# Evaluation of emerging contaminants in drinking water and wastewater in South Romania

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*Abstract:* - There are many emerging contaminants with disrupting properties on the endocrine system, including some pesticides, pharmaceuticals and personal care products (PPCPs) that can get into water bodies through leaking due to pesticides use in farming, leaching from landfills or discharge of wastewater into water sources. In Romania, there is a lack of data on the endocrine disrupting compounds (EDC) and PPCPs existing in different types of water. In this study, it was evaluated, by means of high performance liquid chromatography techniques (UHPLC), the drinking water quality, as well as quality of the WWTP effluents, regarding EDCs and PPCPs contamination, in order to provide information about the wastewater impact on receiving surface waters. The results showed the presence of the pharmaceutical chemicals from benzodiazepine class in all analyzed water samples.

*Key-Words:* water quality, endocrine disrupting compounds, PPCP, high performance chromatography technique, WWTP effluent, emerging contaminants

## 1 Introduction

The detection of organic micropollutants, such as endocrine disrupting compounds, pharmaceuticals and personal care products, in wastewater and the aquatic environment has brought increasing concern over their potential adverse ecological and human impacts [1]. Modified surface waters due to climate change, the discharge of domestic wastewater and other output factors might have a negative impact on drinking water quality [2,3,4]. Thus, the potential for in trace pollutant contamination that can get into drinking water is high and continues to increase, despite water treatment improvement in technological processes [5,6,7]. Furthermore, wastewater from wastewater treatment plants (WWTPs) is likely to be a major source for many endocrine disrupting compounds entering the aquatic ecosystems [8,9]. The discharge of these compounds into the aquatic environment has affected all living organisms [10]. Pharmaceuticals are considered to be important environmental contaminants [11,12]. Pharmaceutical pollutants in wastewater are transported through sewage systems to domestic sewage treatment plants. Because these pollutants are highly soluble in water, they will tend not to be removed during the traditional waste water treatment process by biological treatment [13]. Therefore, the pharmaceutical pollutants are discharged into rivers without an adequate treatment, the water discharged from the treatment plants being the main source of the pharmaceutical pollutants in the river basins [9,13]

The presence of pharmaceuticals in aquatic environment known to affect fish behaviour include antidepressants, selective serotonin reuptake inhibitors (SSRIs), hormones, antihistamines and various psychiatric drugs [14]. The presence of pharmaceutical residues in the environment even at ng/l concentrations may adversely impact on a variety of biological systems and has broader negative effects on ecosystems [15].

The number of organic micropollutants considered to pose a threat to aquatic environment is significant and increases. This concern have lead to introduction, in 2013, in the Water Framework Directive (WFD 2000/60/EC) [16] of 12 new substances, by Directive 2013/39/EU (in addition to the 33 existing priority hazardous substances). The WFD is revised to ensure that any potential threats of pollution are properly covered and that existing limits are suitable for maintaining water quality and reduce health threats to humans, other species and environment. Some of the priority hazardous substances have been identified as endocrine disrupting chemicals which interfere with wildlife and human hormones, affecting their normal development and functioning.

Directive 2013/39/EU, which amends Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, stipulates for new dangerous substances belonging to different classes (pesticides, hormones or pharmaceuticals) [17] that should be monitored beginning with 2021, by each Member State and Romania has to be in line with the new requirements. Although the investigation methods have been significantly improved in recent years, they are underdeveloped or even missing, especially for most of the emerging pollutants that may pose a significant risk and require regulation according to their potential ecotoxicological effects on the aquatic environment [18]. In this regard, it is important for institutions designated for monitoring water quality to have available analytical tools for more precise measurements, with high accuracy and reproducibility.

The aim of this study was to evaluate the contamination with endocrine disrupting compounds and pharmaceuticals in drinking water samples and wastewater samples collected from six cities of Romania.

## 2 Problem Formulation

Water samples were taken during October-November 2016 from the urban WWTPs (wastewater treatment plant) of Urziceni, Fundulea, Calarasi, Oltenita, Lehliu and Budesti - cities located in the southern part of Romania. The drinking water samples were collected from the drinking water treatement plants of Urziceni, Fundulea, Calaraşi and Oltenita cities. The sampling points locations are shown in Figure 1.

