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Direct DOC and nitrate determination in water using dual pathlength and second derivative UV spectrophotometry

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ABSTRACT

UV spectrophotometry is largely used for water and wastewater quality monitoring. The measurement/estimation of specific and aggregate parameters such as nitrate and dissolved organic carbon (DOC) is possible with UV spectra exploitation, from 2 to multi wavelengths calibration. However, if nitrate determination from UV absorbance is known, major optical interferences linked to the presence of suspended solids, colloids or dissolved organic matter limit the relevance of UV measurement for DOC assessment. A new method based on UV spectrophotometric measurement of raw samples (without filtration) coupling a dual pathlength for spectra acquisition and the second derivative exploitation of the signal is proposed in this work. The determination of nitrate concentration is carried out from the second derivative of the absorbance at 226 nm corresponding at the inflexion point of nitrate signal decrease. A short optical pathlength can be used considering the strong absorption of nitrate ion around 210 nm. For DOC concentration determination the second derivative absorbance at 295 nm is proposed after nitrate correction. Organic matter absorbing slightly in the 270–330 nm window, a long optical pathlength must be selected in order to increase the sensitivity. The method was tested on several hundred of samples from small rivers of two agricultural watersheds located in Brittany, France, taken during dry and wet periods. The comparison between the proposed method and the standardised procedures for nitrate and DOC measurement gave a good adjustment for both parameters for ranges of 2–100 mg/L NO3 and 1–30 mg/L DOC.

1. Introduction

Nutrient monitoring in water bodies is still a challenge. The knowledge of nutrient concentrations as nitrate and dissolved organic carbon (DOC) in freshwater bodies is important for the assessment of the quality impairment of water resources touched by eutrophication or harmful algal blooms for example. The export of these nutrients in freshwater is often characterized on one hand, by a high spatio-temporal variability regarding seasonal change, agricultural practices, hydrological regime, tourism and on the other hand, by the nature and mode of nutrient sources (punctual/diffuse, continuous/discontinuous) (Causse et al., 2015). In this context the monitoring of nitrate and DOC must be rapid and easy to use on the field and UV spectrophotometry is certainly the best technique for that, given the great number of works, applications and systems proposed in the last decades.

Nitrate monitoring with UV sensing is a much more mature technique than DOC assessment by UV because nitrate ion has a specific and strong absorption. Several methods are available for drawing a relationship between UV absorbance and nitrate concentration using wavelength(s) around 200–220 nm, usually after sample filtration to eliminate interferences from suspended solids. Considering the presence of potential interferences such as dissolved organic matter (DOM) in real freshwater samples, the use of at least two wavelengths increases the quality of adjustment. The absorbance measurement at 205 and 300 nm was proposed by (Edwards et al., 2001) and the second derivative absorbance (SDA) calculated from three wavelengths was promoted by Suzuki and Kuroda (1987) and Crumpton et al. (1992). A comparison of the two methods (two wavelengths and SDA) carried out on almost 100 freshwater samples of different stations in a 35 km^2 watershed, gave comparable data with ion chromatography analysis (Olsen,

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2008). Other methods based on the exploitation of the whole UV spectrum were also proposed in the last decades, namely for wastewater and sea water, with the aim of a better treatment of interferences. Several multiwavelength methods were thus designed such as the polynomial modelisation of UV responses of organic matter and colloids (Thomas et al., 1990), a semi deterministic approach, including reference spectra (nitrate) and experimental spectra of organic matter, suspended solids and colloids (Thomas et al., 1993), or partial least square regression (PLSR) method built-into a field portable UV sensor (Langergraber et al., 2003). Kröckel et al. (2011) proposed a combined method of exploitation (multi component analysis (MCA) integrating reference spectra and a polynomial modelisation of humic acids), associated to a miniaturized spectrophotometer with a capillary flow cell. More recently, a comparison between two different commercials in situ spectrophotometers, a double wavelength spectrophotometer (DWS) and a multiwavelength one (MWS) with PLSR resolution was carried out by Huebsch et al. (2015) for groundwater monitoring. The findings were that the MWS offers more possibilities for calibration and error detection, but requires more expertise compared with the DWS.

