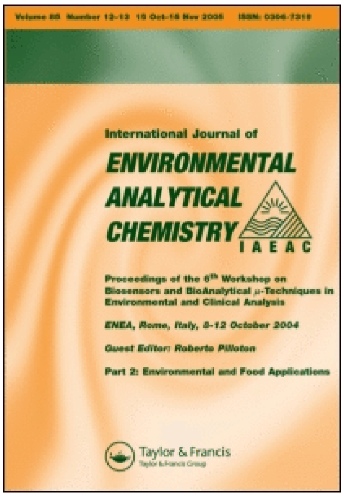

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Rapid estimation of TOC in a marine urban sewage area by UV spectral deconvolution

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A simple and rapid procedure for on-site qualitative and quantitative analysis of organic matter from discharges of municipal wastewater in seawater has been developed. This method is based on the knowledge of the UV signal of both seawater and anthropogenic absorbing matter and on the mathematical deconvolution of the sample spectrum using reference spectra. The main application is the estimation of TOC at the direct outlet of the discharge. This quantitative application is obviously limited by the nature of organic compounds, but the UV estimation allowed us to have an overview of the composition and evolution of organic matter into the polluted area. The application of this procedure has been carried out to study the wastewater dilution into an area receiving urban discharges. Experiments showed satisfactory analytical features with a range of TOC values from 75 to 1500 μM C, and the comparison of the results with those obtained by reference method presented a reasonable correlation ($r^2 = 0.9636$) in the marine discharge. The results have also allowed us to quickly estimate the plume evolution at the sea surface and in depth. This alternative method could be integrated in a portable device for on-site analysis and multiplication of measurements for relevant results, or in a continuous flow analyser.

Keywords: UV spectral deconvolution; TOC; Seawater; Urban sewage

1. Introduction

On the eastern French Mediterranean coast, small towns are not all equipped with wastewater treatment plants (WWTP), and when they exist, they are often under-equipped when the population increases during the summer. The rocky coasts in the

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area are not suitable for building or extending WWTPs, and the discharges of urban wastewaters constitute one of the principal sources of coastal marine pollution [1], and the source of serious problems of public health and degradation of seawater and coastal-ecosystem quality.

The quality of receiving seawaters can be evaluated by various physical, physico-chemical, and biological parameters such as total, dissolved, or particulate organic carbon (TOC, DOC, POC). The TOC is a better-adapted parameter for the determination of organic pollution of seawater and wastewater, and probably the most commonly used worldwide. The TOC determination can be achieved by high-temperature catalytic oxidation (HTCO, with various detection methods) or by chemical oxidation coupled or not with UV irradiation [2]. Some HTCO techniques have been optimized for shipboard measurements [3], but these analytical procedures are difficult and time-consuming. Usual HTCO or chemical oxidation methods require discrete sampling and intensive analytical calibration, and are thus not easily adaptable to on-site analysis.

In this way, different studies have reported the use of UV spectrophotometry for seawater analysis, especially for nitrate determination and organic matter study. For example, the determination of DOM or DOC and the qualitative follow-up of organic matter have been carried out by 220 nm [4], 250 nm [5], or 254 nm [6] absorptiometry, by absorbance ratio [7, 8] or by the study of isosbestic points [9]. A multiwavelength procedure was proposed for ion determination (nitrate, bromide, sulphide, etc.) [10] but rarely for organic-matter quantification in seawater.

Recently, research has focused on dissolved organic matter (DOM), which represents the largest fraction of the organic carbon pool in the ocean, and from which a major part is absorbing and is known as chromophoric dissolved organic matter (CDOM). A number of researchers have studied the relation between DOC or TOC and CDOM [11, 12], spatial and seasonal variations [13], and optical properties of CDOM [14]. Time-resolved and steady-state fluorescence (or absorbance) measurements, by *in situ* or remote sensing techniques, were used in these studies to characterize CDOM. A good correlation between CDOM and DOC or TOC concentration and a linear inverse relationship to salinity have often been observed. CDOM measurements are well adapted to the characterization of terrestrial inputs [15] to the rapid mapping of wide geographical areas and to the study of production or degradation of dissolved organic matter by photochemical [16, 17] and biochemical processes in oceans. However, CDOM measurement does not seem to be adapted to the study of urban sewage at sea, which can be the source of specific compounds such as surfactants [18].

In this article, a procedure for the fast estimation of TOC in marine areas receiving urban sewage is described. The TOC determination was achieved by the exploitation of UV response of samples related to well-known reference spectra. The reference spectra and deconvolution parameters are discussed, and the results are compared with TOC reference method measurements. The analytical tool developed herein was used to monitor Marseille sewage in the discharge marine area of Cortiou creek (France). The results were compared with the mapping of iron in the studied area, chosen as an anthropogenic tracer (ferric chloride used in WWTP for the coagulation-flocculation process).