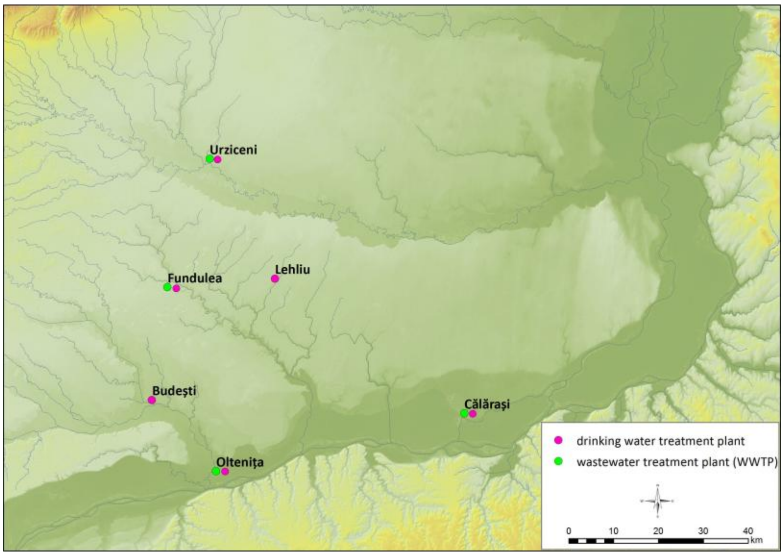


Fig. 1. Sampling points located in 6 cities of Romania

All water samples were collected in glass containers and transported directly to the laboratory, kept cold in freezers at 4°C during transport and the analysis was performed within 24 h after receiving the samples in the laboratory.

***Laboratory Analysis***

Sampling, processing and preservation of samples were performed taking into account national and international standards. The method for analyzing the PPCP/EDC is a hybrid of several methods considered representative by experts in this field.

EPA 1694 Method and Thermo Fisher Scientific analysis protocol were used in this study[19-24]. Combining the sample preparation process of SPE, which concentrates and purifies water samples, with chromatography and MS enables the highly sensitive applied analytical method [13]. An Ultimate 3000 UHPLC Thermo Scientific™ Equan Max Plus system coupled to TSQ Quantiva™ triple quadrupole QqQ-MS/MS tandem mass spectrometer equipped with an electrospray source was used for identifying the PPCP/EDC compounds. Data processing, calibration, and quality control were performed using Thermo Scientific™TraceFinder™ software version 3.2.

## 3 Problem Solution

The UHPLC method was applied for the screening of some pharmaceutical residues in drinking water and WWTP effluents. The prevalence of the pharmaceutical chemicals from benzodiazepine class (% samples) in analyzed water samples is presented in Figure 2. The study has shown the presence of the pharmaceutical chemicals from benzodiazepine class in all analyzed water samples. The large scale use and the great resistance of pharmaceutics to biological and chemical degradation under aerobic conditions can be one of the reasons for its presence in the analyzed samples [25]. Benzodiazepines are a group of anxiolytic drugs that contaminate many surface waters, via treated wastewater effluence [26].

