

A RAPID UV DETECTION METHOD FOR DISSOLVED ORGANIC CARBON (DOC) IN MARINE PORE WATERS USING NANOLITER SAMPLES

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Abstract - A simple flow injection technique for measuring DOC on few nanoliter of marine pore waters has been developed to complement existing high temperature oxidation techniques. Samples of 60-500 nanoliter of interstitial water are introduced with a loop injector directly into a capillary tube connected to a scanning UV-VIS detector. A nano flow cell detection device (35 nL) allowed for the acquisition of a complete UV-VIS spectrum or an absorbance measurement at a specific wavelength. Results obtained in this study with the UV method correlate significantly with those obtained using the high-temperature catalytic oxidation (HTCO) method. The UV method described addresses the HTCO limits and offers the possibility of near real-time DOC measurements onboard ship with a throughput of 30 samples per hour. The method has been used successfully to study the distribution of DOC in Saguenay fjord (Quebec, Canada) sediments following a major flood event in July 1996. Results comparable to HTCO method were obtained more rapidly and with only a few nanoliter sample of marine pore waters.

Introduction

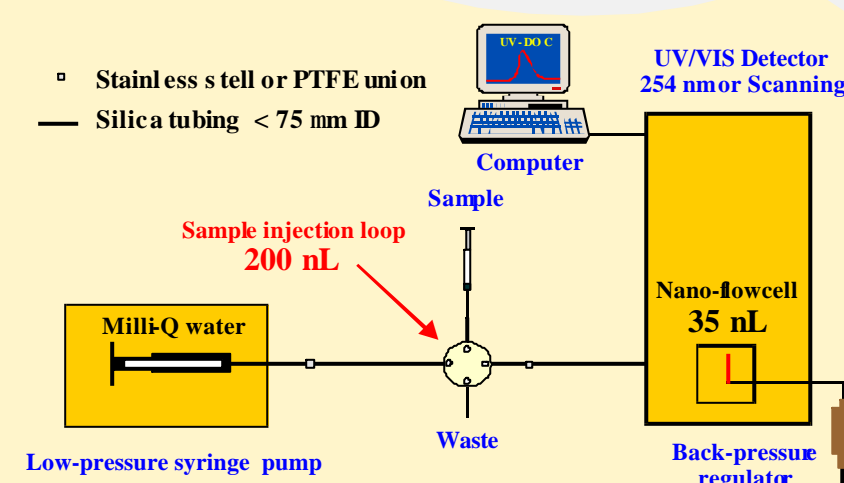
DOC is an important component of the organic carbon reservoir in the marine sediments and the understanding of its behavior is an important key to comprehend the carbon cycle in marine environments. Its study is often limited by the analytical technique employed and the availability of sample volume required for most DOC analyzers.

One of the first analytical methods used for DOC was non-destructive using UV detection¹. It is based on a specific evaluation of physico-chemical characteristics of organic compounds termed chromophores (i.e. "mobile" outer shell electrons that can absorb UV radiation). Such a method allows a rapid estimation of DOC in sedimentary environments². Brandstetter et al.³ used UV absorbance at 254 nm to estimate DOC in natural waters. However, limitations observed in quantifying DOC at a specific UV wavelength initiated the development of destructive techniques that transform the DOC into carbon dioxide by combustion. The HTCO method was recognized as the most precise and efficient technique (1991 Seattle DOC workshop)⁴ for DOC measurements. But, this method has several drawbacks: i) sample storage, sample manipulations and incomplete sparging of inorganic carbon^{5,6}, ii) assessment of the analytical blank⁷⁻⁹, iii) quantitative oxidation efficiency¹⁰⁻¹² and iv) the large sample volume necessary for analyses. Moreover, HTCO commercial instruments are generally too unstable for routine shipboard use^{13,14} reducing the possibilities of online real-time analysis. Recently, Alvarez-Salgado and Miller¹⁵ indicated that rapid and highly precise shipboard HTCO measurements can be routinely performed by coupling commercially available instruments, but the proposed analytical system is not easy to install on a benchtop for field measurements. Considering that the UV method has certain potential advantages over HTCO method, particularly, its simplicity for a rapid estimation of DOC distribution, we have looked into the possibility of using UV-based method for field measurements. In doing, we have optimized an UV detection method for DOC that uses just a few nanoliter of marine pore waters. This method is considered to be complementary to combustion techniques, not to replace it. In the following, we used the term UV-DOC for DOC analyzed by our UV detection method and HTCO-DOC for the one measured by HTCO method.

