Spectrophotometric characterization of human impacted surface waters in the Moselle watershed

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ABSTRACT

In order to characterize the pollution discharged into the Moselle River and some of its tributaries, spectroscopic techniques, namely UV–vis spectroscopy and synchronous fluorescence spectroscopy, have been combined. UV–visible spectra were analysed using the maximum of the second derivative at 225 nm (related to nitrates), the SUVA$_{254}$ and E2/E3 indices (related to the nature of organic matter). Synchronous fluorescence spectra (Δλ = 50 nm) presented different shapes depending upon the type of pollution. The pollution results from anthropogenic activities: untreated domestic sewage due to misconnections in a periurban river, effluent from urban WWTPs, agricultural runoff (nitrates) in several streams, discharge from a paper mill (humic-like substances due to wood processing) and from steel mills (PAHs).

Key words | nitrate, paper mill, steel mill, synchronous fluorescence, UV–visible spectroscopy

INTRODUCTION

In 2000 the European Union established a general framework for the protection and management of water bodies (directive 2000/60/EC). In a watershed, river pollution results from the various uses of water. In order to achieve the final goal of good ecological and chemical status, river pollution sources should be identified and reduced.

Recently spectrophotometric methods have been proposed to characterize water pollution features. Turbidity, UV–visible and fluorescence spectroscopy are rapid and environment-friendly techniques. 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 absorbance at 254 nm (Mrkva 1985). The region of the spectrum around 215 nm is related to nitrates (Ferree & Shannon 2001). Many compounds such as proteins, steroids, phenols, oils, surfactants, vitamins, humic and fulvic acids, etc. emit fluorescence after excitation by visible or near-UV light. Thus the fluorescence spectrum of a water sample can bring information relative to the chromophoric substances it contains (Hudson et al. 2007), such as natural and anthropogenic organic matter. Fluorescence spectroscopy has been suggested to detect pollution related to discharges of untreated sewage in water bodies (Nam & Amy 2008; Kusakabe et al. 2008) or to cross-connections in water reuse systems (Hambly et al. 2010a, b), based on tryptophan-like fluorescence (λ$_{exc}$ ≈ 280 nm and λ$_{em}$ ≈ 340 nm) (Baker et al. 2005). Two other fluorescence centres are in general examined to compare water samples: fulvic-like fluorescence (around λ$_{exc}$ = 320–340 nm/λ$_{em}$ = 410–430 nm) and humic-like fluorescence (around λ$_{exc}$ = 370–380 nm/λ$_{em}$ = 460–480 nm) (Baker 2001). Although modern devices can provide excitation–emission matrices in a relative short time (~1 min according to Baker 2001), synchronous fluorescence (SF), with a constant difference between excitation and emission wavelengths have also been promoted (Miano & Senesi 1992; Ahmad & Reynolds 1995; Sierra et al. 2005): the SF spectra are better resolved than emission or excitation spectra and are fast to collect.

The goal of this contribution is to show the potentialities of the combination of UV–visible and fluorescence spectroscopy to detect different types of anthropogenic pollution, related to domestic, agricultural and industrial water use in a watershed. Examples are taken in the Moselle watershed, in the northeastern part of France (Figure 1(a)). From its source in the Vosges Mountains at the Bussang Pass, the Moselle River, as well as its tributaries, crosses areas of various anthropogenic activities: forestry, agriculture (crops such as wheat and rapeseed, cattle), industries (textile, paper and steel mills, salt extraction, power plants, etc.) as
well as urban centers (Remiremont (22,600 inhabitants), Epinal (89,500), Greater Nancy (410,500), Metz Métropole (430,000), Thionville (156,000), etc.). 1.5 billion m³ of water are extracted yearly from the Moselle watershed for potable water production. 70% of this amount is devoted to industrial use. 47% comes from surface waters and 15% from the Moselle itself. Greater Nancy consumes daily 60,000 m³ of water directly pumped from the Moselle. The quality of the surface water is therefore an important issue.

WATERSHED DESCRIPTION

The Moselle is a 550 km-long left tributary of the Rhine, flowing across France, Luxembourg and Germany (Figure 1(b)). Between its source and Nancy, 100 km downstream, it flows across forests and fields. The textile industry which was once flourishing along this part of its course is nowadays very limited and industrial activities are now mostly related to timber and pulp and paper. The largest paper mill (Norske Skog Golbey) is located near Epinal, some sixty kilometers upstream from Nancy. It produces about 600,000 t of newspaper per year. After its junction with the Meurthe, a few kilometres north of Nancy, the Moselle flows across an industrial valley once devoted to coal and iron mines and steel mills. The mines are all closed and only a few steel mills are still active, especially in the Fensch valley. The Fensch, a 16 km long tributary of the Moselle, is fed by rainfalls and by water overflowing from the former ‘Mine de la Paix’ in Knutange. Part of this overflow is first used in the steel mills before being discharged into the Fensch. Nancy itself is located on the Meurthe, a 160 km long river, whose source is located in the Vosges Mountains. Gremillon (3.5 km) is one of the few remaining periurban rivers in Greater Nancy. It flows successively across three types of area: agricultural, residential and mixed (residential – commercial). Several sections have been piped. Just upstream of Nancy, on the Meurthe, lies a large industrial basin devoted to salt and sodium carbonate. The industrial effluents are first treated in large lagoons and finally discharged into the Meurthe, causing a strong increase of its salinity. The Madon is a 97 km long river, whose source is located in the Vosges Mountains (Monts Faucilles). It flows through a series of villages and small towns (the largest is Mirecourt with 6,000 inhabitants) in a landscape devoted to polyculture (cattle and crops). It joins the Moselle in Pont-Saint-Vincent.

