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Multi-analytical approach to investigate sources of dissolved organic matter in a peri-urban watershed

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Dissolved organic matter DOM corresponds to a complex mixture of molecules and macromolecules playing a major role in terrestrial and aquatic biogeochemical process. DOM heterogeneous composition allows it to have innumerable interactions with organic and inorganic compounds, affecting both their bioavailability and mobility in the environment. At the watershed scale, there are many sources of DOM towards the river such as diffuse inputs by leaching of different types of soils (e.g. forest, meadows, crops, urban impermeable areas...) or urban point inputs (storm overflows, WWTP discharges, stormwater discharges....). However, the influence of all these sources on the composition of the aquatic DOM remains poorly understood to this day.

In this context, the main objective of this study was to build a methodology to detect the different sources of DOM in the rivers. Using a detailed characterization of DOM, the aim was to identify physicochemical markers and construct source-specific fingerprints. For this purpose, approximately 150 samples were collected from natural and anthropogenic sources of DOM (forest, agricultural, wastewater and urban runoff). All samples were analyzed using an innovative approach based on the use of a wide range of analytical techniques: dissolved organic carbon measurement, optical properties (UV-Visible, 3D fluorescence, size exclusion chromatography coupled with UV-fluorescence detection) and molecular composition (high-resolution mass spectrometry coupled with liquid chromatography). A large amount of data has been generated, and processed by classical (Anova, TukeyHSD) and multivariate (PCA, MFA, DFA) statistical approaches.

The results obtained allowed highlighting optical and molecular markers relevant for the identification of the selected sources. These markers inform on specific characteristics of DOM, such as the size of the molecules, the aromaticity content, the degree of humification, polarity and reactivity. In addition, complementarities and redundancies between optical and molecular characterization techniques is investigated. This research also contributes to select relevant markers for geochemical tracing models.