



Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Use of fluorescence EEM to monitor the removal of emerging contaminants in full scale wastewater treatment plants

Massimiliano Sgroi^a, Paolo Roccaro^a, Gregory V. Korshin^b, Valentina Greco^c, Sebastiano Sciuto^c, Tarun Anumol^{d,e}, Shane A. Snyder^d, Federico G.A. Vagliasindi^{a,*}

^a Department of Civil Engineering and Architecture, University of Catania, Viale A. Doria 6, 95125, Catania, Italy

^b Department of Civil and Environmental Engineering, University of Washington, Box 352700, Seattle, WA 98195-2700, USA

^c Department of Chemical Science, University of Catania, Viale A. Doria 6, 95125, Catania, Italy

^d Department of Chemical and Environmental Engineering, University of Arizona, 1133 E. James E. Rogers Way, Tucson, AZ 85721, USA

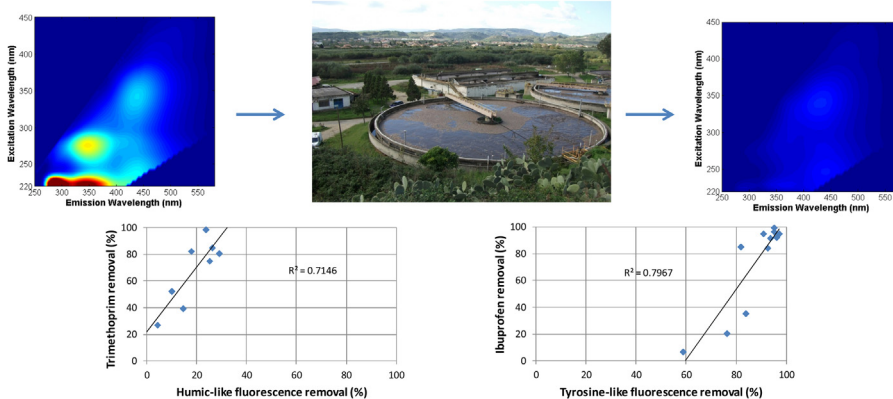
^e Agilent Technologies Inc., 2850 Centerville Road, Wilmington, DE 19808, USA

HIGHLIGHTS

- Comparison of different techniques for fluorescence EEMs data interpretations.
- Fluorescence components of different DOM fractions have different fate in WWTPs.
- Fluorescence indexes were correlated with the removal of selected emerging contaminants.

GRAPHICAL ABSTRACT

Monitoring the removal of emerging trace organic contaminants in wastewater treatment plants using fluorescence EEMs



ARTICLE INFO

Article history:

Received 4 March 2016

Received in revised form 9 May 2016

Accepted 11 May 2016

Available online xxx

Keywords:

Parafac

Fluorescence regional integration

Pharmaceuticals

Personal care products

Dissolved organic matter

ABSTRACT

This study investigated the applicability of different techniques for fluorescence excitation/emission matrices data interpretations, including peak-picking method, fluorescence regional integration and PARAFAC modelling, to act as surrogates in predicting emerging trace organic compounds (ETOCs) removal during conventional wastewater treatments that usually comprise primary and secondary treatments. Results showed that fluorescence indexes developed using alternative methodologies but indicative of a same dissolved organic matter component resulted in similar predictions of the removal of the target compounds. The peak index defined by the excitation/emission wavelength positions ($\lambda_{ex}/\lambda_{em}$) 225/290 nm and related to aromatic proteins and tyrosine-like fluorescence was determined to be a particularly suitable surrogate for monitoring ETOCs that had very high removal rates (average removal >70%) (i.e., triclosan, caffeine and ibuprofen). The peak index defined by $\lambda_{ex}/\lambda_{em} = 245/440$ nm and the PARAFAC component with wavelength of the maxima $\lambda_{ex}/\lambda_{em} = 245, 350/450$, both identified as humic-like fluorescence, were found remarkably well correlated with ETOCs such as atenolol, naproxen and gemfibrozil that were moderately removed (51–70% average removal). Finally, the PARAFAC component

* Corresponding author.

E-mail address: fvaglias@dica.unict.it (F.G.A. Vagliasindi).

<http://dx.doi.org/10.1016/j.jhazmat.2016.05.035>

0304-3894/© 2016 Elsevier B.V. All rights reserved.

with wavelength of the maxima $\lambda_{ex}/\lambda_{em} = <240, 315/380$ identified as microbial humic-like fluorescence was the only index correlated with the removal of the antibiotic trimethoprim (average removal 68%).

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The occurrence of pharmaceuticals, steroid hormones, pesticides and personal care products, collectively termed as emerging trace organic contaminants (ETOrCs) or contaminants of emerging concern (CECs), has been consistently reported for over a decade in different water matrices, including wastewater, surface water and drinking water [1–4]. While effects of many ETOrCs on public health remain largely unknown, studies have shown that some of these contaminants can have drastic effects on aquatic organisms at concentrations typical for wastewater discharges [5].