Contrary to UV measurement of nitrate in water, DOC is associated with a bulk of dissolved organic matter (DOM) with UV absorption properties less known and defined than nitrate. The study of the relation between absorbing DOM (chromophoric DOM or CDOM) and DOC has given numerous works on the characterisation of CDOM by UV spectrophotometry or fluorescence on one hand, and on the assessment of DOC concentration from the measurement of UV parameters on the other hand. Historically the absorbance at 254 nm (A254), 254 nm being the emission wavelength of the low pressure mercury lamp used in the first UV systems, was the first proxy for the estimation of Total organic carbon (Dobbs et al., 1972), and was standardised in 1995 (Eaton, 1995). Then the specific UV absorbance, the ratio of the absorbance at 254 nm (A254) divided by the DOC value was also standardised ten years after (Potter and Wimsatt, 2005). Among the more recent works, Spencer et al. (2012) shown strong correlations between CDOM absorption (absorbance at 254 and 350 nm namely) and DOC for a lot of samples from 30 US watersheds. Carter et al. (2012) proposed a two component model, one absorbing strongly and representing aromatic chromophores and the other absorbing weakly and associated with hydrophilic substances. After calibration at 270 and 350 nm, the validation of the model for DOC assessment was quite satisfactory for 1700 filtered surface water samples from North America and the UK. This method was also used for waters draining upland catchments and it was found that both a single wavelength proxy (263 nm or 230 nm) and a two wavelengths model performed well for both pore water and surface water (Peacock et al., 2014). Besides these one or two wavelengths methods, the use of chemometric ones was also proposed at the same time as nitrate determination from a same spectrum acquisition (Thomas et al., 1993); (Rieger et al., 2004); (Etheridge et al., 2014). A comparison of multiwavelengths exploitation methods for DOC determination including MLR/PLS was recently carried out by Avagyan et al. (2014) from the signal of a UV–vis submersible sensor with the recommendation to create site-specific calibration models to achieve the optimal accuracy of DOC quantification.

Among the above methods proposed for UV spectra exploitation, the second derivative of the absorbance (SDA) is rather few considered even if SDA is used in other application fields to enhance the signal and resolve the overlapping of peaks (Bosch Ojeda and Sanchez Rojas, 2013). Applied to the exploitation of UV spectra of freshwaters SDA is able to suppress or reduce the signal linked to the physical diffuse absorbance of colloids and particles and slight shoulders can be revealed (Thomas and Burgess, 2007). If SDA was proposed for nitrate (Crumpton et al., 1992), its use for DOC has not been yet reported as well as a simultaneous SDA method for nitrate and DOC determination of raw sample (without filtration). This can be explained by the difficulty to obtain a specific response of organic matter and nitrate, in particular in the presence of high concentration of nitrate or high turbidity that cause spectra saturation and interferences. In this context, the aim of this work is to propose a new method to optimize the simultaneous measurement of DOC and nitrate using both dual optical pathlength and second derivative UV spectrophotometry.

2. Material and methods

2.1. Water samples

Water samples were taken from the Ic and Frémur watersheds (Brittany, France) through very different conditions during the hydrological year 2013–2014. These two rural watersheds of 86 km^2 and 77 km^2 respectively are concerned by water quality alteration with risks of green algae tides, closures of some beaches and contamination of seafood at their outlet. 580 samples were taken from spot-sampling (342 samples) on 32 different subwatersheds by dry or wet weather (defined for 5 mm of rain or more, 24 h before sampling) and by auto-sampling (233 samples) during flood events on 3 subwatersheds. For wet weather, sampling was planned by spot-sampling before the rain, or programmed according to the local weather forecast to ensure a sample collection proportional to the flow. Samples were collected in 1 L polyethylene bottles (24 for auto-sampler ISCO 3700) following the best available practices. Samples were transported to the laboratory in a cooler and stored at 5^{+}_{-} 3 °C (NF EN ISO 5667-3, 2013).

2.2. Data acquisition

Nitrate concentration was analyzed according to NF EN ISO 13395 standard thanks to a continuous flow analyzer (Futura Alliance Instrument). Dissolved organic carbon (DOC) was determined by thermal oxidation coupled with infrared detection (Multi N/C 2100, Analytik Jena) following acidification with HCl (standard NF EN 1484). Samples were filtered prior to the measurement with 0.45 μm HA Membrane Filters (Millipore®).

Turbidity (NF EN ISO 7027, 2000) was measured in situ for each sample, with a multiparameter probe (OTT Hydrolab MS5) for spot-sampling and with an Odeon probe (Neotek-Ponsel, France) for auto-sampling stations.

Finally discharge data at hydrological stations were retrieved from the database of the national program of discharge monitoring.

2.3. UV measurement

2.3.1. Spectra acquisition

UV spectra were acquired with a Perkin Elmer Lambda 35 UV/Vis spectrophotometer, between 200 and 400 nm with different Suprasil® quartz cells (acquisition step: 1 nm, scan speed: 1920 nm/min). Two types of quartz cells were used for each sample. A short path length cell of 2 mm was firstly used to avoid absorbance saturation in the wavelength domain strongly influenced by nitrate below 240 nm (linearity limited to 2.0 a.u.). On the contrary, a longer pathlength cell (20 mm) was used in order to increase the signal for wavelengths outside of the influence of nitrates (>240 nm approx.). Regarding a classic UV spectrophotometer with a pathlength cell of 10 mm, these dual pathlength devices act as a spectrophotometric dilution/concentration system, adapted to a high range of variation of nitrate concentrations in particular.

