Investigations Regarding The Contamination with Emerging Pharmaceutical Pollutants in Representative Rivers and Lakes in Romania

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Abstract. The presence of emerging pharmaceutical pollutants in the aquatic environment is generally related to anthropogenic activities such as domestic, industrial and hospital wastewater discharges and landfills. Special attention should be paid to the contamination of surface waters, as they are partly used for drinking water supply, since they directly collect partly untreated wastewater from wastewater treatment plant. Within this paper, the identification, quantification and distribution of pharmaceutical micropollutants, from different complex environmental matrices, respectively: surface water, sediment and biota in the river basins of Arges-Vedea, Buzau-Ialomita and Dobrogea-Litoral and of the Danube River, were achieved. Also, preliminary investigations were carried out regarding the contamination of lakes with active pharmaceutical ingredients (APIs) the metropolitan area of the municipality of Bucharest. Among the pharmaceutical micropollutants identified in the Arges-Vedea river basin, the most frequently detected was paracetamol with a frequency of 69% and antibiotics with a frequency of 65.52%, in the Dobrogea-Litoral basin paracetamol was detected with a frequency of 74.2% and antibiotics with a frequency of 54.84%, while antibiotics were identified in all surface water samples and paracetamol with a frequency of 80% in the Buzau-Ialomita river basin. Considering the contamination of sediments with pharmaceutical residues, these were identified in all studied areas and in biota samples (fish) up to 18.21 ng/g were detected. The preliminary identification of active pharmaceutical ingredients (APIs) from Lakes Plumbuita, Carol, Morii, Alexandru Ioan Cuza (IOR), Herastrau and Tei indicated the frequent presence of several items, such as paracetamol, tinidazole, carbamazepine, moxifloxacin, clarithromycin, and caffeine.

1 Introduction

Pollution due to the presence of pharmaceuticals in the environment is an emerging problem because of potential risks to aquatic ecosystems and humans. Residues of pharmaceuticals can enter the environment during their manufacture, use and disposal. As noted by the

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European Commission [1] and UNESCO [2] there are limited databases on the consumption of pharmaceuticals, their concentrations in environment and emissions from various sources. The potential risk associated with emerging pharmaceutical compounds to aquatic ecosystems has been noted in various scientific research papers [3, 4, 5, 6, 7, 8, 9, 10].

Advanced analytical methods such as UHPLC-MS/MS and GC-MS/MS, have enabled the identification and quantification of over 3000 pharmaceutical pollutants [11] in concentrations ranging from µg/L to ng/L, which pose a potential risk to human and environmental health [12, 13, 14]. These pharmaceutical compounds from numerous therapeutic classes such as antibiotics, anti-inflammatories, hormones as well as cholesterol-lowering and blood pressure-lowering drugs are pseudopersistent as a result of frequent presence in various environmental matrices through release into the environment especially from wastewater treatment plants. The high solubility of pharmaceutical micropollutants in surface water, their persistence, bioaccumulation and possible toxic and carcinogenic effects on aquatic organisms contribute to the need for risk assessment of the aquatic environment. Pharmaceutical residues in low concentrations have both acute and long-term chronic effects on aquatic micro-organisms, flora and fauna. Experimental research indicates that pharmaceuticals can cause adverse effects such as morphological, metabolic and sexual changes in aquatic organisms, induction of antibiotic resistance in aquatic pathogenic microorganisms and disruption of biodegradation processes in wastewater treatment plants [15].

Antibiotics such as oxytetracycline and trimethoprim induce toxic effects on daphnia magna, the pseudokirchneriella subcapitata green algae and anabaena Flos-aque cyanobacteria. According to the World Health Organisation (WHO), antimicrobial resistance is a major challenge to human and animal health worldwide, with the prospect of worsening in the coming years unless effective measures are implemented [16]. In this paper, our aim was to identify, quantify and distribute emerging pharmaceutical pollutants in the aquatic environment of the Arges-Vedea, Buzau-Ialomita, Dobrogea-Litoral and Danube River basins and lakes of the metropolitan area of the municipality of Bucharest.