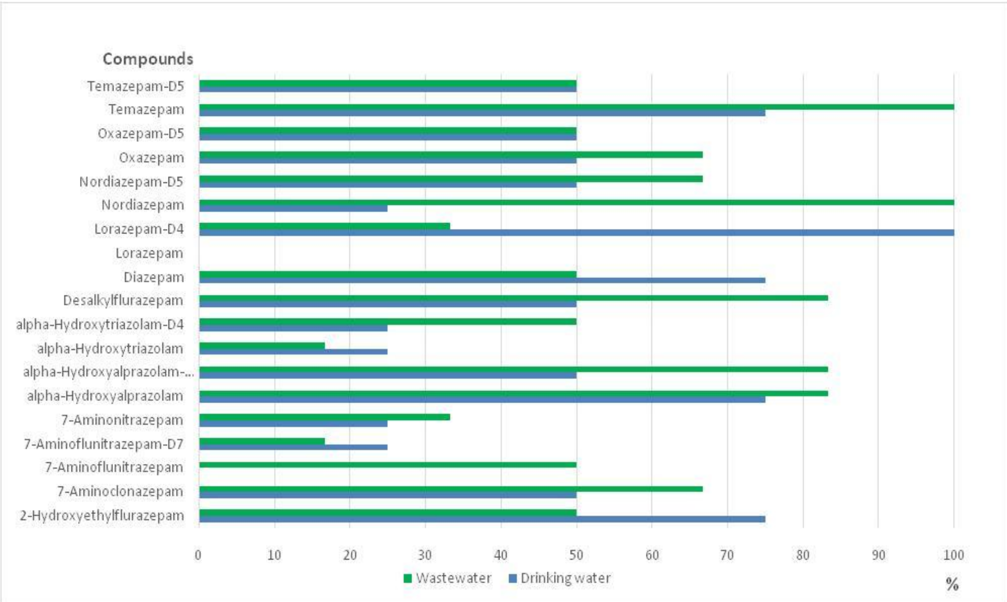


Fig. 2 – The prevalence of benzodiazepine class pharmaceutical products (% samples) in drinking water and wastewater samples

The *screening* of organic micro-pollutants using analytical methods developed and tested by UHPLC (high performance liquid chromatography) highlighted the presence in drinking water samples taken from the treatment plants of Urziceni, Fundulea, Călăraşi and Olteniţa of the following pharmaceutical chemicals from benzodiazepine class and its metabolites: 2-Hydroxyethylflurazepam, 7-Aminoclonazepam, 7-Aminoflunitrazepam-D7, 7-Aminonitrazepam, alpha-Hydroxyalprazolam, alpha-Hydroxyalprazolam-D5, alpha-Hydroxytriazolam, alpha-Hydroxytriazolam-D4 Desalkylflurazepam, Diazepam, Lorazepam-D4 Nordiazepam, Nordiazepam-D5, Oxazepam, Oxazepam-D5, Temazepam, Temazepam-D5 (Fig. 3,4,5). Compounds like 7-aminoflunitrazepam and Lorazepam were tested but they were not identified in the analyzed samples (Fig. 2).

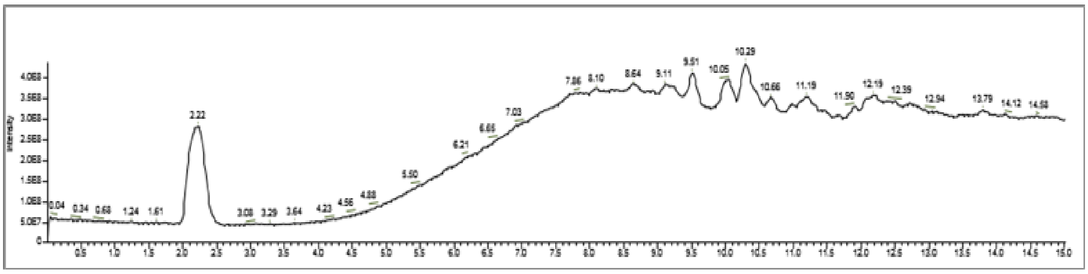

Fig. 3 – *Screening* of pharmaceuticals from benzodiazepine class – drinking water sample taken from the treatment plant of Calarasi

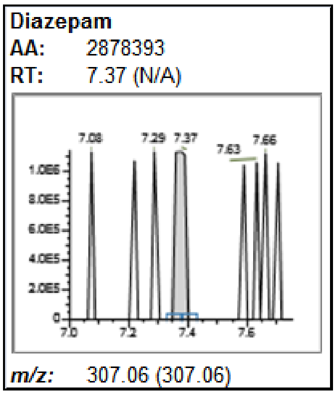


Fig. 4 – Chromatogram for diazepam – drinking water sample from the treatment plant of Calarasi