2. Experimental

2.1 *Sampling processing*

Three cruises were conducted from February to May 2004 in Cortiou creek where two sewers collecting urban wastewater and runoff waters of the urban area of Marseille are discharged at the sea surface. Seawater samples were collected from multiple depths at a series of stations located on three transects (A, B, and C), according to the bathymetry and the direction of the wind during the cruise considered (figure 1): transects A and B correspond to a north wind, which generates upwellings and a circulation of the plume towards the south-east under the combined action of the currents and the wind; transect C characterizes a fine weather or a light east wind, where the plume is preferentially oriented from east to west by the Liguro-Provençal current. Two reference stations were chosen 10 km from the urban discharge. Table 1 presents the physico-chemical characteristics of the stations located on transect A, as an example, and reference stations during the cruise conducted on May 2004. The results obtained during sampling on transects B and C presented similar profiles.

Surface and deep samples were collected in polyethylene bottles at the different stations and kept in the dark at 4°C until analysis (about 2 days). In-depth sampling was carried out using acid-washed 1 L Go-Flo® type PVC bottles deployed on a wire.

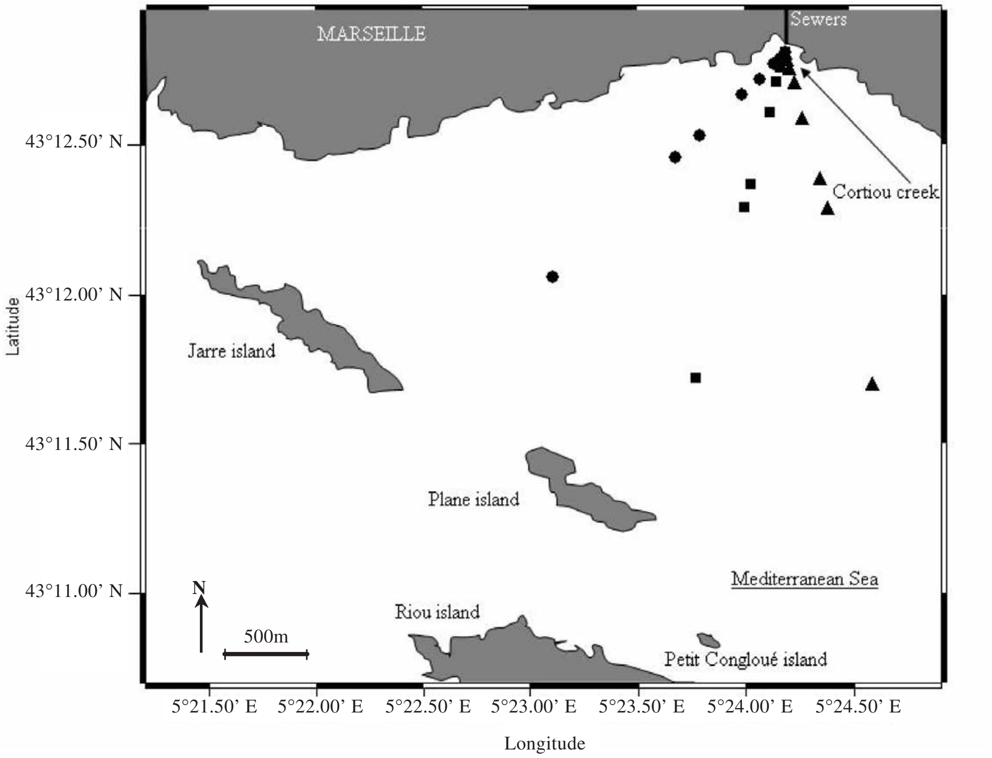

Figure 1. Locations of sampling stations along transect A (▲), B (■), and C (●).

Table 1. Physico-chemical characteristics of stations located on transect A and reference stations, in Cortiou Creek, France.

Stations	Latitude north	Longitude east	Distance from discharge point (m)	Depth (m)	Salinity (g L^{-1})	Iron (μM)
A10	43°12.81′	5°24.18′	10	0	31.3	3.52
A50	43°12.79′	5°24.19′	50	0	33.2	3.41
				2	35.3	0.19
				5	37.5	<0.1
A100	43°12.76′	5°4.20′	100	0	34.1	3.34
				2	35.1	0.27
				5	37.6	<0.1
A200	43°12.71′	5°4.22′	200	0	36.2	3.04
				2	36.1	1.09
				5	37.3	<0.1
				7	37.4	<0.1
				10	37.5	<0.1
A400	43°12.59′	5°24.26′	400	0	36.5	3.01
				2	37.2	0.22
				5	37.3	0.18
				7	37.5	0.9
				10	37.5	0.17
A800	43°12.39′	5°24.33′	800	0	35.9	3.71
				2	36.2	0.31
				5	36.9	0.41
				7	37.5	0.27
				10	37.5	<0.1
A1000	43°12.29′	5°24.38′	1000	0	36.6	3.69
				2	37.5	0.36
				5	37.5	0.29
				7	37.4	0.21
				10	37.5	<0.1
A2000	43°11.76′	5°24.53′	2000	0	37.5	0.38
				2	37.4	0.21
				5	37.5	0.18
				7	37.5	<0.1
				10	37.5	<0.1
R1	43°07.50′	5°26.35′	10 000	0	37.5	<0.1
				2	37.5	<0.1
				5	37.5	<0.1
				7	37.4	<0.1
				10	37.5	<0.1
R2	43°08.60′	5°19.10′	10 000	0	37.5	<0.1
				2	37.5	<0.1
				5	37.4	<0.1
				7	37.5	<0.1
				10	37.5	<0.1

A preliminary UV spectroscopy study on unfiltered and filtered samples (Millipore 1 μm and 0.45 μm pore), collected in a zone far away from the sewage, has shown that the particulate and colloidal phases are negligible. TOC and iron measurements and UV spectroscopy were thus carried out on unfiltered samples. The samples for TOC measurements were acidified with phosphoric acid (1.25 mL of H_3PO_4 50% v/v, added to 250 mL of samples) and then purged with pure nitrogen for 10 min, and samples for iron measurements were acidified with hydrochloric acid (0.5 mL of HCl 36% v/v, added to 100 mL of samples). Samples for UV spectroscopy were maintained without acid.