2.3.2. Preliminary observation

Before explaining the proposed method, a qualitative relation between UV spectra shape and water quality can be reminded. Fig. 1 shows two spectra of raw freshwaters with the same nitrate concentration (9.8 mgNO3/L) taken among samples of the present work. These spectra are quite typical of freshwaters. If the nitrate signal is well identified with the half Gaussian below 240 nm, the one of organic matter responsible for DOC is very weak with a very slight shoulder above 250 nm. In this context, the use of SDA already proposed for nitrate determination (Crumpton et al., 1992) and giving a maximum for any inflexion point in the decreasing part of the signal after a peak or a shoulder can be useful. However, given the absorbance values above 250 nm, the use of a longer optical pathlength is recommended in order to increase the sensitivity of the method.

2.3.3. Methodology

The general methodology is presented in Fig. 2. Firstly, a UV spectrum is obtained directly from a raw sample (without filtration nor pretreatment) with a 2 mm pathlength (PL) cell. If the absorbance value at 210 nm (A210), is greater than 2 u.a., a dilution with distilled water must be carried out. If not, the second derivative of the absorbance (SDA) at 226 nm is used for nitrate determination. The SDA value at a given wavelength λ is calculated according to Equation (1) (Thomas and Burgess, 2007):

$$SDA_{\lambda} = k * \frac{(A_{\lambda-h} + A_{\lambda+h} - 2*A_{\lambda})}{h^2} \quad [1]$$

where A_{λ} is the absorbance value at wavelength λ, k is an arbitrary constant (chosen here equal to 1000) and h is the derivative step (here set at 10 nm).

Given the variability between successive SDA values linked to the electronic noise of the spectrophotometer, a smoothing step of the SDA spectrum is sometimes required, particularly when the initial absorbance values are low (<0.1 a.u.). This smoothing step is based on the Stavitsky-Golay's method (Stavitsky and Golay, 1964).

For DOC measurement, the SDA value at 295 nm is used if A250 is greater than 0.1 a.u. If A250 is lower than 0.1, the intensity of absorbances must be increased with the use of a 20 mm pathlength cell. After the SDA295 calculation, a correction from the value of SDA226 linked to the interference of nitrate around 300 nm is carried out. This point will be explained in the DOC calibration section.

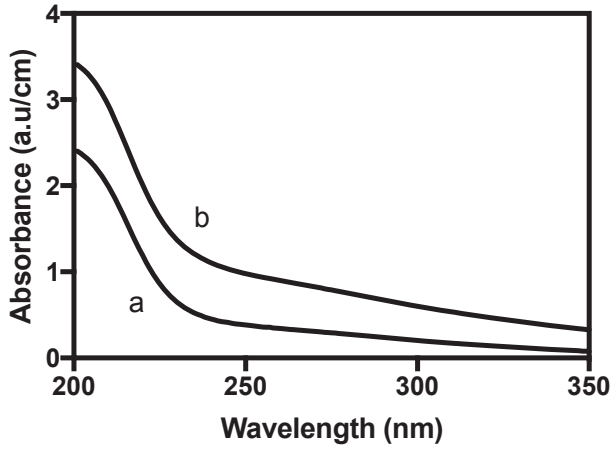

Fig. 1. Example of UV spectra of raw freshwaters with the same concentration of nitrate (9.8 $mgNO_3/L$) and different DOC values (10.9 and 18.3 mg C/L for sample "a" and "b" respectively).

2.3.4. Nitrate calibration

A mother solution of 100 mg NO_3^-/L was prepared from a Nitrate Standard solution Certipur at 1 g/L. Solutions of 2.5, 5.0, 10.0, 20.0, and 50.0 mg NO_3^-/L were prepared with UHQ water. Fig. 3 shows spectra and second derivatives of standard nitrate solutions. Nitrate strongly absorbs around 200–210 nm with a molar absorption coefficient of $8.63*10^5$ m^2/mol at 205.6 nm (Thomas and Burgess, 2007) and a maximum at 226 nm corresponding at the inflexion point of absorbance spectrum, is observed for the second derivative signal. However if nitrate strongly absorbs around 210 nm for concentration usually found in freshwaters (below 100 $mgNO_3/L$), a peak of absorbance can also be observed for higher concentrations of nitrate with a much lower molar absorption coefficient of $1.71*10^3$ m^2/mol at 301 nm (Thomas and Burgess, 2007).