Analytical system

The detection principle is based on the UV absorbance of chromophores present in DOC. As shown in the figure, a low-pressure pump was used to carry degassed Milli-Q-water at a flow rate of 1 $\mu\text{L}/\text{min}$; its absorption can be neglected above 190 nm (UV cutoff < 190 nm). Samples were injected (from aliquots of 10 to 500 nL) with a Valco 4-port injection valve equipped with an internal loop of 200 nL. Several loop volumes (60, 200 and 500 nL) have been tested and results indicate that each of them can be used. We have set the injection volume at 200 nL for two reasons: i) working with volume as small as 60 nL is difficult because the sample may contain just few picograms of DOC and ii) it is not always easy to collect large volumes of marine pore waters. Moreover 200 nL is about 1000 times less than the volume necessary for HTCO. To wash out the sample loop and perform replicate analysis, we only need about 1 μL of sample.

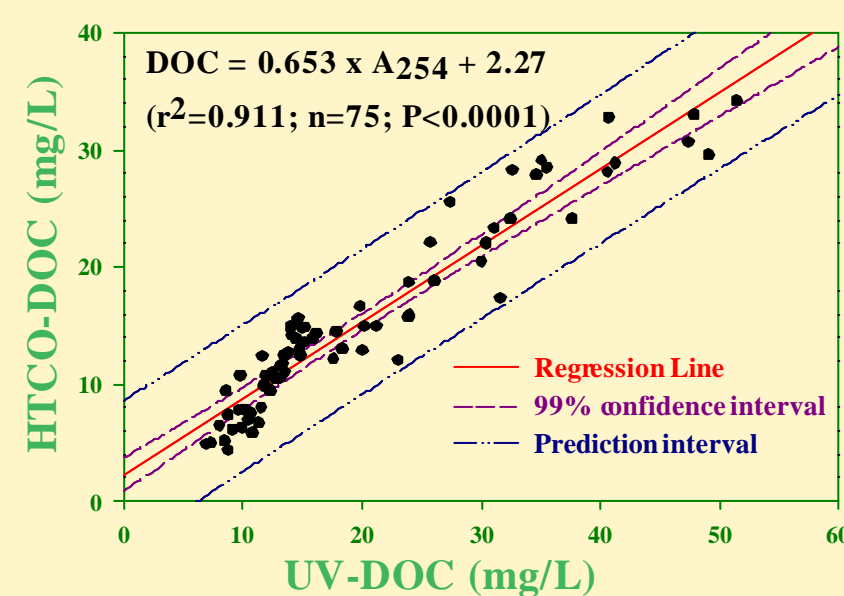
Dimensions of the deactivated silica capillary used throughout the system were evaluated to optimize the system. The scanning UV-VIS detector is equipped with a special 35 nL flow cell detection device for high-sensitivity UV detection allowing the acquisition of an UV-VIS spectrum or a specific wavelength signal. We have chosen 254 nm wavelength because i) it provides an acceptable absorbance for various chromophores present in DOC, and ii) the mobile phase does not contribute to the signal at this wavelength. The nano flow cell is connected to a back-pressure device to prevent the presence of gas bubbles which cause problems in the detector. Spectral treatment was handled with PC1000 software (TSP, Canada) using peak height integration. A single analysis can be completed in less than two minutes with a reproducibility better than 1%. Easy to set up and physically robust, this system can be readily used aboard ship with a throughput of 30 samples per hour. No salt effect has been observed. Moreover, since the analytical blank give no significant response at 254 nm, we conclude that both the salt effects and the blank determination encountered in HTCO method do not interfere in UV method.