In order to minimize organic contamination of samples [19], the polyethylene and PVC bottles were previously cleaned with HCl 0.25 N and thoroughly rinsed with deionized water (MilliQ, Millipore, $\rho > 18\,\mathrm{m\Omega\,cm}$).

2.2 *TOC determination*

Total organic carbon (non-purgeable organic carbon, NPOC) measurements were made using high-temperature catalytic oxidation techniques (Shimadzu TOC 5050A). The pretreated sample was injected (50 µL) into the TOC-5050A furnace filled with an Al_2O_3/Pt preconditioned catalyst (Shimadzu). The combustion was carried out at 680°C, and the combustion products were carried by high-purity oxygen (Linde Gas) through an infrared detector, which performed a CO_2 analysis. Each sample was injected three times, and the average was reported as the total organic carbon value (TOC, in µM C). Up to five injections were performed if the coefficient of variation was greater than 3%. The response of the detector was linear and was calibrated with potassium hydrogen phthalate solutions (Shimadzu) of a well-known TOC concentration before analysis of the samples. The instrument blank was $15.1 \pm 2.7\,\mu\mathrm{M}$ over the entire study.

2.3 *Iron determination*

Atomic absorption spectrometry measurements of iron were carried out on a Perkin-Elmer 1100B spectrometer equipped with an HGA700 graphite furnace. A Perkin-Elmer iron hollow-cathode lamp was operated at 25 mA. Argon flow was $300\,\mathrm{mL\,min^{-1}}$ except during sample atomization ($50\,\mathrm{mL\,min^{-1}}$). Pyrolytically coated graphite tubes were used.

Furnace settings were: drying at 110°C, ramp for 10 s, holding for 30 s, cracking at 800°C, ramping for 10 s, holding for 30 s, atomizing at 2400°C, with no ramp and holding for 5 s; then, cleaning at 2600°C with a ramp for 1 s and holding for 2 s.

2.4 *UV spectroscopy*

2.4.1 Apparatus. UV spectra of undiluted samples (three replicates) were recorded using a single-beam Secomam Anthelie spectrophotometer (Alès, France) controlled by UVPro® software (Secomam). The spectra acquisition was carried out between 200 and 350 nm, with 1 nm bandwidth and a scan speed of $1800\,\mathrm{nm\,min^{-1}}$. The baseline was measured on deionized water and renewed for samples of each sampling station (approximately 15 spectra were thus processed with a given baseline). Cells were made of quartz suprasil (Hellma) with an optical pathway of 10 mm.

2.4.2 UV spectra deconvolution (UVSD). The shape of any UV spectrum of seawater (S_w) can be considered as a vector whose components for n wavelengths are the absorbance values. This column vector can be mathematically expressed as a linear combination of i reference spectra ($\mathrm{Ref}_1, \ldots, \mathrm{Ref}_i$) related to characteristic states or compounds of seawater [20]. The sample absorbance at each wavelength can thus be computed as a linear combination of the absorbances of reference spectra at the same wavelength by following the relation:

$$S_{\mathrm{w}} = \sum_{i=1}^{n} a_i \cdot \mathrm{Ref}_i \pm r, \tag{1}$$

where a_i is the contribution coefficient of the concerned reference spectrum, and r is the spectrum restitution error.

The calibration of the method consists in a multiple linear regression between measured TOC values (reference method) and computed a_i contribution coefficients, allowing the determination of the PAR*i* value of each reference spectrum. This calibration defines a parameter file which is used for the quantification of TOC associated to an unknown sample spectrum, computed from equation (1):

$$P_{\mathrm{S}} = \sum_{i=1}^{n} a_i \mathrm{PAR}i \pm r, \tag{2}$$

where PAR*i* denotes the values associated with the reference spectra ($\mathrm{Ref}_1, \ldots, \mathrm{Ref}_i$), and r is the error on the computation.

The TOC quantification by the UV spectral deconvolution (UVSD) procedure was achieved using a two-step procedure: after a first deconvolution procedure carried out with the i selected reference spectra, the q negative contribution coefficients computed are set to zero. Then, a second deconvolution procedure is applied with $i-q$ reference spectra (removal of negative contributing reference spectra), allowing the determination of other contribution coefficients. This two-step deconvolution computation was also used by Escalas *et al.* [21]. The calculations were performed with UV-Pro® software (Secomam) but would have been performed with any commercial spreadsheet.

