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Photodegradation-based detection of fluorescent whitening agents in a mountain river

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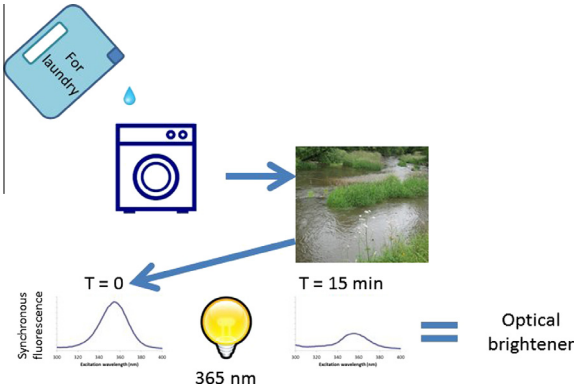
HIGHLIGHTS

- Synchronous fluorescence decay over 15 min is suitable to monitor optical brighteners.
- Humic substances and dilute dyes do not hinder the detection.
- Optical brightener presence was correlated with urban and industrial discharges.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluorescent whitening agents (FWAs) are highly soluble and poorly biodegradable ingredients used in laundry detergents and in industries (paper, textile, plastic manufacturing). They are likely to pass through biological wastewater treatment systems. The presence of FWAs in a mountain river was detected by monitoring the decay of synchronous fluorescence intensity at λ_{ex} = 360 nm after exposing samples to ultraviolet (UV) light (365 nm), for mimicking sunlight, for 15 min. The method was first validated on four commercial FWAs (DAS-1, FB28, DMA-X and CBS-X) in different water matrices (deionized water and pristine river water in the presence of humic acid and dyes). A 40% decay was observed after 15 min for the least photosensitive FWA (CBS-X). A field application was then performed on samples collected along a mountain river in which impacts of FWAs from domestic sources (laundry greywater) and industrial sources (paper and textile mills) were suspected. Variations of fluorescence decay at λ_{ex} = 360 - nm could be explained by these potential sources of pollution. It is suggested that the fluorescence decay at λ_{ex} = 280 nm also be considered as an indicator, as some FWAs can exhibit fluorescence at that excitation wavelength.

1. Introduction

Since the discovery by Krais in 1929 (Anliker, 1975) demonstrating that a natural substance called "esculin" could be attached to clothing to increase its whiteness, substantial progress has been made in the development of industrial optical brighteners. Optical brighteners (OBs) used in the chemical industry, also called fluorescent whitening agents (FWAs) in the detergent industry, are compounds that, after excitation (or activation) in the near-ultraviolet (near-UV) range (360–365 nm), emit light in the blue range (400–440 nm) (Poiger et al., 1998). FWAs are present in most modern laundry detergents and are thus discharged in substantial quantities with household wastewater (HERA project,

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2004). For example, in the United States, 97% of all laundry detergents contain one or both of two types of fluorescent whitening agents: 1) DAS-1 (CAS 24231-46-7) or FB-28, 2) DSBP also called Tinopal CBS (CAS 27344-41-8) (Hartel et al., 2007). Laundry wastewater is the largest contributor of FWAs to wastewater systems because it retains a large portion of dissolved optical brighteners. Laundry effluent is predominantly associated with grey wastewater (Dixon, 2009). FWAs are also used, to a far lesser extent (less than 10% in total), in the textile and paper industries. Toilet paper contains optical brighteners. When toilet paper breaks down, FWAs are released into sanitary water. FWAs are not readily biodegradable, but due to their ability to absorb part of terrestrial sunlight, they can be photochemically degraded in natural surface waters (Kramer et al., 1996).

There are several methods for detecting optical brighteners in waterways. One method involves placing cotton pads in waterways and allowing them to adsorb optical brighteners for a certain period of time. After collection, the pads are dried, and when they are exposed to ultra-violet (UV) light, they will fluoresce if optical brighteners are present. This method is both inexpensive and simple but has low sensitivity and poor quantification power (Sargent and Castonguay, 1998). Another method is high-performance liquid chromatography, which is highly sensitive but is expensive and requires a trained technician (Shu and Ding, 2005). A third approach involves taking measurements with a fluorometer, which is relatively inexpensive and easy to use (Hartel et al., 2007). Fluorometric measurement of FWAs is an inexpensive, simple, and fast method for distinguishing sources of human fecal contamination from non-human sources (Hartel et al., 2008).

Dissolved natural organic matter (DNOM) occurs ubiquitously in surface water and consists of humic and non-humic components (Volk, 2001). Between 40% and 60% of DNOM is fluorescent (Beck et al., 1993). In surface waters, DNOM may be combined with dissolved organic matter from anthropogenic sources such as wastewater. However, because the fluorescence of FWAs decays much faster than that of dissolved organic matter (DOM) under UV light, Cao et al. (2009) have proposed that the two can be distinguished by comparing fluorescence measurements before and after UV exposure.