UV method validation : UV vs. HTCO

In the absence of a certified DOC standard that could be used for calibration in both the HTCO and UV methods, we have compared the signal obtained with two methods on replicate samples. The HTCO-DOC concentrations were performed on a Shimadzu TOC-5050 Total Organic Carbon Analyzer with a Pt catalyst at 680°C¹⁶.

As shown in the figure, UV absorbance (254 nm) was strongly correlated to HTCO-DOC concentrations with $r^2 = 0.911$. The intercept of the regression line in the current study indicates that approximately 2 mg/L of non-UV-absorbing DOC is present. This is probably due to the presence of organic matter that contains no active chromophores at 254 nm such as saturated aliphatic compounds or low molecular weight fatty acids (i.e. acetate). The good correlation between the absorbance at 254 nm and HTCO-DOC allowed us to estimate the UV-DOC concentrations using regression equation shown in the figure.



Environmental applications

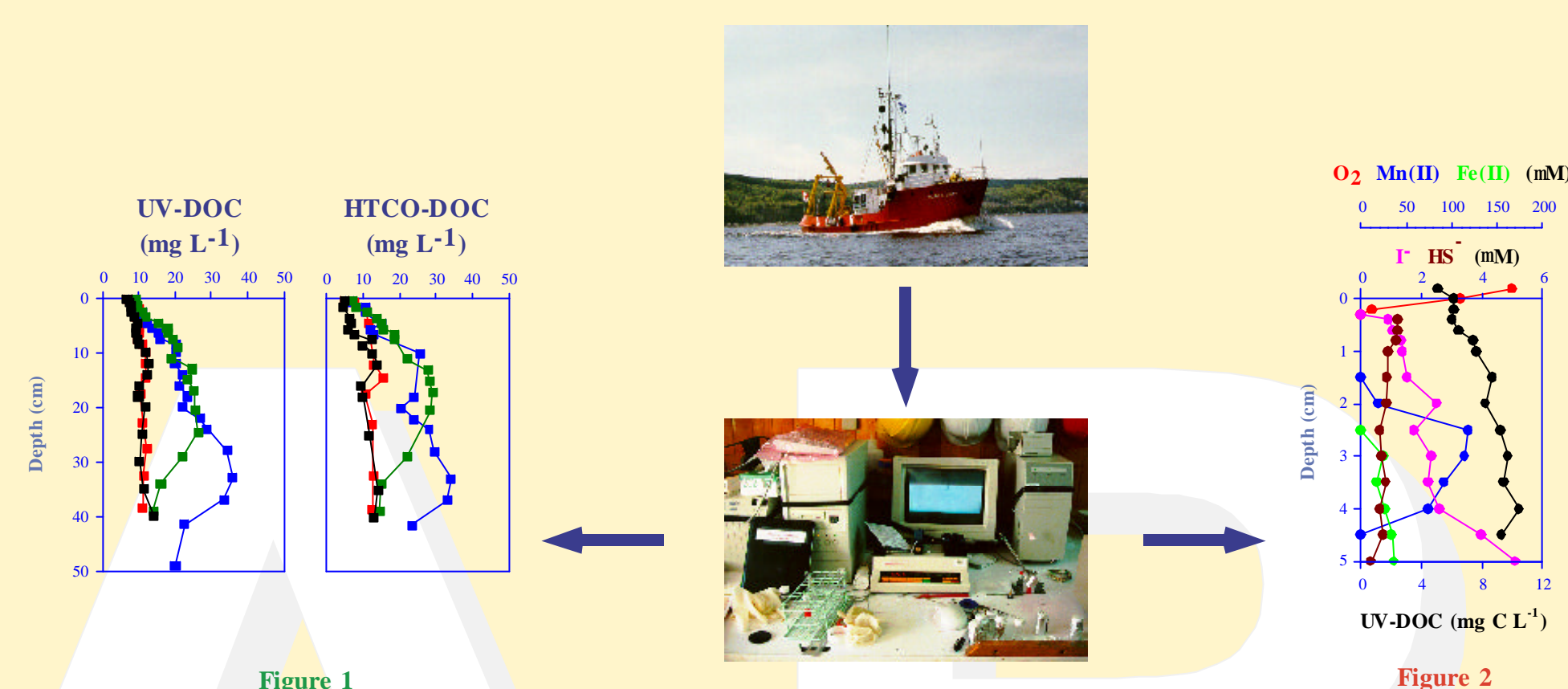


Figure 1

Figure 2

The UV method has been used to investigate the distribution of DOC in the Saguenay fjord (Quebec, Canada). Four sediment cores were collected in August 1998. Aliquots of 10 to 500 mL were taken for immediate UV-DOC analyses. Larger 5 mL aliquots were acidified and stored for subsequent HTCO analyses in laboratory. The sediment accumulation rate is about 0.2 cm/yr in this area but, during an important sedimentation event in July 1996, the head region of the Saguenay received a large deposit of new sediments over few days. The sediments at stations ST2 and ST17 were greatly perturbed, receiving 30 to 40 cm of new deposits. Stations ST15 and ST30 were less perturbed, receiving about 5 cm. Figure 1 indicates that the UV-DOC and HTCO-DOC distributions are similar in the four cores and show an increase in DOC with depth. The DOC increase seems to be related to the thickness of newly deposited sediment. DOC concentrations at 30 cm depth were up to 5 times that of the surface concentration in a perturbed area (ST2 and ST17) and only twice