In this study, two reference spectra selection methods have been applied in order to achieve UVSD procedure: automatic and semi-deterministic selection. In the first procedure, the reference spectra are statistically chosen by UVPro software using a Gaussian method [9]. This method allows the separation of the most independent spectra representing characteristic absorbing compounds or groups of absorbing compounds inside a set of seawater samples. In the semi-deterministic procedure, several reference spectra are selected in a deterministic way according to knowledge related to the type of water studied. These are the spectra of specific compounds known to be present in studied water, such as nitrate or detergents. The other reference spectra are chosen by studying real sample spectra of various phases (dissolved, colloidal and particulate) or by isolation of characteristic UV response of compounds or groups of compounds.

3. Results and discussion

3.1 *UVSD procedure*

The discrimination of organic matter in seawater was tested according to two models, M0 and M1, respectively resulting from the automatic and semi-deterministic procedures for reference spectra selection. In both cases, the deconvolution computation was carried out in the 220–350 nm range, to strongly reduce the interferences of major ions, especially of chlorides and bromides.

3.1.1 Automated reference spectra selection (model M0). The number of reference spectra in the automatic selection procedure can be selected manually between 2 and 8. The reference spectra are selected by a step-by-step regression. The number of reference spectra is increased step by step, and the corresponding model is evaluated in each stage. In this study, the optimum number of reference spectra selected by this method is 2. In order to identify and validate these reference spectra (M0-SW1 and M0-SW2), these latter were standardized and introduced into a set of real-sample standardized spectra. Each spectrum is standardized, i.e. the sum of the absorbance values of the exploited wavelength range (220–350 nm) is fixed in order to attribute the same area to all spectra [22].

For a small acquisition step (e.g. 1 nm), the standardization of a given spectrum consists in a computation of a normalized absorbance $A_{\mathrm{N}}(\lambda)$ following the relation:

$$A_{\mathrm{N}}(\lambda) = A(\lambda)\frac{N}{\sum_{\lambda=220}^{350} A(\lambda)} \tag{3}$$

where N is the value of the chosen norm ($N = 10$ in this study). The standardization procedure can be carried out using a commercial spreadsheet software.

This standardization procedure corresponds to a dilution compensation and reveals on figure 2 the presence of an isosbestic point closed to 234 nm. This isosbestic point indicates the presence of two independent major mixtures made of absorbing compounds in changing proportions [22]. The reference spectra M0-SW1 and M0-SW2 correspond to the two extremes of real-sample spectra, i.e. to reference seawater and highly polluted seawater (closed to the sewage), respectively.

3.1.2 Semi-deterministic reference spectra selection (model M1). The semi-deterministic spectra deconvolution procedure requires several reference spectra to be defined, which will be either characteristic of specific compounds or a group of compounds with a significant absorbance, or representative of previously selected particle phases, as described in previous works on urban sewage spectra restitution [23].

Three types of reference spectra can be taken into account in this study: spectra intended for the restitution of the mineral and organic matrix of uncontaminated seawater, constituting a spectral background; spectra defined for the restitution of anthropogenic organic matter; and spectra allowing us to take into account the potential existence of a few specific compounds (nitrate and detergents).

As shown above, UV spectra of unfiltered and filtered seawater reference samples (sampling stations R1 and R2; see table 1) have shown that the particulate and colloidal phases are negligible. Moreover, the spectra of these reference samples have been compared with an artificial seawater spectrum (following the ASTM D1141 standard). Indeed, in seawater, anions, essentially bromide and chloride, are responsible for a very high absorbance in the 200–220 nm range. Consequently, the reference spectrum for the restitution of mineral and organic matter of seawater (M1-SW1) is representative

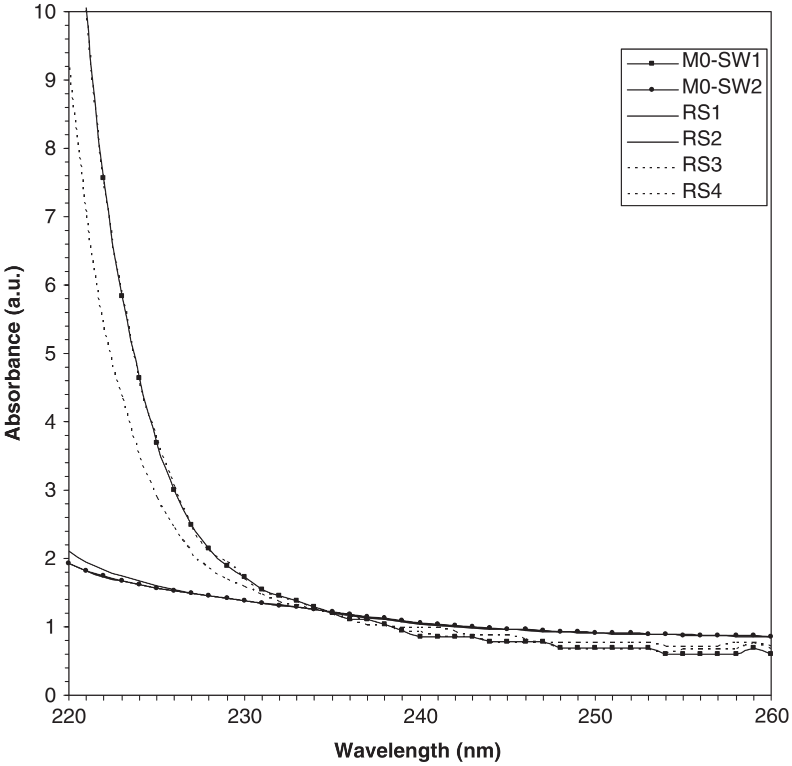

Figure 2. Reference spectra M0-SW1 and M0-SW2 in a set of real samples spectra (RS1 and RS2 are polluted seawater samples and RS3 and RS4 are reference seawater samples).

of saline matrix absorbance of seawater (220–240 nm range) and absorbance background above 240 nm due to dissolved natural organic matter.

