



UV–vis spectral modifications of water samples under irradiation: Lake vs. subterranean water

Silvia Berto^a, Marco Isaia^{b,2}, Babita Sur^{a,c}, Elisa De Laurentiis^{a,1}, Francesco Barsotti^a, Roberto Buscaino^a, Valter Maurino^{a,1}, Claudio Minero^{a,1}, Davide Vione^{a,d,*}

^a Università degli Studi di Torino, Dipartimento di Chimica, Via Pietro Giuria 5-7, Torino 10125, Italy

^b Università degli Studi di Torino, Dipartimento di Scienze della Vita e Biologia dei Sistemi, Via Accademia Albertina 13, Torino 10123, Italy

^c Department of Chemical Engineering, Calcutta University, 92 Acharya P. C. Road, Kolkata 700009, India

^d Università degli Studi di Torino, Centro Interdipartimentale NatRisk, Via Leonardo da Vinci 44, Grugliasco 10095, TO, Italy

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ABSTRACT

Water samples from subterranean systems (caves and abandoned mines) and from lake epilimnion were optically characterised and irradiated under simulated sunlight, to study the effects that sunlight exposure before sampling may have on the properties and photochemical behaviour of chromophoric dissolved organic matter (CDOM). Differently from lakes, absorption spectra of subterranean water samples showed variations from the typically observed, featureless exponential decay of absorbance vs. wavelength. Fluorescence spectra suggested that, compared to lake water and with a single exception, subterranean water had higher proportion of aquagenic/autochthonous CDOM (e.g. proteinaceous material) compared to pedogenic/allochthonous one (e.g. humic and fulvic substances). Irradiation of subterranean water produced very significant spectral changes, and finally yielded lakewater-like exponential absorption spectra. In contrast, irradiation of lake water produced photobleaching (decrease of the absorbance), but the shapes of absorption spectra underwent very limited variations. Tyrosine and humic acids were irradiated as proxies of the CDOM fractions identified by fluorescence. Irradiated tyrosine underwent a significant increase of the absorbance and finally yielded an exponential absorption spectrum, with close resemblance to the behaviour of a protein-rich and humic-poor sample of subterranean water. In contrast, irradiated humic acids underwent photobleaching in a similar way as lake water, but they retained their typical exponential spectrum. The present findings suggest that exposure of CDOM to sunlight may play a key role in shaping the exponential absorption spectra that are typically observed in surface waters.

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1. Introduction

Chromophoric (or Coloured) Dissolved Organic Matter (CDOM) is the fraction of organic material dissolved in natural waters that is able to absorb radiation. CDOM can be optically characterised by means of its absorption of radiation above 200 nm, although absorption above 250 nm is usually preferred to avoid interference by nitrate [1]. However, from an environmental point of view it is the CDOM ability to absorb sunlight that is most important. CDOM

is usually the main radiation absorber in water in the 300–500 nm wavelength interval, and its ability to absorb UVA and UVB radiation has important consequences for aquatic organisms. Indeed, CDOM protects the aquatic biota from exposure to UV radiation [2], which can be very significant during summertime in CDOM-poor environments such as mountain lakes located above the tree-line [3]. Another important issue is that radiation absorption by CDOM yields reactive species, such as $\cdot\text{OH}$, $^1\text{O}_2$ and the triplet states $^3\text{CDOM}^*$, which can be involved into transformation of dissolved compounds, including xenobiotics, as well as into the photoprocessing of CDOM itself [4–7].

CDOM absorption spectra in surface waters usually show an almost featureless exponential decrease with wavelength, which accounts for the widespread use of the spectral slope S for a qualitative or semi-quantitative description of CDOM characteristics such as molecular weight and aromaticity [8,9]. Note that S values are obtained by fitting the absorbance (A_λ) spectra of natural waters with the equation $A_\lambda = A_0 \cdot e^{-S \cdot \lambda}$. The small deviations of the CDOM

* Corresponding author at: Università degli Studi di Torino, Dipartimento di Chimica, Via Pietro Giuria 5-7, Torino 10125, Italy. Tel.: +39 011 6705296; fax: +39 011 6705242.

E-mail address: davide.vione@unito.it (D. Vione).

URLs: <http://www.natrisk.org> (D. Vione),

<http://chimica.campusnet.unito.it/do/docenti.pl/Show?id=dvione> (D. Vione).

