

# Determination of Emerging Contaminants in Surface Water Resources of EYDAP following wide-scope Target and Non-Target Screening

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## Abstract

The aim of the study was to perform extended monitoring of emerging contaminants in the water samples from three reservoirs of drinking water of EYDAP, Evinos, Mornos and Marathonas. Solid-Phase Extraction (SPE) by mixed-mode sorbent was used during the sample preparation to ensure the extraction of compounds with a wide range of physicochemical properties and very low limits of detection. The extracts were analyzed by complimentary chromatographic techniques, including Reversed Phase (RP) and Hydrophilic Interaction Liquid Chromatography (HILIC) coupled to Quadrupole-Time-of-Flight Mass Spectrometry (QToF-MS) due to its increased selectivity. Wide-scope target screening was performed by in-house databases consisting of 3,000 compounds, including several classes of emerging contaminants, naturally occurring compounds and endogenous metabolites. For the suspect screening, a database of approximately 40,000 compounds (REACH chemicals, industrial chemicals, biocides, PPCPs, surfactants and compounds from the NORMAN network monitoring programs) was used. Non-target screening was also performed for the identification of unknown unknowns in the analyzed samples.

**Keywords:** *Emerging Contaminants, Extended Monitoring, Surface Water Resources, HRMS*

## 1. Introduction

The quality of drinking water is crucial in order to protect the public health. Local and European guidelines provide standards and regulations for priority pollutants, but the effort for risk assessment of new compounds is a burning environmental issue. Previous studies have demonstrated that emerging contaminants are ubiquitous in surface water, mainly due to insufficient removal by the wastewater treatment plants (WWTPs) and the subsequent release of effluents into rivers and lakes [Cahill et al., 2004; Kasprzyk-Hordern et al., 2007]. The aim of the study was to perform an extended monitoring study of the emerging contaminants in the water samples from three drinking water reservoirs of EYDAP, Evinos, Mornos and Marathonas.

## 2. Methods

### 2.1. Sampling

Sampling was carried out by EYDAP personnel from three water reservoirs, Evinos, Mornos, Marathonas. Daily composite water samples were collected for each water reservoir for three consecutive days (Evinos: EYH 1-3, Mornos: MOR 1-3 and Marathonas: MAR 1-3).

### 2.2. Sample Preparation

The samples were stored in the dark at 4 °C until the extraction after the adjustment of the pH to 6.5 ( $\pm 0.2$ ). 2.5L of each water sample was filtered through regenerated cellulose filters to separate total suspended matter from the water sample. A mix of Internal Standards solution was spiked in each sample. Sample clean-up and pre-concentration was realized by Solid-Phase Extraction (SPE) with mixed-mode sorbent. This approach was used to ensure the extraction of compounds with a wide range of physicochemical properties and very low limits of detection. The elution of the analytes from the sorbent material was performed by a basic solution, followed by an acidic solution. The extract was evaporated to dryness under a gentle nitrogen stream and was reconstituted to a final volume of 250  $\mu$ L (MeOH-Milli-Q water, 50/50 v/v). The extract was filtered into a vial using a syringe fitted with a RC membrane filter and was ready for being analyzed in Liquid Chromatography High Resolution Mass Spectrometry [Gago-Ferrero et al., 2015].

### 2.3. Instrumental Analysis

The extracts were analyzed by the complimentary chromatographic techniques, achieving chemical characterization of the samples, facilitating the detection and separation of compounds with wide range of polarity in the samples including Reversed Phase Liquid Chromatography (RPLC) and Hydrophilic Interaction Liquid Chromatography (HILIC) coupled to Quadrupole-Time-of-Flight Mass Spectrometry (QToF-MS) due to its increased selectivity. For RP analysis an

Acclaim™ C18 column was used and a gradient elution program of the mobile phase (ratio and flow rate) for both ionization modes. For HILIC analysis, the samples were analyzed after reconstitution of the extract with a final proportion of ACN-Milli-Q water, 95/5 v/v, using an Acquity UPLC® BEH Amide column [Gago-Ferrero et al., 2015]. The MS data were acquired through Data Dependent and Independent Acquisition modes (DDA and DIA). The same extract was used for wide-scope target, suspect and non-target screening.

#### 2.4. Data Treatment

In-house databases consisting of 3,000 compounds (including different classes of emerging contaminants, naturally occurring compounds and endogenous metabolites) was used for the wide-scope target screening and the detection criteria was based on retention time, mass accuracy, isotopic pattern of the precursor ions and MS/MS fragmentation pattern [Gago-Ferrero et al., submitted]. Moreover, for the suspect analysis, “AutoSuspect”, an in-house automated suspect screening workflow, was used for the screening of emerging contaminants and their transformation products, using a database of approximately 40,000 compounds (REACH chemicals, industrial chemicals, biocides, PPCPs, surfactants and other compounds from the NORMAN network monitoring programs), (<https://www.norman-network.com/>) [Aalizadeh et al., 2017]. Non-target screening was also performed to search known (Pubchem was used as the online public chemical database) and unknown unknowns in the analyzed samples.

### 3. Results

#### 3.1. Target Screening

In total 25 compounds were detected through wide-scope target screening. Out of them, 15 belonged to the category of industrial chemicals mainly from the classes of Benzotriazoles, Benzothiazoles, Perfluorinated Alkylated Substances, Phenols and Phthalate esters. Moreover, pharmaceuticals and personal care products, plant protection products and stimulants, were also detected. 2-OH-benzothiazole, Dimethyl-phthalate and Sulfadiazine were detected in high concentration levels (µg/L) whereas Nicotine, Metformin, PFHxA, 2-OH-benzothiazole, Dimethyl-phthalate and Sulfadiazine, had high detection frequency.

#### 3.2. Suspect and Non-Target Screening

Concerning the suspect screening results, surfactants from the classes of Alkyl Ether Sulfates (AES) and Linear Alkylbenzene Sulfonates (LAS) were detected. From all the aforementioned surfactant categories, the samples from Evinos showed the highest frequency of detection. The AES-C12, n=0-8, class was detected in all samples from all tested reservoirs, were detected only in the samples from the reservoirs of Evinos and Marathonas, C9-13-LAS were detected only in the samples from the reservoirs of Evinos and Mornos. Other industrial chemicals such as 1,3-benzothiazole-2-sulfonic acid, Phthalic acid and Phenyl benzimidazole

sulfonic acid, which is used as an UV-filter, were among the most abundant compounds found in the analyzed samples. Four out of nine emerging contaminants identified through non-target screening belong to the category of Sulfophenyl Carboxylic Acids (SPCs) which are the oxidation products of LAS detected through suspect screening. Moreover, Propylparaben which is a preservative in cosmetics and personal care products was detected in the highest intensity in EYH 3. Finally, a new compound (a derivative of trimesic acid) was identified tentatively (level of identification 3) by the aid of in silico MS/MS fragmentation tool [Allen et al., 2015] and predicted LC retention time indices [Aalizadeh et al., in preparation].

#### 3.3. Conclusions

In total 34 compounds were detected through wide-scope target, suspect and non-target screening. Most of the known analytes were present in low concentrations, at ng/L levels. DEHP was detected only in EYH 3, in concentration below the set Environmental Quality Standard (1.3 µg/L), as indicated by the Directive 2013/39/EU. Last but not least, Dimethyl-phthalate and Sulfadiazine in the tested samples exceeded the range of concentration values that have been reported in recent literature [Liu et al, 2014; Hu et al., 2018]. Although the results of this research show that there are no concerns relevant to regulated substances in drinking water, they are particularly useful as they indicate potential sources of emerging, less studied contaminants.

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