The anthropogenic organic matter linked to urban sewages and likely to be present in marine environment was already studied in previous works [20]. In this study, fractionation was limited to the particulate (M1-SW2) and dissolved (M1-SW3) phases, separated by filtration with 0.45-μm-pore filters. M1-SW2 and M1-SW3 were experimentally determined from a study of Marseille wastewater samples. The particulate phase is responsible for a diffuse absorbance, whereas the UV spectrum of dissolved phase shows a shoulder at about 280 nm.

Moreover, nitrates and surfactants, which present a maximum absorbance of about 220 and 225 nm, respectively, are compounds linked to the composition and the biological treatment of the sewage, and must be included in the model (respectively M1-SW4 and M1-SW5).

Figure 3 shows the sets of standardized reference spectra for models M0 (figure 3a) and M1 (figure 3b). The sets include two reference spectra selected by the automatic procedure (model M0) and five reference spectra for model M1 based on the semi-deteministic procedure selection. We can see that the reference spectra SW1 and SW2 of M0 model are very similar to the reference spectra SW1 and SW3 of M1 model respectively and are related to mineral and natural organic matter of seawater and anthropogenic organic matter.

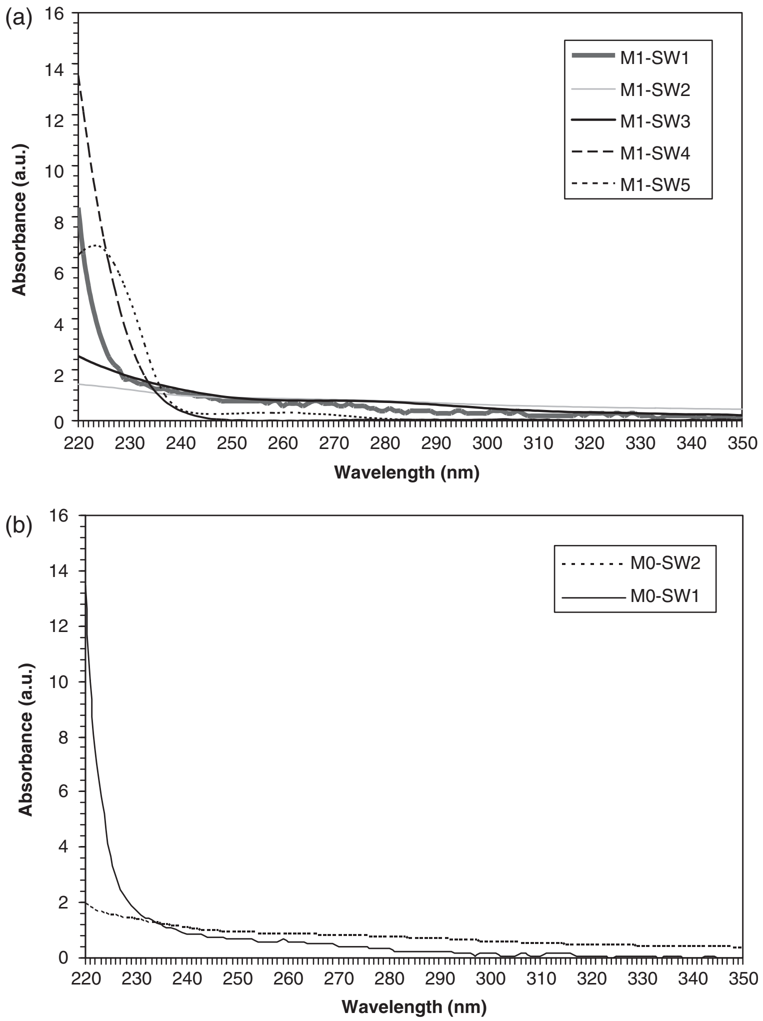

Figure 3. Sets of reference spectra for models (a) M0 and (b) M1.

3.2 *Establishment of parameter files*

The estimation of TOC by models M0 and M1 was achieved by a calibration step of parameter files as seen previously. The PAR*i* value of each reference spectrum of the linear combination (2) was determined by HTCO measurement (M1-SW1 and M1-SW5) or by stepwise linear regression (M0-SW1, M0-SW2, M1-SW2, and M1-SW3). The results are listed in table 2. The values have been computed using normalized reference spectra following relation (3).

The values attributed to M0-SW1 and M1-SW1 standardized reference spectra (191.7 and 250, respectively), which are linked to the mineral and natural organic matter of sea water, thus correspond to a real TOC concentration of 19.1 and 25 µM C and are in the range of those quoted from literature, between 10 and 80 µM C, according to the depth and area concerned [24, 25].