¹ <http://www.environmentalchemistry.unito.it>

² <http://www.personalweb.unito.it/marco.isaia/>

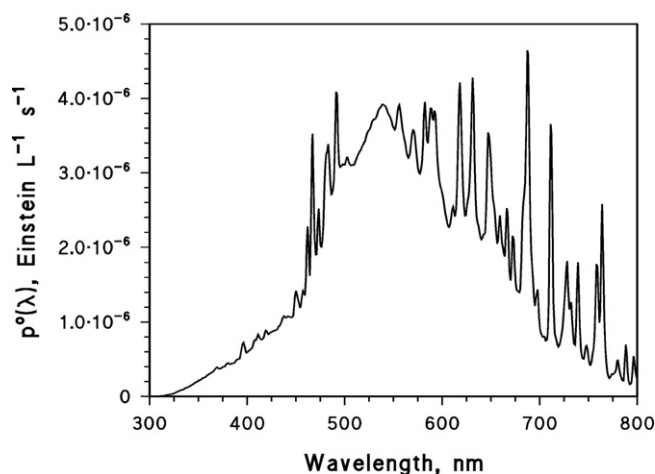


Fig. 1. Spectral photon flux density ($p^\circ(\lambda)$) of the adopted solar simulator.

spectrum from a purely exponential decay, which can be evidenced by considering the S trend with wavelength ($S(\lambda)$) and/or $\partial S/\partial \lambda$, can be used to differentiate between “different CDOM environments” [10]. However, the amount of knowledge that is presently available is still too limited to enable the full exploitation of $S(\lambda)$ or $\partial S/\partial \lambda$ as tools for CDOM characterisation. Another very useful technique for the study of CDOM is the emission–excitation matrix of fluorescence (EEM). EEM is only capable of detecting fluorophores in CDOM (thus yielding the so-called FDOM, Fluorescent Dissolved Organic Matter), but it is very useful for distinguishing between humic and fulvic substances, proteinaceous material, plankton pigments, and even man-made fluorescent xenobiotics (e.g. whitening agents) [11].

Sunlit CDOM undergoes a decrease of the absorbance (photobleaching), because sunlight-absorbing compounds are often transformed into less- or non-absorbing ones [12–14]. Photoinduced mineralisation (loss of dissolved organic carbon, DOC) can also be observed [15–17]. Interestingly, CDOM in subterranean water (groundwater that was collected and irradiated, without pre-exposure to sunlight before sampling) was much more susceptible to photomineralization than CDOM in lake water [18]. A possible explanation is that groundwater CDOM is shielded from sunlight, which could prevent photolabile species from undergoing photo-transformation/mineralisation. In contrast, lake water undergoes exposure to sunlight prior to sampling, which could transform photolabile species and cause the remaining CDOM to be rather photostable [18].

This paper reports on a study of spectral CDOM variations upon irradiation under simulated sunlight, comparing lake water samples with samples taken from ponds located in mines and caves. In the latter case, the relevant water as well as its CDOM stayed for prolonged time (months to some years) away from sunlight exposure. The experimental procedures allowed differences to be highlighted, both in the initial samples and in water samples after irradiation.

2. Experimental

Humic acid sodium salt, L-tyrosine (98%) and H_2O_2 (30%) were purchased from Aldrich. Water samples were collected in ponds present in the studied caves/mines or from the epilimnion of the studied lakes. Table 1 reports sampling sites and dates. The samples, kept in the dark, were transported to the laboratory under refrigeration, vacuum filtered on $0.22 \mu\text{m}$ cellulose acetate membranes, and stored at 4°C until analysis or irradiation.

Table 1
Features of the studied lake and subterranean water samples. The error bounds represent $\pm \sigma$ of runs carried out at least in quadruplicate on different aliquots of the same sample.

Sample acronym	Sample source	Location municipality (province)	Coord UTM	Sampling date	DOC, mg C L ⁻¹	IC, mg C L ⁻¹	A_{254nm} DOC ⁻¹ , L cm ⁻¹ (mg C) ⁻¹
1	Abandoned Talc Mine Santa Barbara	Prali (Torino)	32T 348074 4977205	26 March 2010	1.28 ± 0.02	27.2 ± 0.3	$0.037 \pm (6 \times 10^{-4})$
2	Abandoned Talc Mine Gianfranco	Prali (Torino)	32T 348059 4977358	26 March 2010	2.75 ± 0.05	74.7 ± 0.6	$0.030 \pm (5 \times 10^{-4})$
3	Baròn Litron Cave	Valdieri (Cuneo)	32T 373117 4902365	25 April 2010	0.58 ± 0.02	24.6 ± 0.2	$0.006 \pm (2 \times 10^{-4})$
A	Candia Lake	Candia (Torino)	32T 414676 5019591	22 Sep 2010	5.74 ± 0.11	16.5 ± 0.2	$0.014 \pm (3 \times 10^{-4})$
B	Avigliana Lake (Grande)	Avigliana (Torino)	32T 372999 4991538	13 June 2010	3.28 ± 0.03	49.1 ± 0.2	$0.020 \pm (2 \times 10^{-4})$
C	Laghetto Lake	Coazze (Torino)	32T 357492 4989084	18 June 2010	1.30 ± 0.05	1.45 ± 0.01	0.025 ± 0.001

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