based on these centres, Natural Organic Matter (NOM) has been extensively characterized using excitation-emission matrices (EEM) in rivers (Parlanti et al., 2002), coastal zones (Parlanti et al., 2002), seas (Sierra et al., 2005) or reservoirs (Goslan et al., 2004). Finally turbidity is related to particulate matter.

These techniques have been applied to the monitoring of periurban creeks during rain events. The monitoring is based on sampling trips regularly organized along the creeks and for one of them by the set-up of two permanent monitoring stations. Comparison between classical and spectroscopy-derived parameters is presented.

The absorbance and fluorescence spectra are large datasets whose manipulation is not easy. Chemometrics provide tools to extract meaningful information either for analysis or fingerprinting and have been proposed in many applications dealing with EEMs (He et al., 2003; Li et al., 2004; Sikorska et al., 2005). Principal Components Analysis (PCA) belongs to these tools and is able to summarize the information contained in the full UV-visible and synchronous fluorescence spectra within a small number of variables. The method is applied here to datasets combining the synchronous fluorescence and the UV-visible spectra to monitor the temporal and/or spatial variability of the water quality of periurban streams.

## 1 MATERIALS AND METHODS

The main creek of interest (Grémillon) has a total length of about 5,9 km, corresponding to a watershed larger than 1200 ha. 25% of the surface is impervious (Figure 1). It is located in the eastern part of Greater Nancy. Upstream toward downstream, it crosses fields (crops such as wheat and rapeseed, cattle) (Zone A: sampling points 1 to 8), a residential area (individual homes) (Zone B: sampling

points 9 to 11), a small lake (Masserine) originally planned as a retention basin (Zone C: sampling point 12), and a mixed zone of small and medium companies (shopping malls, car dealers) and houses (Zone E: sampling points 13 to 17). The Grémillon is canalized underground in Zone D (between C and E) and Zone F, up to its junction with the Meurthe river, as well as in some locations for road crossings. Trips are organized every two weeks in average and daily in case of rain events. The two permanent stations are located at the interface between Zones A and B (station 1, sampling points 19 and 20) and at the beginning of Zone F (station 2, sampling point 18). Limnimeters have been installed. Flowrate, pH, conductivity and dissolved oxygen are permanently monitored, as well as nitrates for station 1 and ammonia for station 2. Automated samplers triggered by rain meters in the vicinity of the Grémillon enable to collect samples during rain events. Two other streams (Fléville Village, Prays), located in the western part of Greater Nancy, have been also monitored on a less frequent time basis.

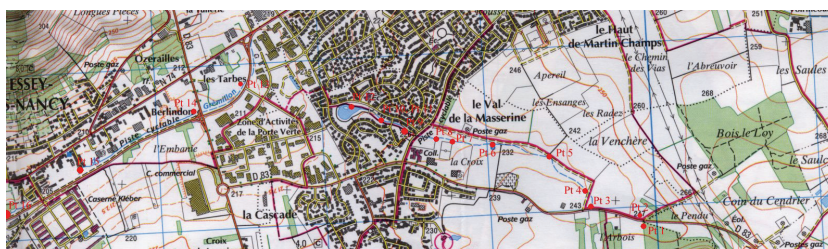


Figure 1: Localization of the sampling points along the Gremillon

Samples were collected in 500 ml polyethylene bottles, transferred to the laboratory within 2 hours and stored in the cold room. In the laboratory pH was measured with a Epoxy InLab 417 pH probe (Prolabo, Paris, France) connected to a Meterlab PHM220 (Radiometer Analytical, Villeurbanne, France). Electrical conductivity was measured with a CDC565 probe connected to a Meterlab CDM220 (Radiometer Analytical). Turbidity was obtained with a Hach DR/2400 spectrophotometer (Loveland, Colorado) at 450 nm, calibrated with a formazine solution. COD was determined using the HACH mini method or by the normalized method. After filtration, ammonium and nitrates were analyzed according to Nessler and cadmium reduction methods respectively on a HACH spectrophotometer. UV-visible spectrum was collected between 200 and 600 nm on a Anthelie Light spectrophotometer (Secomam, Domont, France) with a quartz cuvette (pathlength = 10 mm). Synchronous fluorescence spectra were collected on a Hitachi F2500 device with  $\Delta\lambda = \lambda_{em} - \lambda_{exc} = 50$  nm and a 2.5 nm slit size (SF50 spectra).