Table 2. TOC values (μM) attributed to normalized reference spectra for deconvolution computation (PARi coefficients).[a]

	Reference spectra				
	SW1	SW2	SW3	SW4	SW5
Model M0	191.7	1083.3	–	–	–
Model M1	250[a]	775	1241.7	0	1400[b]

[a] For the significance of reference spectra SW1–SW5 for both models, see figure 3.
[b] Measured values.

Table 3. Calibration of models M0 and M1 for TOC determination.

	Intercept[a]	Slope[a]	R^2	$r_{\min} - r_{\max}$ (r_{average})[b]	Standard error[a]	n
Model M0	−0.275	0.7955	0.9628	0.001–0.013 (0.003)	1.19	10
Model M1	0.221	0.8724	0.9787	0.001–0.004 (0.003)	0.99	10

[a] μM.
[b] Spectrum restitution error (a.u.).

The models M0 and M1 have been applied on some real samples ($n = 10$) collected during the first cruise (transect A), and the results were compared. As can be seen in table 3, the spectrum restitution error is acceptable in both models, i.e. the reference spectra selected by automated or semi-deterministic procedures are characteristic of the mixture between sewage and seawater. The semi-deterministic model M1 shows better results than the automated model M0, with regard to slope, correlation coefficient, and residual standard error. The automated procedure for reference spectra selection probably needs more sample spectra for statistical improvement. The model M1 was thus retained for further experiments. The TOC detection limit of the model M1 was found to be 75 μM C (three times the standard deviation of the blank). The detection limit found shows the limit of the method for 'unpolluted' seawater samples but is adapted to the study of the dilution plume of an urban sewage.

3.3 *Validation and discussion*

The TOC estimation with model M1 has been tested on several surface and depth real samples collected within 2 km distance from the sewage-discharge point (transects B and C). For surface and subsurface samples (depth < 5 m) near the sewage-discharge point ($n = 35$), the results are presented in figure 4. The TOC determination by proposed method is in agreement with the reference method for the samples collected on surface and subsurface ($r^2 = 0.9636$).

However, the same comparison between results obtained by proposed and reference methods, for samples collected at a depth below 5 m or on the surface far from the sewage, showed a great underestimation of TOC, even for samples with a measured TOC above the detection limit of the proposed method. We can propose three hypotheses to explain this underestimation of TOC.

First, the presence of unknown absorbing compounds would have induced higher restitution errors ($r > 0.1$). However, in this study, the restitution errors

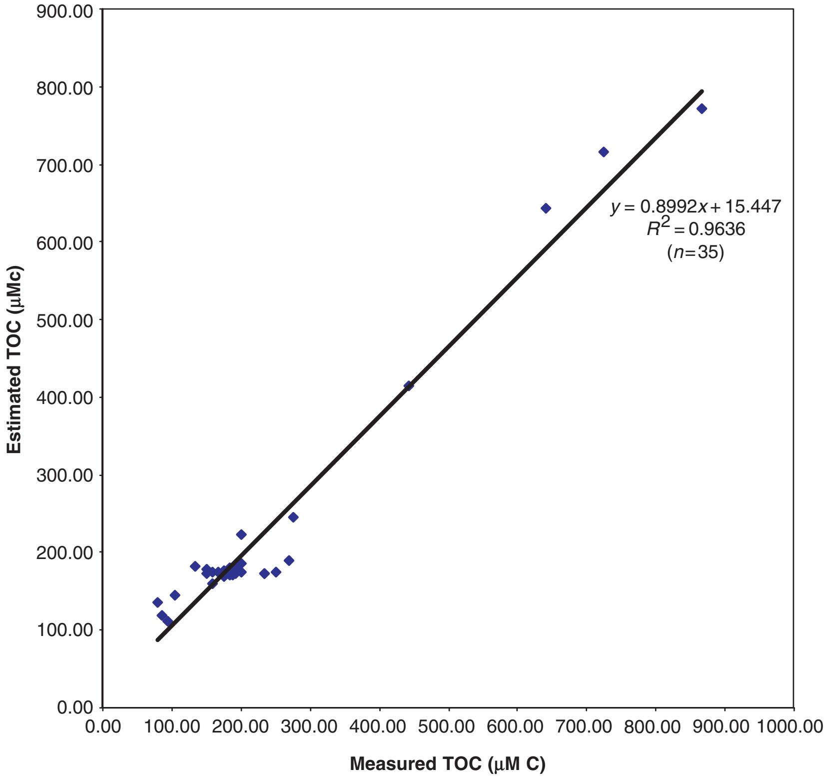

Figure 4. TOC estimated by UV spectra deconvolution *vs*. TOC measured by the HTCO method.

of deconvolution calculations showed no difference between surface and deep samples, near to or far from the sewage, allowing us to eliminate the hypothesis of the presence of an unknown absorbing compound and thus to validate the choice of reference spectra.

Second, a study of the evolution of deconvolution coefficients a_i *versus* measured TOC was performed for the underestimated samples. The study of the values of the coefficients a_i makes it possible to check the nature of the absorbing matrix of the samples. For example, for a given sample, if the coefficient a_1 is dominating, one can say that the sample presents an important saline matrix and a low level of anthropogenic organic matter, and inversely if the coefficients a_2 and a_3 are higher than a_1. As shown on figure 5, the coefficients were overall constant, implying the stability of the absorbing matrix characteristic of the samples. This absorbing matrix seemed to be composed of a saline and natural organic matrix of seawater (a_1) and of nitrates (a_4). We can see the very low levels of anthropogenic particular or dissolved organic absorbing matter (a_2 and a_3, respectively), except for some specific samples. Moreover, the TOC values measured are not correlated with coefficients, and we can thus confirm the good calibration of parameter file for the deconvolution model M1.