MATERIALS AND METHODS

Sampling trips have been undertaken under various flow and weather conditions along the Moselle (0 to 100 km), two of its tributaries (the Madon and the Fensch) and the Grémillon. The samples were collected with a bailer from bridges or banks. Occasionally an automated sampler was used to collect samples over 24 h. They were stored in clean polyethylene bottles and quickly transported to the laboratory where they were kept at 4 °C until analysis. Turbidity, pH and conductivity were assessed on unfiltered samples. After filtration (pore size = 1.5 μm), UV–vis and synchronous fluorescence (Δλ = λ_em – λ_exc = 50 nm) spectra as well as excitation–emission matrices (EEMs) were collected. Based on the analysis of EEMs obtained on several samples, Δλ = 50 nm was found to be the best compromise to detect the various types of substances present in the samples. Δλ in the range 30 to 80 nm are commonly used in literature. Anions and cations were analyzed by ion chromatography (Dionex) and DOC on a Shimadzu VCHS.

Figure 1 | Localization of the watershed (a) and of the rivers under study (b).
RESULTS AND DISCUSSION

An agricultural river: the Madon

Figure 2 summarizes the results obtained along the Madon. A good correlation ($R^2 = 0.9$) is obtained between the second derivative of the UV–vis spectrum (observed at 224 nm) and the nitrate concentration measured by ion chromatography. The nitrate concentration increased quickly as the river quits the forest (at Le Void d’Escles) and flows across cultivated zones. Up to 14 mg NO$_3$/L are measured in the upper part of the river (up to Mattaincourt). Then the nitrate concentration decreases and levels off at about 3 mg NO$_3$/L. The improved quality downstream has permitted a small colony of European beavers to settle in Ambacourt.

The increase in conductivity along the course of the Madon could be due to pollution discharge, but the geological component (from granite and sandstone to Dogger limestone) should be taken into account. The concentrations in minerals such as calcium, sodium and magnesium increase from the source to the mouth. The SF50 spectra (Figure 3(a)) show two maxima, one related to T-like fluorescence ($\lambda_{exc} = 290$ nm) and the other one to H-like fluorescence ($\lambda_{exc} = 360$ nm) and a shoulder ($\lambda_{exc} \approx 325$ nm), which can be associated to fulvic substances. The T-like/H-like ratio increases slightly along the course of the river. Globally the fluorescence level is low, with a total fluorescence (integral of the SF50 spectrum between $\lambda_{exc} = 250$ nm and 600 nm) varying between 4,000 and 5,000 a.u., once the Madon has left the forest. The small increase of the T-like fluorescence could be due to untreated domestic sewage in the villages as well as some farm wastes (Baker 2002b). The average ammonium concentration along the Madon is 1 mg NH$_4$/L ($\sigma = 0.3$). No clear trend can be defined for the SUVA$_{254}$ ($\text{mean} = 2.97$, $\sigma = 0.79$). The E2/E3 index (ratio of the absorbance at 250 nm to the absorbance at 365 nm) increases from source to mouth.

A periurban stream: the Grémillon

The upper section of the Grémillon receives the runoff from agricultural activities (mainly crops, some cattle). The nitrates, whose concentration is calculated here by the second-derivative of the UV–vis spectrum method, are washed off from the fields. An increase of A$_{254}$ is
observed at sampling point 12 (corresponding to a small reservoir). Conductivity, total fluorescence and T-like/H-like SF50 increase between points 12 and 13. The shape of SF50 spectra collected along the Gremillon (Figure 3(b)) differs from those collected along the Madon. Two bands ($\lambda_{\text{exc}} = 290 \text{ nm}$ and $\lambda_{\text{exc}} = 350 \text{ nm}$) are clearly seen but there is no shoulder. This indicates a different nature of the H-like fluorescence. The changes observed between points 12 and 13 occur in an underground section, where several misconnections and defects have been found during visits. Untreated sewage is clearly discharged into the stream. T-like/H-like SF50 could reach values as high as 3 on some occasions. Figures 4 and 5(a) depict the variations of T-like and H-like SF50 as well as of ammonium during 24 h in one of the underground pipes (pipe G). T-like SF50 and
ammonium are correlated. The very large H-like SF50 observed in the middle of the night is here related to the discharge of greywater from a washing machine: optical brighteners contained in washing powders also fluoresce in that region (Westerhoff et al. 2001). The series of SF50 collected in another pipe (pipe T) in the same underground section revealed a series of shoulders attached to the T-like fluorescence band. Iridescent spots in the water transported by pipe T were seen when the automated sampler was installed and they led us to suspect the presence of gasoline or combustion by-products such as PAHs. Tests with gasoline and PAHs such as fluoreanthene show that these compounds could modify the appearance of the T-like band (Figure 6).