From the results of SDA values and the corresponding concentration of nitrate, a calibration is obtained for nitrate concentration ranging up to 100 $mgNO_3/L$ (Fig. 4). This high value of nitrate concentration is possible thanks to the use of the 2 mm pathlength cell. Deduced from the calibration line, the R2 value is very close to 1 and the limit of detection (LOD) is 0.32 $mgNO_3/L$.

2.3.5. DOC calibration

For DOC calibration, the procedure is different from the one for nitrate given the absence of standard solution for DOC, covering the complexity of dissolved organic matter. A test set of 49 samples was chosen among samples described hereafter, according to their DOC concentration up to 20 mg C/L. The choice of the SDA value at 295 nm is deduced from the examination of the second derivative spectra of some samples of the test set (Fig. 5). Two peaks can be observed, the first one around 290 nm, and the second one less defined, around 330 nm (Fig. 5a). The maximum of the first peak is linked to the DOC content, but its position shifts between 290 and 300 nm, because of the relation between DOC and nitrate concentration, with relatively more important SDA values when DOC is low (Thomas et al., 2014). Considering that the measurement is carried out with a long optical pathlength for DOC, and that nitrate also absorbs in this region, its presence must be taken into account. On Fig. 5a the second derivative spectrum of a 50 $mgNO_3/L$ of nitrate presents a valley (negative peak) around 310 nm and a small but large peak around 330 nm. Based on this observation, a correction is proposed for the SDA of the different samples (Equation (2)):

$$SDA^* = SDAsample - SDAnitrate \quad [2]$$

Where SDA* is the SDA corrected, SDA sample is the SDA calculated from the spectrum acquisition of a given sample and SDA nitrate is the SDA value corresponding to the nitrate concentration of the given sample.

After correction, the second derivative spectra show only a slight shift for the first peak around 300 nm and the peak around 330 nm is no more present (Fig. 5b). From this observation, the SDA value at 295 nm is chosen for DOC assessment.

Finally, Fig. 6 displays the calibration relation between the SDA value at 295 nm corrected by nitrate (SDA^*_{295}) and the DOC concentration for the test set of 49 samples. The value of R^2 is 0.996 and the LOD is 1.14 mg C/L.

3. Results

3.1. Samples characteristics

For this work, a great number of samples were necessary for covering the different subwatersheds characteristics and the variability of hydrometeorological conditions all along the hydrological

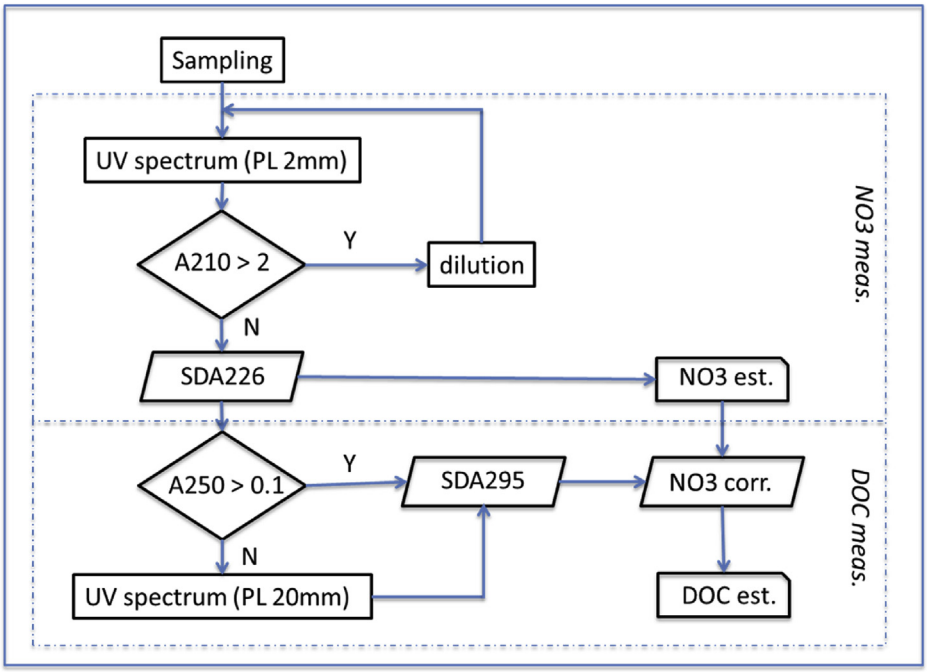

Fig. 2. General methodology.