The underestimation of TOC, for deep samples or samples collected far away from the sewage, thus seems to be related in part to the presence of compounds which do not

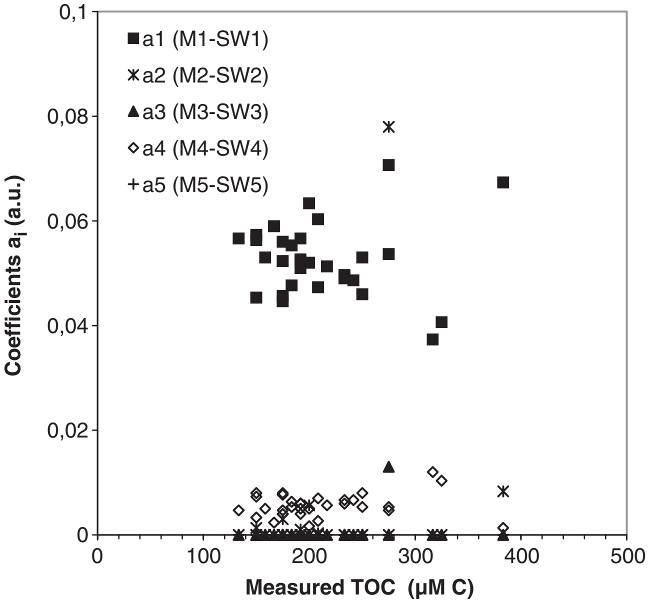

Figure 5. Scatter plot of deconvolution coefficients (a_i) against measured TOC.

absorb in the exploited wavelength range. These compounds can be natural organic compounds of seawater such as carbohydrates or degradation compounds of anthropogenic organic matter. Note that the underestimation can also be related to a high dilution of sewage in seawater.

4. Field applications

The UV spectral deconvolution method developed has been implemented in a portable UV spectrophotometer and used for field measurements during a survey of the Marseille agglomeration sewage. Two applications have been approached: a quantitative approach for the TOC concentration monitoring at sea surface and at depth along distance from the sewage; and a qualitative approach which allows information on sewage behaviour in seawater to be collated by studying the qualitative composition of organic carbon.

The TOC results were confirmed by the determination of iron as an anthropogenic tracer of urban sewage. Stations located near the sewage-discharge point showed iron concentrations up to 3 µM, whereas far away from the sewage-discharge point, reference stations showed concentrations below 0.18 µM.

We can see in figure 6(a) the horizontal dilution of the sewage plume over 2000 m, which is similar to results reported elsewhere [26]. The measured and estimated values of TOC are well correlated for surface and deep samples close to the sewage-discharge point. The horizontal profile of the surface sewage dilution was confirmed by the similar profile of iron. For samples collected far away from the sewage-discharge point, the correlation of measured and estimated TOC values is lower, especially for samples