the surface concentration at the less disturbed stations (ST15 and ST30). We also observed a subsurface decrease in DOC near 30-40 cm depth at the most perturbed stations. We believe that this decrease is associated with the presence of the old sediment-water interface buried by the sedimentation event. These results show that UV-DOC profiles have a better resolution than HTCO-DOC profiles because it requires much smaller pore water volumes. The UV method opens new opportunities for studying DOC on the microscale required to understand the importance of sedimentary microenvironments. Figure 2 shows a set of preliminary results showing a high resolution distribution of UV-DOC coupled with inorganic tracers measured with a voltammetric microelectrode.

References

- Ogura N. and T. Hanya. 1967. Int. J. Oceanogr. Limnol. 1 : 91-102.
- Mattson, J.S., C.A. Smith, T.T. Jones and S.M. Gerchakov. 1974. Limnol. Oceanogr. 19 : 530-535.
- Brandstetter A., R.S. Sletten, A. Mentler and W. Wenzel 1996. Z. Pflanzenernähr. Bodenk. 159 : 605-607.
- Hedges J.I. and C. Lee (eds.). 1993. Mar. Chem. 41 : 121.
- Sharp J.H., E.T. Peltzer, M.J. Alperin, G. Cauwet, J.W. Farrington, B. Fry, D.M. Karl, J.H. Martin, A. Spitz, S. Tugrul and C.A. Carlson. 1993. Mar. Chem. 41 : 37-49.
- Peltzer E.T. and P.G. Brewer. 1993. Mar. Chem. 41 : 243-252.
- Benner R. and M. Strom. 1993. Mar. Chem. 41 : 153-160.
- Wangersky P.J. 1993. Dissolved organic carbon methods: a critical review. Mar. Chem. 41 : 61-74.
- Cauwet G. 1994. Mar. Chem. 47 : 55-64.
- Alperin M.J. and C.S. Martens. 1993. Mar. Chem. 41 : 135-143.
- Bauer J.E., M.L. Occelli, P.M. Williams and P.C. McCaslin. 1993. Mar. Chem. 41 : 75-89.
- Chen W. and P.J. Wangersky. 1993. Mar. Chem. 41 : 167-171.
- Baar H.J.W., C. Brussaard, J. Hegeman, J. Schijf and M.H.C. Stoll. 1993. Mar. Chem. 41 : 145-152.
- Qian, J., and K. Mopper. 1996. Anal. Chem. 68 : 3090-3097.
- Alvarez-Salgado X.A. and A.J.L. Miller. 1998. Mar. Chem. 62 : 325-333.
- Sugimura Y. and Y. Suzuki. 1988. Mar. Chem. 24 : 105-131.

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