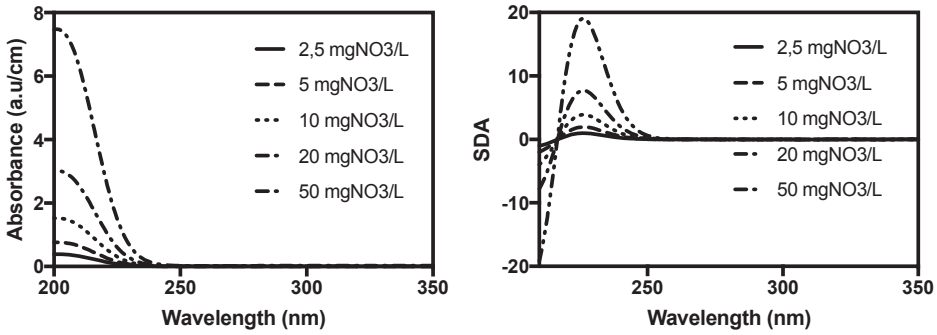

Fig. 3. Spectra of standard solutions of nitrate (raw absorbances left, and SDA right).

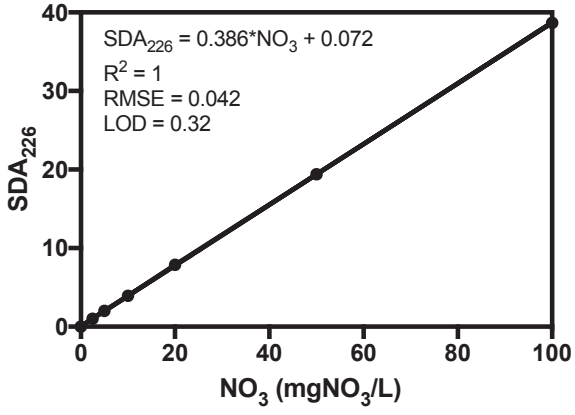

Fig. 4. Calibration line for nitrate determination from SDA at 226 nm (R^2 being equal to 1, 99% prediction bands are overlapped with the best fit line).

year. 580 samples were taken from 32 stations and the majority of samples were taken in spring and summer time with regard to the principal land use of the two watersheds and the corresponding agricultural practices, namely fertilization (Fig. 7). Nitrate and DOC concentrations ranged respectively from 2.9 to 98.5 mgNO3/L and from 0.7 to 28.9 mg C/L. The river flows were between 0.8 L/s and 6299 L/s and turbidity between 0.1 and 821 NTU, after the rainy periods.

3.2. Validation on freshwater samples

The validation of the method for nitrate determination was carried out on 580 samples (Fig. 8). The adjustment between measured and estimated values of nitrate concentration gave a R^2 greater than 0.99 and a RMSE of 2.32 $mgNO_3/L$. The slope is close to 1 and the ordinate is slightly negative (−1.68) which will be explained in the discussion section.

The validation of the method for DOC determination was carried out on 580 samples (Fig. 9). The adjustment between measured and estimated values of DOC concentration gave a R^2 greater than 0.95 and a RMSE close to 1 mg C/L. The slope is close to 1 and the ordinate is low (0.086 mg C/L).

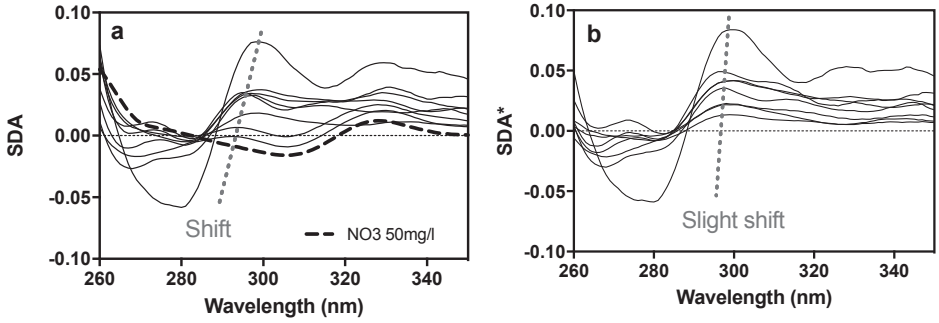

Fig. 5. Second derivative spectra of water samples without nitrate correction (5a with a spectrum of a 50 mgNO3/L nitrate solution, dotted line) and after nitrate correction (5b). Nitrate, DOC and turbidity of samples vary respectively from 5.1 to 49.8 mgNO3/L, 2.9 to 15.4 mg C/L and 4 to 348 NTU.