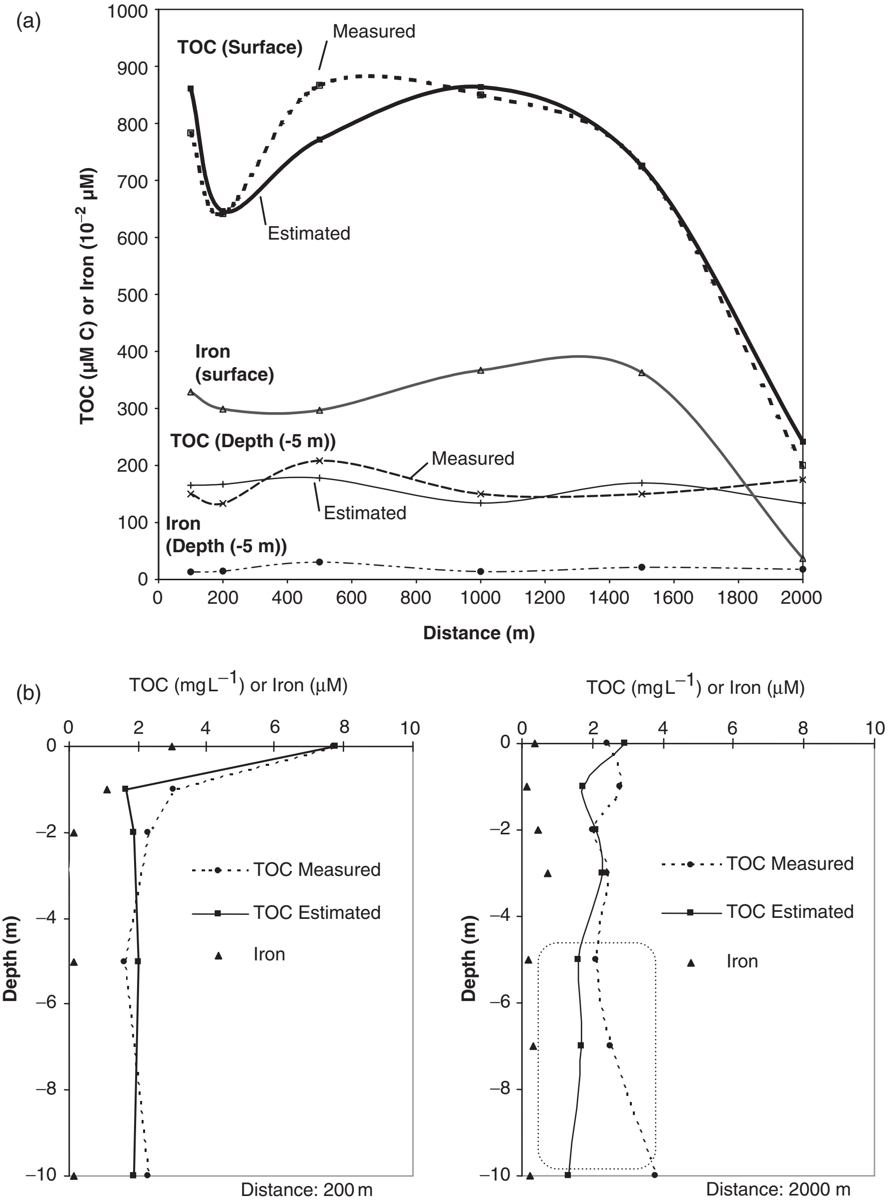

Figure 6. Evolution of TOC and iron along (a) distance and (b) depth.

below 5 m (figure 6b). Notice that in figure 6(b), TOC was reported as mg L^{-1} for a better comparison with iron quantification expressed in μM. As seen previously, the underestimation of TOC for these samples is probably due to non-absorbing compounds or to a great dilution of the sewage in seawater. However, the vertical profile of iron is similar to the vertical profile of estimated TOC, showing that even if the TOC were underestimated by the proposed method, the tool developed could provide useful information on sewage dilution.

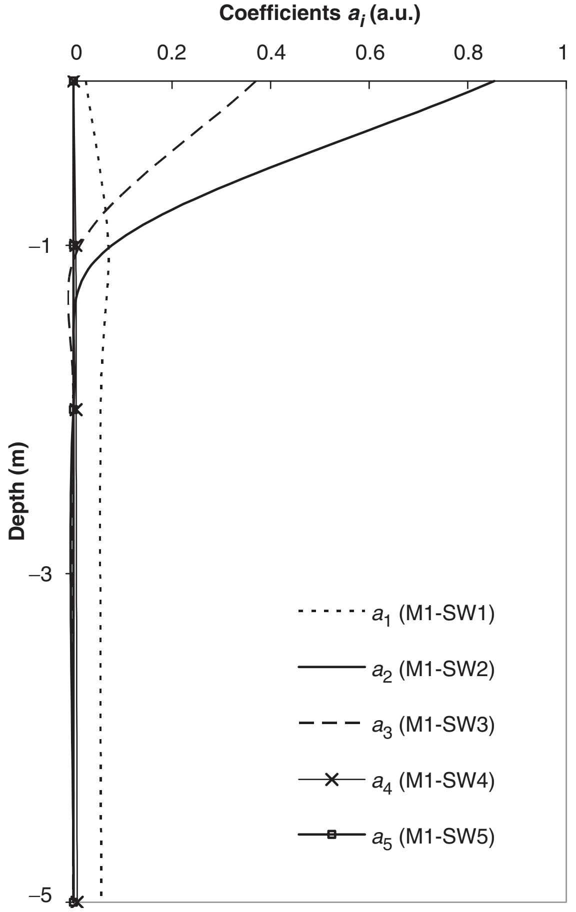

Figure 7. Evolution of a_i deconvolution coefficients at depth, 100 m from the sewage-discharge point.

This qualitative knowledge can be obtained by studying the deconvolution coefficients (a_i). For example, on figure 7, we can observe that the coefficients computed for samples near the sewage-discharge point (100 m) showed that the dilution of the sewage plume was limited to 1 m, and beyond this depth the coefficient a_1 (characteristic of the natural matrix of seawater) became higher than a_2 and a_3 (characteristic of the particular and dissolved phases of anthropogenic organic matter of urban sewage). This qualitative study of coefficients allowed the sewage dilution in the receiving marine area to be monitored in both vertical and horizontal axes.

5. Conclusion

The application of the proposed UV spectral deconvolution method for the TOC quantitative estimate in marine environments associated with urban sewage yielded encouraging results that could be improved by multiplying by the number of analysed samples. Two models of deconvolution procedure were tested, and the model which separates the contribution of the sewage in two spectra representing the particulate phase and the DOM seems to be the most effective. Moreover, with this approach, the method can be extended to estimate TSS and DOC in marine urban sewage areas.

With the the proposed UVSD method, it is possible to study the dilution of the urban sewage in the receiving marine zone in both vertical and horizontal axes but also to obtain information on the qualitative composition and evolution of organic matter. This alternative method, whose advantages such as speed, simplicity, portability, and low cost are obvious, makes it possible to consider on-site measurements with the possibility of integration with a portable device. The tool developed in this study was shown to be helpful for field applications in spite of the restriction induced by the limit of detection. In this respect, the method could be valuable for TOC monitoring in receiving seawater of urban sewage and space–time studies with multiple environmental applications.

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