



# A non-targeted high-resolution mass spectrometry data analysis of dissolved organic matter in wastewater treatment

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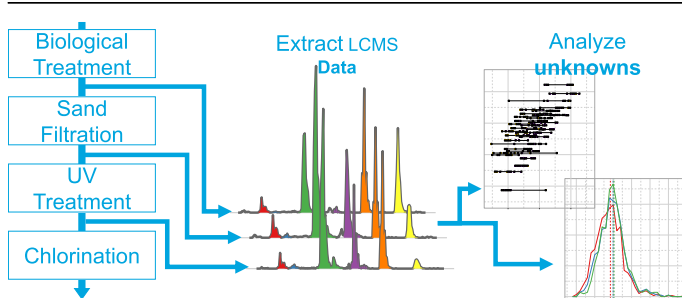
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## HIGHLIGHTS

- Secondary treatment removed 67% influent features while 24% new effluent appeared.
- The biodegradable organic matter differed chemically from the recalcitrant.
- Kendrick plot uncovered the removal of CH<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>O homologs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The dissolved organic matter (DOM) in wastewater is typically described by a limited number of concentration measurements of select DOM fractions or micro-contaminants, which determine the removal efficiency in a wastewater treatment. Current methods do not necessarily reflect the true performance of the treatment with regard to environmental and public health risk. Herein we describe the development and application of a non-targeted liquid chromatography-high resolution mass spectrometry (LC-HRMS) data analysis for the evaluation of wastewater treatment processes. Our data analysis approach was applied to a real wastewater system with secondary biological treatment and tertiary treatment consisting of sand filtration, UV-treatment, and chlorination. We identified significant changes in DOM during wastewater treatment. The secondary treatment removed 1617 of 2409 (67%) detected molecular features (grouped isotopologues belonging to the same molecule) from the influent while 255 of 1047 (24%) new molecular features appeared in the secondary effluent. A reduction in the number of large molecules (>450 Da) and an increase in unsaturated molecular features of the effluent organic matter was observed. Van Krevelen plots revealed the distribution of unsaturation and heteroatoms and Kendrick mass defect plots uncovered  $-CH_2-$  homologous series implying a removal of heavy constituents in that fraction. The demonstrated approach is a step towards a more comprehensive monitoring of DOM in wastewater and contributes to the understanding of current treatment technologies.

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## 1. Introduction

Wastewater DOM represents a complex, heterogenic mixture of polysaccharides, proteins, lipids, nucleic acids, soluble microbial

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products and anthropogenic organic chemicals. Anthropogenic compounds in wastewater include, among others, surfactants, personal care products, pharmaceuticals, biocides, pesticides, and industrial chemicals. Additionally, there is a wide range of biologically active transformation products (TPs), intermediates, metabolites (Michael-Kordatou et al., 2015) and disinfection by-products in the case of tertiary treatment (Richardson and Postigo, 2016). Some of these compounds can be hazardous even at a low concentration and may raise concerns regarding their release into the environment (Daughton, 2004). The composition of wastewater DOM is dependent upon the type of wastewater (municipal, industrial, hospital's effluent, runoff from fields, etc.) and the nature of the treatment process used in wastewater treatment plants (WWTP) (Deblonde et al., 2011). Currently, the efficiency of DOM removal at a WWTP is evaluated through measurements of the chemical oxygen demand (COD), biological oxygen demand (BOD) and the total organic carbon (TOC). Additional specialized technologies for the prioritized fractions of DOM include: measuring the dissolved organic halide to estimate the halogenated organics, the assessment of aromaticity using specific UV absorbance ( $SUVA_{254}$ ), size exclusion chromatography (SEC) to identify mass/size distributions of C- or N-containing constituents or excitation-emission-matrix fluorescence used to identify substance classes in natural OM (Chen et al., 2003; Clesceri et al., 1998; Huber et al., 2011). However, while these techniques reveal the chemical characteristics to a certain extent and the abundance of organics in WWTP influent and effluent, they do not provide information on the presence of unique organic substances and need to be combined into one data stream. Thus there is a need for new strategies to assess the quality of wastewater treatment (Prasse et al., 2015).

Different MS methods were developed for the analysis of wastewater treatment constituents. Initially, those focused on the detection of a small number of contaminants and occasionally on their TPs (Richardson and Ternes, 2014). By definition, these approaches omit thousands of DOM constituents which are present in the influent or emerge during the treatment process. Since some are potentially hazardous, overlooking these compounds limits the understanding of the impact of the effluent organic matter on the environment. Moreover, monitoring of the entire molecular complement or even a sub-complement of wastewater offers a possibility for a more comprehensive evaluation of the organic content in wastewater and a deeper understanding of the treatment processes and DOM transformation (Hollender et al., 2017). This new understanding will allow us to learn about the shortcomings of the treatment processes themselves and propose evidence-based improvement strategies.