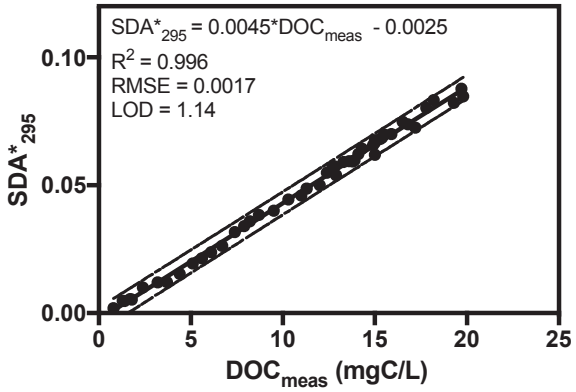

Fig. 6. Calibration between SDA at 295 nm corrected by nitrate (SDA^*_{295}) and DOC concentration (dotted lines define the 99% prediction band). DOC, nitrate, and turbidity of samples vary respectively from 0.8 to 19.8 mg C/L, 2.9–65.7 mg NO3/L and 4 to 348 NTU.

4. Discussion

4.1. Interferences

Except for DOC assessment for which the value of SDA at 295 nm must be corrected by the presence of nitrate, different interferences have to be considered in nitrate measurement. Nitrate absorbing in the first exploitable window of UV spectrophotometry (measurement below 200 nm being quite impossible given the strong absorption of dioxygen) the presence of nitrite with a maximum of absorption at 213 nm could be a problem. However the molar absorption coefficient of nitrite is equal to the half of the value of nitrate (Thomas and Burgess, 2007) and usual concentrations of nitrite are much lower in freshwaters than nitrate ones (Raimonet et al., 2015). For other interferences linked to the presence of suspended solids or colloids (for raw samples) and organic matter for nitrate determination, Fig. 10 shows some example of spectral responses for some samples of the tests set taken under contrasted conditions (dry and wet weather) and corrected from nitrate absorption (i.e. the contribution of nitrate absorption is deduced from the initial spectrum of an each sample). The spectral shape is mainly explained by the combination of physical (suspended solids and colloids) and chemical (DOM) responses. Suspended solids are responsible for a linear decrease of absorbance up to 350 nm and more, colloids for an exponential decrease between 200 and 240 nm and the main effect of the presence of DOM is the shoulder shape between 250 and 300 nm the intensity of which being linked to DOC content. Thus the spectral shape is not linear around the inflexion point of the nitrate spectrum (226 nm) and the corresponding second derivative values being low at 226 nm give a theoretical concentration under 2 $mgNO_3/L$ at maximum. This observation explains the slight negative ordinate of the validation curve (Fig. 8).

In order to confirm the need of nitrate correction of SDA at 295 nm for DOC determination the adjustment between DOC and SDA at 295 nm without nitrate correction was carried out for the same set of samples than for DOC calibration (Fig. 6). Compared to the characteristics of the corrected calibration line, the determination coefficient is lower (0.983 against 0.996) and the slope is greater (1.2 times) as well as the ordinate (7.9 times), the RMSE (5.6 times) and the LOD (5.4 against 1.1 mgNO3/L. These observations can be explained by the shift of the peak (around 290–295 nm) and the hypochromic effect of nitrate on the SDA value of the sample at 295 nm (see Fig. 5), showing the importance of the nitrate correction for DOC determination.

Another interfering substance can be free residual chlorine absorbing almost equally at 200 nm and 291 nm with a molar absorption coefficient of $7.96*10^4$ m^2/mol at 291 nm (Thomas and Burgess, 2007), preventing the use of the method for chlorinated drinking waters.

4.2. DOM absorption

The peak around 295 nm for the second derivative spectra reveals the existence of an inflexion point at the right part of the slight shoulder of the absorbance spectrum, between 250 and 300 nm. This observation can be connected with the use of the spectral slope between 265 and 305 nm (Galgani et al., 2011) to study the impact of photodegradation and mixing processes on the optical properties of dissolved organic matter (DOM) in the complement of fluorescence in two Argentine lakes. Fichot and Benner (2012) also used the spectral slope between 275 and 295 nm for CDOM characterisation and its use as tracers of the percent terrigenous DOC in river-influenced ocean margins. Helms et al. (2008) propose to consider two distinct spectral slope regions (275–295 nm and 350–400 nm) within log-transformed absorption spectra in order to compare DOM from contrasting water types. The use of the log-transformed spectra was recently proposed by Roccaro et al. (2015) for raw and treated drinking water and the spectral slopes between 280 and 350 nm were shown to be correlated to the reactivity of DOM and the formation of potential disinfection by-products. Finally a very recent study (Hansen et al., 2016) based on the use of DOM optical properties for the discrimination of DOM sources and processing (biodegradation, photodegradation), focused on the complexity of DOM nature made-up of a mixture of sources with variable degrees of microbial and photolytic processing and on the need for further studies on optical properties of DOM. Thus, despite the high number of samples