## 2 PRINCIPAL COMPONENTS ANALYSIS

In PCA, an original matrix of data  $\mathbf{X}$  ( $n$  rows or individuals and  $p$  columns or features) is approximated by the product of two smaller matrices,  $\mathbf{T}$  (score matrix) and  $\mathbf{L}$  (loading matrix):

$$\mathbf{X}(n, p) = \mathbf{T}(n, d) \times \mathbf{L}^T(d, p) + \mathbf{E}(n, p)$$

where  $\mathbf{T}$  is the transpose of a matrix,  $\mathbf{E}$  is the error matrix and  $d$  the number of principal components.  $d$  is determined so that a given percentage of the variance of the original data set is retained (Otto, 1999). The new coordinates are linear combinations of the original variables. These combinations can be used to build a

model that can be applied to supplementary data, which have not been included in the original data, for validation or comparison purpose.

PCA was programmed using Scilab (Inria, Rocquencourt, France). For each individual the feature vector consists in 26 SF50 data (from  $\lambda_{exc} = 250$  nm to 500nm, with a wavelength step of 10 nm) followed by 30 UV-visible data (from  $\lambda = 200$  to 350 nm, with a wavelength step of 5 nm). These values were selected in order to obtain feature vectors able to grasp the main characteristics of the spectra with a equivalent weight for both spectroscopic techniques.

### 3 RESULTS

Figure 2 presents typical UV-visible and synchronous fluorescence spectra obtained along the Grémillon on a dry weather day in winter (Jan 6th, 2006). Sampling points 1 and 2 were frozen on that day. Figure 3 summarizes the water quality data in dry weather spring conditions (April 12th, 2005) along the stream.

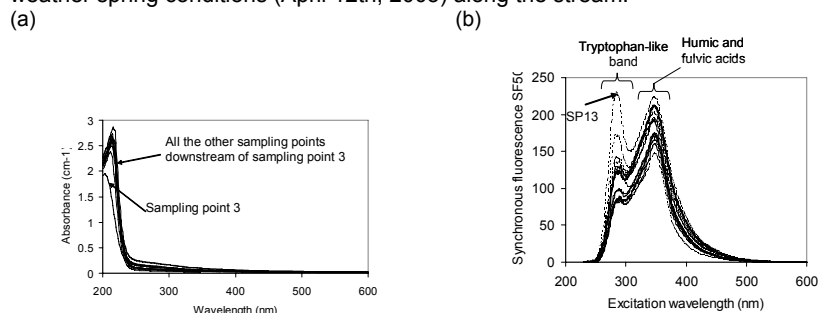


Figure 2: Typical UV-visible (a) and synchronous fluorescence (b) spectra along the Grémillon (dry winter weather)

After an increase in the Zone A at the junction with a tributary, pH decreases along the stream. The tributary collects water from cultivated fields and is a source of nitrates as shown by the increase in the absorbance at 215nm (Figure 2a and Figure 3c), in agreement with literature data (Royer et al., 2006). Conductivity increases along the stream, with a sudden increase between points 12 and 13. Except at the first sampling point, COD remains below 100 mg/L. COD variations are in agreement with the variations observed for the absorbance at 254 nm (Figure 2c). Most of the COD is soluble, as the turbidity is low in dry weather (< 50 NTU). A sharp increase in ammonia is observed at Point 13 (Figure 3b). It corresponds to a large increase of the tryptophan-like fluorescence, around  $\lambda_{exc} = 285$ nm, which is an indicator of the presence of untreated domestic sewage. An increase in nitrates is also observed at Point 13. The humic and fulvic like fluorescence (band around  $\lambda_{exc} = 350$ nm) can be considered as stable along the stream. From these results it can be concluded that the upper part of the Grémillon is mainly affected by agriculture and that untreated sewage discharged is observed in the underground section between Point 12 and Point 13. A good agreement is observed between the classical chemical parameters obtained by wet chemistry (N-NH<sub>4</sub>, COD and nitrates) and the spectroscopic techniques in dry weather conditions.

Figure 4 depicts the variations of the classical and surrogate parameters during a summer storm for samples collected at the station located downstream (station 2). The storm intensity was not sufficient to have station 1 autosampler triggered. The ammonia related to the discharge of untreated domestic sewage is flushed away by

the rain water. The T-like synchronous fluorescence variations matches those of ammonia measured by the on-line probe. On the contrary the F-like fluorescence, mostly related to soil nature, is diluted, as well as nitrates, as estimated by the absorbance at 215 nm. These data confirms the ability of spectroscopic techniques to monitor easily the water quality in any weather conditions.