An industrial river: the Fensch

The deformation of the T-like band is also visible on the SF50 spectra collected along the Fensch river, especially in its downstream part, where it collects water used in the steel mills (Figure 7). Here again PAHs are suspected. The Fensch is known to be polluted by these substances (Jeanneau et al. 2008), especially near its mouth. Iridescent spots were also clearly visible during the March 24, 2009 campaign.

Due to the shape of the SF50 spectra, it is difficult to calculate a T-like/H-like SF50. It can be seen on Figure 8 that the total fluorescence increases drastically between sampling points S1 and F4, where the part of the mine water which is used for cooling in the steel mills starts to be discharged into the Fensch (Figure 8(a)). The other part of the mine water is directly discharged to the stream at point K1 and dilutes the pollution (nitrates). A good correlation is again obtained between the second derivative of the UV–visible spectrum (maximum at 225 nm) and the nitrates concentration measured by ion chromatography (Figure 8(d)). The mine water contains a lot of sulphates (Figure 8(c)). The average SUVA254 along the Fensch is 1.62 (σ = 0.79) and it is difficult to see a clear trend (Figure 8(b)). A slight global increase can be detected between point S11 and the mouth. E2/E3 is also globally increasing in that section. Absorbance around 270–280 nm is related to π–π* electronic transitions in aromatic structures, such as those found in PAHs. The increase of E2/E3

![Figure 6](https://iwaponline.com/wst/article-pdf/64/3/602/444282/602.pdf)  
**Figure 6** SF50 spectra of gasoline (a) and fluoreanthene (b). To facilitate the comparison the grey line corresponds to the SF50 spectrum of a wastewater sample.

![Figure 7](https://iwaponline.com/wst/article-pdf/64/3/602/444282/602.pdf)  
**Figure 7** SF50 spectra collected along the Fensch under two weather conditions. (a) Heavy rain conditions (March 24, 2009) and (b) Dry weather conditions (April 23, 2010).
in the downstream section is in agreement with the presence of PAHs (Jeanneau et al. 2008). The fluorescence index (ratio of the emission intensity at 450 nm to that at 500 nm for excitation at 370 nm) (McKnight et al. 2001) was measured for three sampling points (FI_{F18} (source) = 1.93, FI_{K0} = 1.99 and FI_{F1} = 2.06). An increase is observed between the source and the mouth. Further work is needed to relate these variations to specific anthropogenic inputs (domestic or industrial).

**A wild river: the Moselle**

The data presented in Figures 9 and 10 refer to a section of the Moselle. Between km 53 and km 93.4, the Moselle is considered to be a wild river, with a Natura 2000 protection area (European beaver, Great Crested Newt, etc). The SF50 spectra present three bands: T-like ($\lambda_{exc} = 290$ nm), F-like ($\lambda_{exc} = 325$ nm) and H-like ($\lambda_{exc} = 360$ nm). The total fluorescence is low except in the vicinity of the discharge points of the city WWTP (domestic pollution) and the paper mill. After the Golbey-Epinal zone it is close to its upstream value without ever going back to it. The strong H-like fluorescence is due to the humic substances derived from wood processing. The signature is different from the one observed in Kraft pulp mill effluent (Duarte et al. 2005) and is similar to that described by Baker (2002a). The sudden increase of E2/E3 at km 37.1 and km 53 can be related to the presence of small industrial discharges (small paper mill, agro-food plant). Between km 59 and km 93.4, SUVA$_{254}$, E2/E3, $A_{254}$, nitrates (UV$_{225}$) increase steadily, in response to the discharge of pollution directly into the Moselle or through its tributaries.

**CONCLUSIONS**

UV–visible spectroscopy and synchronous fluorescence were used to characterize the pollution (nitrates, organic matter) of various streams in the Moselle watershed. The method of the second derivative of the UV–visible spectrum was used to determine the nitrate concentration and gave good results on the different river matrices, even on the
highly polluted samples such as those of the Fensch. SUVA$_{254}$ and E2/E3 presented variations which need more work for full interpretation as natural as well as anthropogenic organic matter is present. Synchronous fluorescence spectra presented different shapes depending upon the river under study as well as the type of pollution. Pollution due to PAHs or related substances (gasoline) disturbs the tryptophan-like band usually associated with untreated domestic sewage. Optical brighteners contained in greywater participate in the humic-like fluorescence. Humic substances related to the processing of wood in paper mills are easily detected and their progressive disappearance in the river (due to dilution or photolysis (Carvalho et al. 2009)) could be monitored.

Although several points could still be discussed and the understanding of the underlying phenomena related to UV–visible and fluorescence spectroscopies improved, these techniques have been and are currently used in several projects related to the improvement of the surface water quality in the Moselle watershed.

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**REFERENCES**