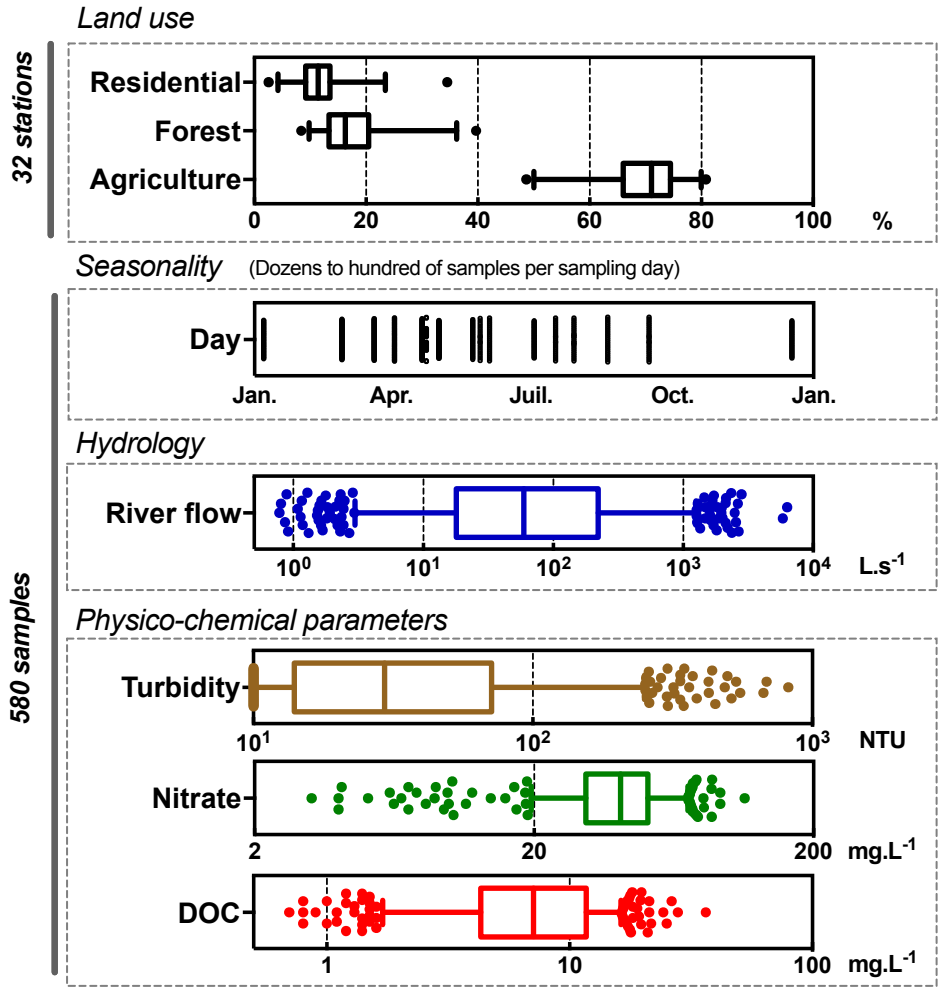

Fig. 7. Relevance of samples in relation to land use, seasonality, land use and physic-chemical parameters (box plots for inferior and superior quartile and median, whiskers for minimum and maximum of 90% of data, and points for the 5% lower or greater measurements).

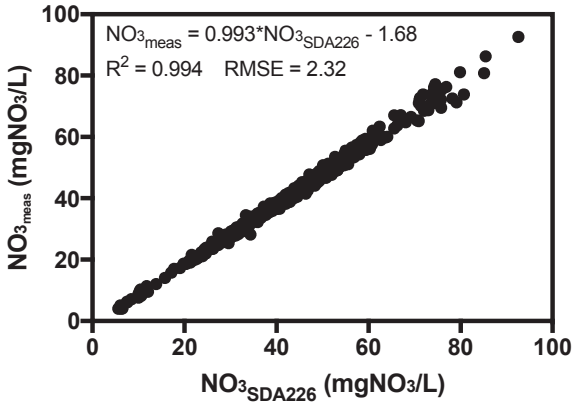

Fig. 8. Relation between measured and estimated (from SDA_{226}) NO_3 concentrations for 580 freshwater samples.