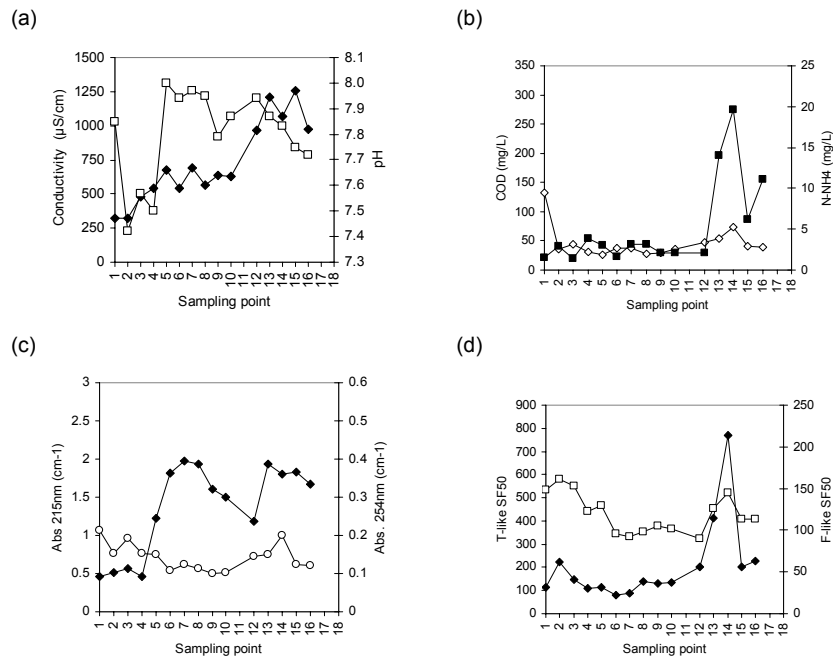
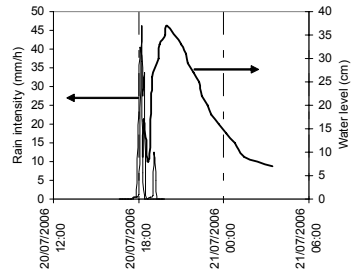


Figure 3: Variations of water quality parameters along the Grémillon stream; (a) Conductivity (◆) and pH (□); (b) COD (◇) and N-NH<sub>4</sub> (■); (c) Absorbance at 215 nm (◆) and 254 nm (○); (d) Tryptophan-like (◆) and fulvic-like (□) synchronous fluorescence.

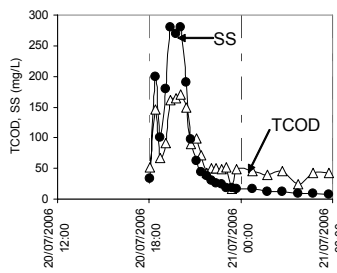
As spectroscopic techniques provide large amounts of data it is useful to try to summarize the information they contain by making use of chemometrics, such as PCA. In Figure 5, the PCA approach is applied to the monitoring of the water quality of two periurban stream over a period of 12 days. A rain event occurred on the fifth day. The sampling points are located some 100 m one from another. The Fléville Village stream crosses a village, when the Prays stream is flowing through farming lands (crops, cattle). The PCA was applied to the total set of data.

The water quality, which is similar for both streams at the beginning of the period of investigation, changes during the rain event, with the discharge of some tryptophan-like substances in the Fléville Village creek and the washing out of nitrates from fields in the Prays creek. During the drying out period, the water quality of both creeks returns gradually to its initial state, the return being slower for the Prays stream than for the Fléville Village stream.

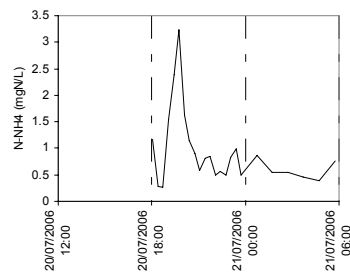
(a)



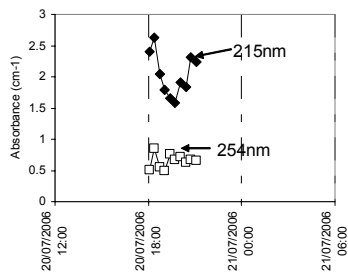
(b)



(c)



(d)



(e)