The ability of high-resolution mass spectrometry (HRMS) to identify small amounts of organic chemicals from increasingly complex mixtures can provide information on wastewater DOM. For example, HRMS suspect screenings attempted to identify dominant signals using chemical databases and *in silico* prediction to find the structure of unique chemicals (Causanilles et al., 2017). Due to the complexity of wastewater, an HRMS analysis yields  $10^3$ – $10^5$  signals. This makes a manual structural identification of so many unique substances nearly impossible. Therefore this HRMS methodology generally uncovers only a small fraction of compounds and omits the unknown majority of wastewater DOM (Wode et al., 2015). Even without a tentative structural identification of particular substances, the large number of signals with assigned elemental compositions can be used to uncover physicochemical changes in wastewater treatment (Maizel and Remucal, 2017; Nürenberg et al., 2015).

Non-targeted analysis reduces the challenge of manual data treatment as for example present in a suspect screening, however without omitting it completely. The described HRMS data

treatment emerged from the fields of petroleomics and characterization of natural organic matter (NOM) (Hughey et al., 2001; Remucal et al., 2012; Sleighter and Hatcher, 2008) and was applied for the organic matter in processed water (Fang et al., 2017) and wastewater (Maizel and Remucal, 2017; Phungsai et al., 2016). Yet, the challenges of a non-targeted method remain the incomplete exclusion of noise signals from datasets and the exclusion of true DOM signals. These arise from the necessarily complex HRMS data acquisition, extraction, and clean-up methodology. Often DOM analyses do not include a chromatographic separation that might enhance the resolution of the spectral data. A direct infusion, without a separation on a chromatographic column, can simplify the procedure. Yet, the retention time is an additional variable to distinguish molecular features and an advantage of LC over an injection without a separation. The separation on the column is also beneficial for the reduction of the matrix effect compared to a direct infusion. Separation simplifies the mixture thus increases the chance of detecting low-intensity signals (Iparraguirre et al., 2014; Taylor, 2005). Meanwhile, measurement without sample pre-concentration does not lead to a loss of DOM, which is inevitable during a pre-concentration step (Li et al., 2016). Also, the use of LC-ESI-MS additionally reduces the discovered DOM, since it mostly detects medium-polar compounds (Aral et al., 2017).

HRMS non-targeted analysis includes a series of methods to sieve through large amounts of data. For example, in the van Krevelen diagram the atomic ratio X/C, where X is an element of interest, is plotted against H/C. In petroleomics and NOM chemistry the correlation between areas in this plot and functional classes of compounds led to the elucidation of the chemical composition of organic matter (Kim et al., 2003; Lu et al., 2010; Minor et al., 2012; Zhang et al., 2012a). A comparison of multiple samples revealed the transformation of matter (as oxidation of DOM) (Cortés-Francisco and Caixach, 2013; Herzsprung et al., 2012). Van Krevelen plot applied to wastewater treatment revealed a possible transformation of DOM (Maizel and Remucal, 2017). On the other hand, heterogeneous DOM (found in wastewater or eutrophic river) leads to a less structured distribution of points obscuring the graphic nature of the van Krevelen plot. For instance, the difficulty of exploring the graphical nature of the van Krevelen plot of the heterogeneous organic matter was experienced outside the field of water chemistry (Marshall et al., 2018).

The monitoring of double bond equivalents (DBE) in wastewater treatment can be applied to estimate the quality of the process and to recognize hydrophobicity-altering reactions as hydrolysis or oxidation (Cortés-Francisco et al., 2014). DBE reflect the level of unsaturation by double bonds in an organic molecule using only the counts of H, C, O, N, and halogen atoms in a molecule. DBE do not always apply to predict aromaticity since they can include double bonds with heteroatoms. Other models to predict unsaturation of a molecule as DBE divided by the number of C atoms, DBE minus oxygen atoms (DBE-O) and the aromaticity index were proposed (Cortés-Francisco and Caixach, 2013; Koch and Dittmar, 2006). DBE-O correlate especially well with the saturation of oxygen-rich organic compounds, but they represent a more abstract measure of unsaturation than DBE.

Mass defects are widely applied in HRMS analysis. Identification of homolog series using a non-targeted mass defect analysis was used to map surfactants in wastewater (Loos and Singer, 2017). Homologs occur in NOM (Hughey et al., 2001) but more importantly in classes of anthropogenic substances like surfactants, polyfluorinated compounds or chlorine substitute series (Jobst et al., 2013). The Kendrick Mass Defect (KMD), which sets the exact mass of a chosen molecular fragment to a nominal value (like 14.015 Da–14.000 Da for  $-CH_2-$ ) is able to identify homologous series for various structural moieties as  $-C_2H_4O-$  or  $-H/ + Cl$ . The

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