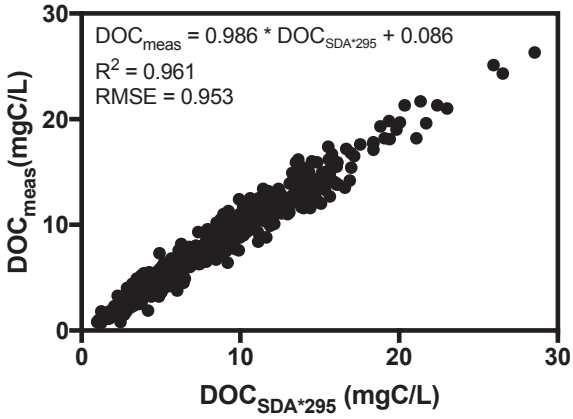

Fig. 9. Relation between measured and estimated (by SDA^*_{295}) DOC concentrations for 580 freshwater samples.

considered for this work and the contrasted hydrological conditions covered, the relevance of DOM nature as representing all types of DOM existing in freshwaters is not ensured. The transposition of the method, at least for DOC assessment, supposes to verify the existence of the second derivative peak at 290–300 nm and the quality of the relation between the SDA value at 295 (after nitrate correction), and the DOC content.

4.3. Optical pathlength influence for NO3 and DOC

Two optical pathlengths are proposed for the method, a short

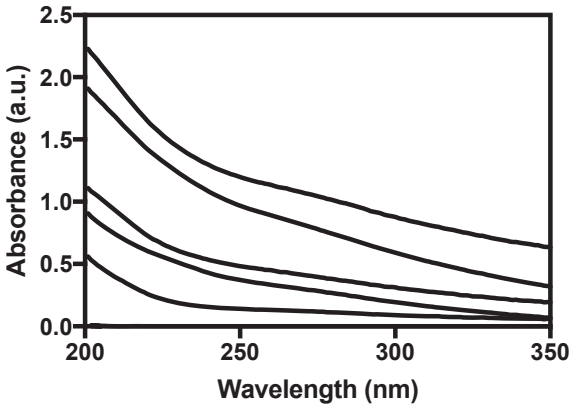

Fig. 10. Spectra of freshwater samples corrected from nitrate absorbance. Nitrate, DOC and turbidity of samples vary respectively from 19.8 to 49.8 mgNO3/L, 4.9 to 15.4 mg C/L and 6 to 116 NTU.

one (2 mm) for nitrate determination and a longer one (20 mm) for DOC (Fig. 2). However, considering that the optimal spectrophotometric range UV spectrophotometers between 0.1 and 2.0 a.u. (O Thomas and Burgess, 2007) must be respected, other optical pathlengths can be chosen for some water samples depending on their UV response. If the absorbance value of a sample is lower than 0.1 a.u. at 200 nm with the 2 mm optical pathlength, a 20 mm quartz cell must be used. Respectively, if the absorbance value is lower than 0.1 at 300 nm with the proposed optical pathlength of 20 mm, a 100 mm one must be used. This can be the case when nitrate or DOC concentration is very low given the inverse relationship often existing between these two parameters (Thomas et al., 2014). A comparison of the use of different optical pathlength for DOC estimation gives an R^2 value of 0.70 for the short pathlength (2 mm) against 0.96 for the recommended one (20 mm). Finally, the choice of a dual pathlength measurement was recently proposed by Chen et al. (2014) to improve successfully the chemical oxygen demand estimation in wastewater samples by using a PLS regression model applied to the two spectra.

5. Conclusion

A simple and rapid method for the UV determination of DOC and nitrate in raw freshwater samples, without filtration, is proposed in this work:

- Starting from the acquisition UV absorption spectra with 2 optical pathlengths (2 and 20 mm), the second derivative values at 226 and 295 nm are respectively used for nitrate and DOC measurement.
- After a calibration step with standard solutions for nitrate and known DOC content samples for DOC, LODs of 0.3 mgNO3/L for nitrate and 1.1 mg C/L were obtained for ranges up to 100 mgNO3/L and 0–25 mg C/L.
- The method validation was carried out for around 580 freshwater samples representing different hydrological conditions in two agricultural watersheds.
- Given its simplicity, this method can be handled without chemometric expertise and adapted on site with field portable UV sensors or spectrophotometers.

It is the first UV procedure based on the use of the second derivative absorbance at 295 nm for DOC determination, and calculated after correction of nitrate interference from the acquisition of the UV absorption spectrum with a long optical pathlength (20 mm or more). This is a simple way to enhance the slight absorption shoulder around 280–300 nm due to the presence of organic matter. Moreover the interferences of suspended matter and colloids being negligible on the second derivative signal, the measurement can be carried out for both parameters on raw freshwater samples without filtration. Finally, even if the validation of the method was carried out on a high number of freshwater samples covering different hydrological conditions, further experimentations should be envisaged in order to check the applicability of the method to the variability of DOM nature.

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