Wastewater treatment plants (WWTPs) have been recognized as significant hotspots for the transfer of ETOrCs into the environment [6,7]. This group of compounds offer a large variation in physical-chemical properties and usage rates, which affect their concentration levels in municipal wastewater and their corresponding fate in WWTPs. The removal efficiency of ETOrCs in WWTPs is also affected by the temperature, characteristics of the influent and treatment process employed (e.g., the sludge retention time, the nitrifying and denitrifying conditions) [7–9]. Traditional WWTPs usually utilize only primary and secondary treatments, with the latter often based on conventional activated sludge. These treatments tend to provide poor removal for most ETOrCs in wastewater [6–8]. Modern WWTPs often employ tertiary and advanced treatments that are generally efficient in removal of most ETOrCs. However, these advanced technologies are seldom applied due to large capital and operating costs [10].

The synthesis, production, and usage of a wide range of synthetic chemical compounds are occurring at an unprecedented pace. This likely leads to increasing concentrations and diversity of chemicals that are regularly released into the environment and the water cycle. As a consequence, the analytical effort to detect all the potential contaminants in the environment is not practical and economically feasible. Progress in analytical techniques partly compensates for this by more efficient methods, but the analysis of ETOrCs at trace levels in water remains laborious, time-consuming and expensive. Consequently, interest is increasing in using rapid and easy to measure bulk organic parameters (BOPs) of water useful for ETOrCs monitoring. For example, UV absorbance and fluorescence excitation/emission spectroscopy has shown good promise in predicting the removal of ETOrCs during advanced wastewater treatments [11–15].

Fluorescence spectroscopy is considered a useful tool for characterizing dissolved organic matter (DOM) in various natural and engineered aquatic systems [16,17]. Its potential to discriminate among various types of DOM is based on differences in light emission following excitation of fluorophores present in aquatic DOM (e.g., humic and fulvic acids, proteinaceous material, microbial by-products, pigments and various anthropogenic chemicals). Fluorescence data are presented in three-dimensional excitation-emission matrices (EEMs) in which fluorescence intensities are given as a function of excitation and emission wavelengths. Over the last two decades, a series of methods have been developed to interpret the complex information in EEMs, including peak-picking method, in which different fluorescence peaks are selected from several defined wavelength ranges of EEM [17,18]; fluorescence regional integration (FRI), where EEMs are divided in five regions and the integrated volumes under the five regional EEM surfaces,

normalized to the projected excitation-emission area of that region, are calculated and treated as individual fluorescence DOM components [19], and parallel factor analysis (PARAFAC), which is a technique of multivariate data analysis that can mathematically decompose the complex fluorescence spectra into chemically independent but spectrally overlapping fluorescent components for quantitative and qualitative analysis [20,21].

Fluorescence spectroscopy has been investigated in previous studies for its use as an indicator of water treatment efficacy and treated water quality [16,17,20,22,23]. Particularly, correlations have been determined between the fluorescence intensity of various EEM peaks or PARAFAC components and typical water quality parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total carbon (TC) and dissolved organic carbon (DOC) [17,22–24]. However, no study has investigated the possibility to employ fluorescence indices for monitoring the behaviour of ETOrCs in conventional WWTPs that generally include primary and secondary treatments.

Objectives of this work are: i) to examine possible relations between removal of fluorescence indices and ETOrCs in conventional WWTPs characterized by different secondary treatments (e.g., presence or absence of nitrification and denitrification processes, use of activated sludge unit or rotating biological contactors (RBCs)); ii) to compare the use of different techniques for fluorescence EEM data interpretations, including peak-picking method, FRI and PARAFAC analysis, and iii) to evaluate their suitability to produce indices that are effective surrogate parameters for ETOrCs monitoring in conventional WWTPs.

2. Materials and methods

2.1. Chemicals and reagents

All purchased solvents, standards, and reagents were of high purity. The details concerning these materials are reported in the Supplementary material section (Text S1).

The selection of ETOrCs analyzed in this study was based on data presented in previous literature that rely on occurrence data, detection frequency, availability of robust analytical methods and removal rate in conventional WWTPs [25–29]. Detailed information about all target analytes used in this study are shown in Table 1.

2.2. Sampling at the wastewater reclamation plants

Ten wastewater treatment facilities located in Sicily (Italy) were selected to evaluate the removal of ETOrCs during conventional WWTPs. These WWTPs had different secondary treatments. Four of the selected WWTPs employ activated sludge units achieving nitrification and denitrification processes. Two other WWTPs have activated sludge oxidation units that perform only nitrification. One selected wastewater treatment facility employs a conventional activated sludge scheme (non-nitrifying) and two WWTPs have rotating biological contactors as secondary treatment. Finally, one selected WWTP has an extended aeration activated sludge unit without primary treatment. The selected facilities serve different population sizes ranging from 5300 to 432500 population equivalent. Detailed information about the treatment trains of the selected WWTPs are shown in Table 2.

Download English Version:

<https://daneshyari.com/en/article/4979968>

Download Persian Version:

<https://daneshyari.com/article/4979968>

[Daneshyari.com](https://daneshyari.com)