To the best of our knowledge, this fluorescence decay method has been applied only in US waters and primarily in saline waters. Our purpose in this study was to evaluate the method by applying it to a mountain waterway exposed to greywater pollution (containing laundry detergents), as well as pollution from paper and textile mills that have existed along its banks since the XIXth century, benefiting from a plentiful water resource.

Fluorescence excitation–emission matrices (EEMs) are largely used for DOM characterization in rivers and detection of pollution sources (see for example Baker, 2001, 2002). However, as synchronous fluorescence yields improved peak resolution (Patra and Mishra, 2002), revealing the various spectral components present in DOM (De Souza Sierra et al., 1994; Sierra et al., 2005; Barker et al., 2009), the method has been adapted to use spectra obtained by this fluorescence technique.

2. Materials and methods

2.1. Water samples

Pristine water samples were collected close to the springs of two rivers (first-order tributaries of the Moselle River) flowing in the Vosges Mountains in northeastern France (Fig. S1 in the supplementary material). The Meurthe River has its source near the Schlucht Pass, at 1190 m above sea level. The pristine 20-L samples were obtained at the Valtin, two km downstream from the source. The Vologne River also has its source near the Schlucht Pass, at 1360 m above sea level, and travels for 50 km before its junction with the Moselle at Jarménil. Its watershed covers an area of 369 km^2. Its main tributary is the Neuné. A pristine 20-L sample was obtained upstream of Lake Retournemer, a few km downstream from the source. Twenty-seven samples (listed with the locations at which they were collected in Table S1 in the Supplementary Materials) were collected along the Vologne River on March 8, 2011, primarily from bridges, using a polyethylene bailer (SDEC, Beignac-sur-Indre, France) (Fig. S1). All of the samples were placed in clean polyethylene bottles and quickly transported in the dark to the laboratory, where they were kept in the dark at 4 °C until they were analyzed within 24 h.

Historical water quality parameter values for the Vologne and the Neuné, as well as information on the wastewater treatment plants (WWTP) in the watershed, were extracted from the Rhin-Meuse Water Board information system (http://rhin-meuse.eaufrance.fr/). Vologne and Neuné flow rate data were obtained from the Hydro database (http://www.hydro.eaufrance.fr).

2.2. Analytical methods

The pH and conductivity of raw samples were assessed using pH210 and CDM210 devices, respectively (Radiometer Analytical, CTB Choffel, Remiremont, France). After filtration (pore size = 10 μm), organic carbon was measured using a VCHS device (Shimadzu, Noisiel, France). N-NH_4 was determined using a miniaturized Nessler method (Hach method 8038 on a DR2400 spectrophotometer, Hach, Loveland, Colorado). UV–visible spectra were collected with an Anthelie Light device (Secomam, Domont, France) using a quartz cuvette (path length = 1 cm). Ultra-pure water was used for the blank. For fluorescence, an F-2500 (Hitachi, Krefeld, Germany) device was used. Synchronous fluorescence spectra were collected in the excitation wavelength range of 230–600 nm with a difference of 50 nm (SF50 = Synchronous Fluorescence with a difference of 50 nm) between excitation and emission, using PMMA cuvettes (Fisher Scientific, Illkirch, France). The difference of 50 nm was chosen as the best compromise for a good separation of the fluorescence peaks, while avoiding the influence of the Rayleigh scatter line. The photomultiplier voltage was set at 700 V, the scanning speed was 300 nm min^{-1}, and the excitation and emission slits were fixed at 2.5 nm. The device stability was checked by measurement of the Raman peak and a synchronous spectrum of ultra-pure water (Lawaetz and Stedmon, 2009). No inner-effect correction was applied. A repeatability test of the SF50 spectrum collection was conducted on one of the river samples: the coefficient of variation (CV) of the total fluorescence (i.e. integral of the SF50 spectrum between λ_{ex} = 230 nm and λ_{ex} = 600 nm) was calculated as 1.3% (for a series of 13 spectra) with a CV of 5.5% (respectively 1.4 for the intensity of fluorescence collected for λ_{ex} = 280 nm (respectively, 360 nm).

2.3. Reagents

Diaminostilbene (DAS-1, CAS 24231-46-7) and Fluorescent Brightener 28 (FB28, CAS 4404-43-7) were obtained from Sigma–Aldrich (Saint-Quentin-Fallavier, France). Tinopal CBS-X (CAS 27344-41-8) and Tinopal DMA-X (CAS 16090-02-1) were graciously provided by Ciba (Rueil-Malmaison, France). Their structures are shown in Fig. S2. Stock solutions (0.03 mg L^{-1}) were prepared for each optical brightener listed above using ultra-pure water and were stored at 4 °C in darkness for further use. A stock humic acid (ref 53680, Sigma–Aldrich, Saint-Quentin-Fallavier, France) solution was prepared at a 10 mg L^{-1} concentration using ultra-pure water and was stored at 4 °C until use. This brand is often used in studies on aquatic DOM (Valencia et al., 2013).