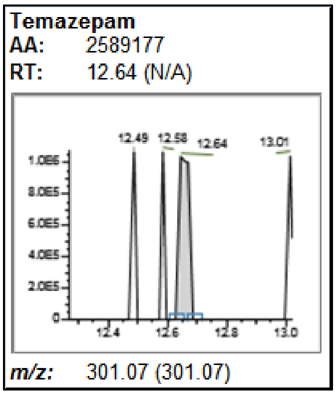


Fig. 5 – Chromatogram for temezapam – drinking water sample from the treatment plant of Calarasi

***In wastewater samples taken from the WWTP*** of Urziceni, Fundulea, Călăraşi, Olteniţa, Lehliu and Budeşti there was revealed the presence of the following organic micro-pollutants belonging to the pharmaceutical chemicals from benzodiazepine class: 2-Hydroxyethylflurazepam, 7-Aminoclonazepam, 7-aminoflunitrazepam, 7-Aminoflunitrazepam-D7, 7-Aminonitrazepam, alpha-Hydroxyalprazolam, alpha-Hydroxyalprazolam-D5, alpha-Hydroxytriazolam, alpha-Hydroxytriazolam-D4, Desalkylflurazepam, Diazepam, Lorazepam-D4, Nordiazepam, Nordiazepam-D5, Oxazepam, Oxazepam-D5, Temazepam, Temazepam-D5 (Fig. 6,7,8). The Lorazepam compound was tested, but it was not identified in the analyzed samples (Fig. 2).

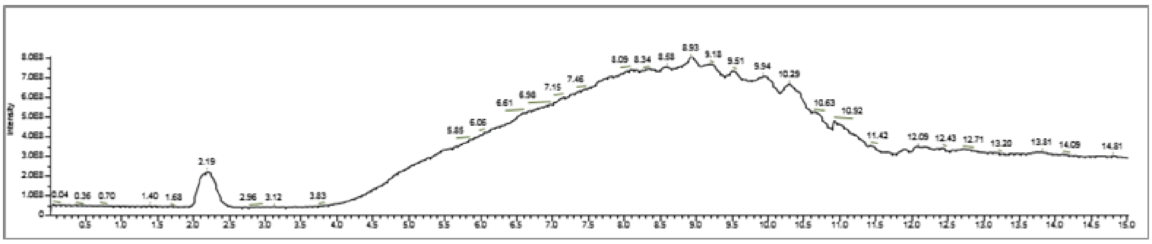

Fig. 6 – *Screening* of pharmaceuticals from benzodiazepine class – wastewater sample taken from the treatment plant of Calarasi

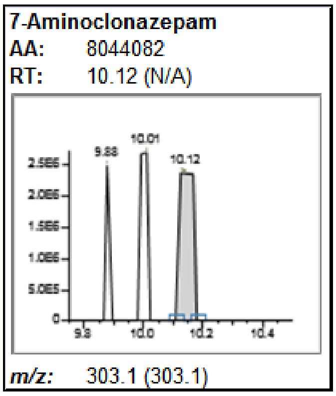


Fig. 7 – Chromatogram for 7-aminoclonazepam – wastewater sample from the WWTP of Calarasi

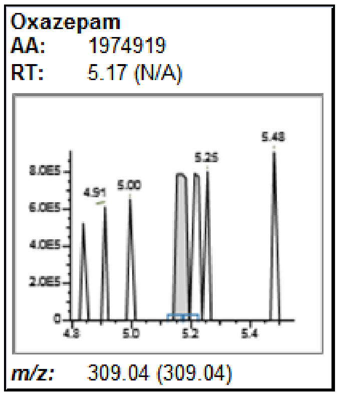


Fig. 8 – Chromatogram for oxazepam – wastewater sample from the WWTP of Calarasi

## 4 Conclusion

Results obtained in this study, by in the field sampling and laboratory testing, will be a useful technical and scientific tool for knowing the complex water pollution level and for the transfer of scientific information to the field of water resources management. In this regard, efforts should be made to develop a monitoring system for detecting the pharmaceuticals in order to assess their impact and environmental effects.

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