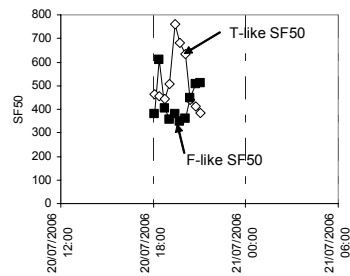


Figure 4: Summer storm: rain intensity and water level at the station 2 (a); Total COD ( $\Delta$ ) and suspended solids ( $\bullet$ ) (b); on-line N-NH<sub>4</sub> (mg/L) (c); absorbance at 215 nm ( $\blacklozenge$ ) and 254 nm ( $\square$ ) (d); T-like ( $\diamond$ ) and F-like synchronous ( $\blacksquare$ ) fluorescence (SF50)

The effect of winter rain in February 2006 on the Gremillon water quality is presented in Figure 6. The PC model was obtained on a dataset combining spectra from a dry weather day (January 31<sup>st</sup>, 2006) and a rain weather day (February 22<sup>nd</sup>, 2006). The resulting model was applied on the supplementary data (samples from 6 different sampling trips). In this example the consideration of the two first PC renders only 83.8 % of the total variance. The third PC has a weight (9.3 %) which is very close to the weight of the second PC (10.5%). For this reason three PCs were considered. A drastic change is observed in the three plots at the onset of the rain event (February 14<sup>th</sup>). PCA1s increase at that time then decrease towards its initial state for all the sampling points. PCA2s decrease for all the sampling points located before the covered section (where most of the sewage discharges are taking place) and increase for the downstream points. After February 17<sup>th</sup>, PCA2s tend toward their initial values. PCA3s decrease at the onset of the rain event but no return to the initial state is observed at the end of the tested period.

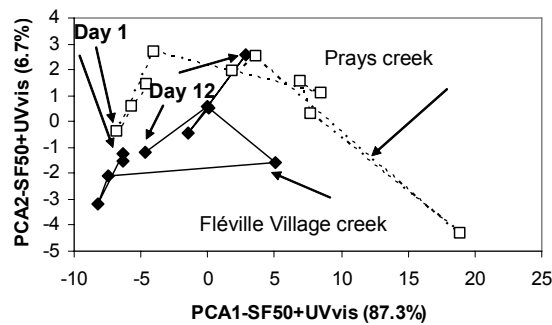


Figure 5: Monitoring of the Fléville Village creek and the Prays creek water quality during a rain event. Variance explained given in brackets.

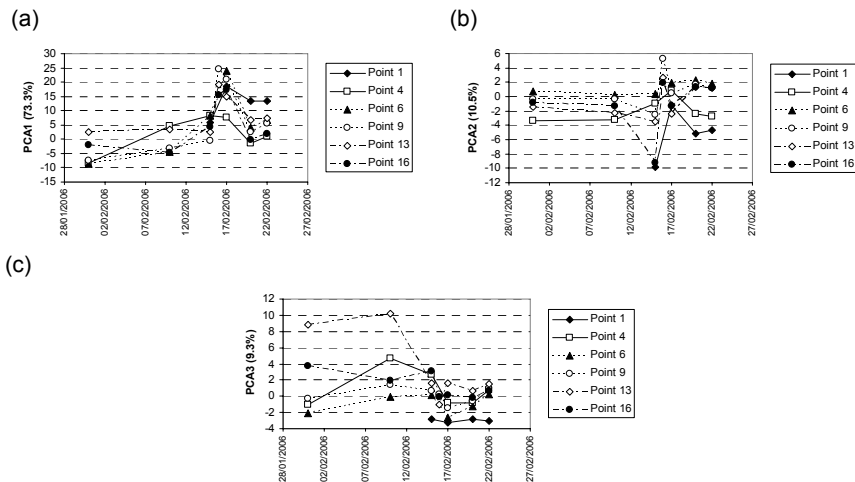


Figure 6: Monitoring of the effect of a rain event on the Gremillon water quality using the three first principle components (PCA1, PCA2 and PCA3). Variance explained in brackets.



#### 4 CONCLUSIONS

UV-visible and fluorescence spectroscopic techniques enable a fast and reagent-free characterisation of the water quality in surface water samples. Although they are usually used separately, they are very complementary as they depict different traits of water quality: COD and nitrates/nitrites for UV-visible spectroscopy, tryptophan-like, humic and fulvic substances for fluorescence. The large sets of data obtained can be examined by principle components analysis, which summarizes the information they contain and allows comparing rapidly the samples. In general the two first principal components are sufficient. The approach has been applied successfully to monitor the water quality with respect to time (effect of rain events) and space (effect of industrial and urban discharges and diffused agricultural pollution) in periurban streams.

#### 5 ACKNOWLEDGEMENTS

The authors thank N. Laurent, A. Maribas, L. Lucas, M. Kessler, Y.B. Pambou for collecting and analyzing the samples.

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