

Toward a better knowledge of domestic sewage fluorescent dissolved organic matter: a study of its biological and physicochemical properties

A Goffin*, S Guérin, V Rocher, G Varrault

*Corresponding author: goffin.angel@gmail.com

Abstract: This study investigates the biological and physicochemical properties of domestic sewage fluorescent dissolved organic matter (DOM). Particular attention was paid on domestic sewage humic substances-like fluorescent components which are poorly known, especially since synthetic organic molecules (e.g. optical brightening agents) are likely to fluoresce in the same excitation-emission wavelength areas of the fluorescence spectrum. Domestic sewage biodegradation experiments highlighted a high biodegradability of protein-like fluorescent components and an increase of humic substances-like fluorescent components observed between 0 and 15 incubation days. Fractionation by DAX-8/XAD-4/AGMP-50/AGMP-1 resins showed that only half of the domestic sewage humic substances-like fluorescent components were observed in the hydrophobic acid fraction. All these observations raised doubts about the attribution of humic substances-like components fluorescence signal to real humic substances in domestic sewage.

Keywords: domestic sewage dissolved organic matter; characterization; excitation-emission matrix fluorescence spectroscopy

The regulatory context in the field of urban wastewater treatment has evolved considerably in the last two decades by presenting a significant increase in the requirements on the water quality returned to the receiving environment. Improvement of online monitoring and characterization of dissolved organic matter (DOM) in sewage is one of the ways envisaged to optimize control and management of treatment facilities. To reach these objectives, Excitation emission matrix (EEM) fluorescence spectroscopy could be used as it is an easy, rapid and cost-less method to characterize DOM in wastewater from diverse origins (Carstea et al., 2016). DOM fluorescence from domestic sewage is most often dominated by the presence of protein-like components with a lowest part of humic substances-like components (Goffin et al., 2018). Particular attention was paid on domestic sewage humic substances-like fluorescent components, which are poorly known, especially since synthetic organic molecules (e.g. optical brightening agents, OBAs) are likely to fluoresce in the same excitation-emission wavelength areas of the fluorescence spectrum. This study (MOCOPEE research program) aims to use physicochemical and biological fractionation methods coupled with excitation-emission matrix (EEM) fluorescence spectroscopy to better understand the origin of humic substances-like fluorescence signature observed in domestic sewage.

Different nature of filtrated samples (0.45 μm ; GF/F filters) were investigated: domestic sewage samples from the “Seine Centre” wastewater treatment plant (240,000 m^3/day ; Colombes, France); samples from French Rivers under low urban pressure; Suwannee River fulvic acid standard (IHSS) and laundry detergent solutions with or without OBAs. All samples were fractionated on DAX-8/XAD-4/AGMP-50/AGMP-1 resins in duplicates following protocol used by Matar (2012). Dissolved organic carbon (DOC) measurements were made for each resin effluents and analysed at pH 8 with EEM fluorescence spectroscopy. Biodegradability experiments were also made on the previous filtered samples (0.45 μm ; GF/F filters) using an Oxitop® respirometer under dark condition for 15 days. EEM fluorescence spectroscopy and DOC measurements were made at 0 and 15 days of experimentations, in triplicates.

Humic substances are known to be retained on DAX-8 resin (Peuravuori et al., 2002) and to be relatively refractory to biodegradation compared to protein. Domestic sewage biodegradation experiments highlighted a high biodegradability of protein-like fluorescent components (-90% of fluorescence intensity) and an increase of humic substances-like fluorescent components (+28% of fluorescence intensity) observed between 0 and 15 incubation days. Fractionation by DAX-8 resins showed only half of the domestic sewage humic substances-like fluorescence (55%) was observed in the hydrophobic acid fraction. All these observations raised doubts about the attribution of humic substances-like fluorescence signal to real humic substances in domestic sewage. According to a mass balance calculation it can be possible that OBAs are emitted in sufficient quantities to cause about 10% of the fluorescence observed for humic substances-like components in domestic sewage.

This study showed that EEM fluorescence spectrometry coupled with biological or physicochemical fractionation steps makes possible to distinguish fluorophores in domestic sewage according to their biodegradability and physicochemical properties. Results obtained also provide a better understanding of domestic sewage fluorescent DOM properties. This could help to better understand their possible evolution during the wastewater treatment plant process but also to consider a better management of the wastewater treatment works based on these elements.

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