2 Materials and Method

2.1 Sampling Locations

In this study, the main watercourses in the hydrographic areas located in the south, south-east of Romania, namely the Arges-Vedea, Buzau-Ialomita and Dobrogea-Litoral river basins, upstream and downstream of the main urban agglomerations, as well as at the level of the Danube River were investigated. The investigated river basins were selected taking into account the sources of pollution such as hospitals; the existence of wastewater treatment plants that collect virtually the entire load of pollutants generated in the area of urban agglomerations, being areas with representative urban agglomerations with about 4 million inhabitants, 80 hospitals and 19 wastewater treatment plants (WWTP), which can influence the contamination of the Danube River with pharmaceutical micropollutants.

Identification and quantification of the 26 compounds of the pharmaceuticals group was performed from different matrices, namely surface water collected from Dambovita R. - Budesti area, upstream and downstream of WWTP Glina of Bucharest, Ialomita R. - upstream and downstream of WWTP Slobozia, Arges R. - Hotarele and Clatesti area, Sabar R., Ciorogarla R. - upstream and downstream of Domnesti, Prahova R. - upstream and downstream of WWTP Campina, Dambu R. - upstream and downstream of WWTP Ploiesti, Danube River - Orsova area, Tulcea (upstream, downstream), Bastroe, Sulina, Sf. Gheorghe, Fetesti (km 43), Bala (km 9.5), km 238 and km 35, Epurasu arm, Izvoarele. Moreover, determinations were carried out for identifying the emerging pharmaceutical pollutants and the sediment sampled from Ialomita R. - WWTP Slobozia area, Arges R. - Clatesti area, Dambu R. - WWTP Ploiesti area, Prahova R. - WWTP Campina area, as well as for biota (fish) samples from Arges R. - Clatesti area, Dambovita R. - Stoenesti area, Danube River-Borcea, km 40 (Figure 1). The identification of emergent pharmaceutical compounds was also carried out from surface water from the lakes in the metropolitan area of Bucharest (Figure 1).

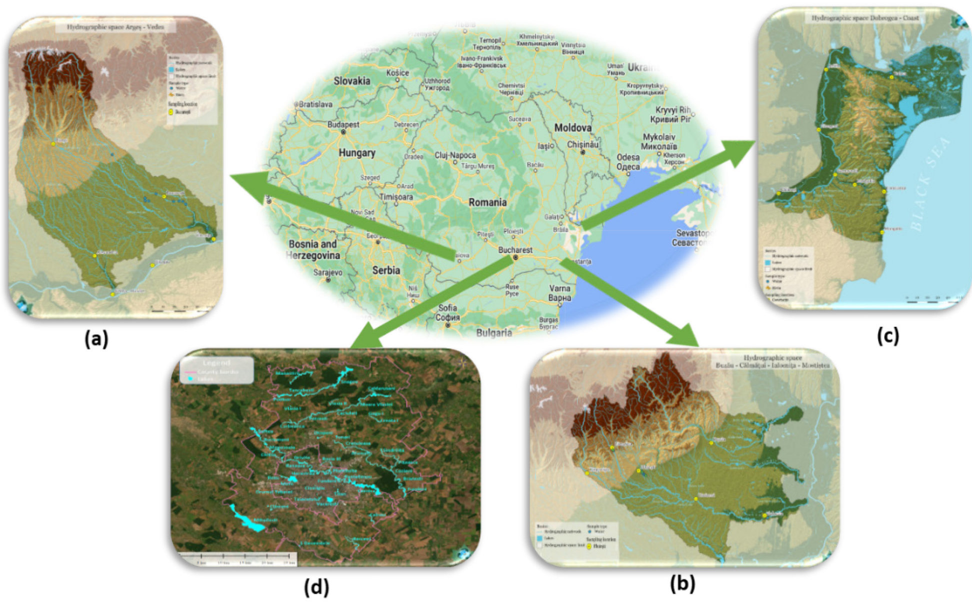

Fig. 1. Sampling locations – river basins of Arges -Vedea (a), Buzau-Ialomita (b), Dobrogea-Litoral and the Danube River (c) and lakes of Bucharest (d)

2.2 Methods

Investigations on the presence of pharmaceutical residues in the aquatic environment at the level of the three investigated river basins and the Danube river, were carried out from 29 representative monitoring sections during June 2019 - May 2022, i.e. 22 sections for surface waters and seven sections in the area of treatment plants of cities such as Bucharest, Slobozia, Calarasi, Ploiesti and Campina. The preliminary identification of the active pharmaceutical ingredients (API) was made from samples taken from Lakes Plumbuita, Carol, Morii, Alexandru Ioan Cuza (IOR), Herastrau and Tei.

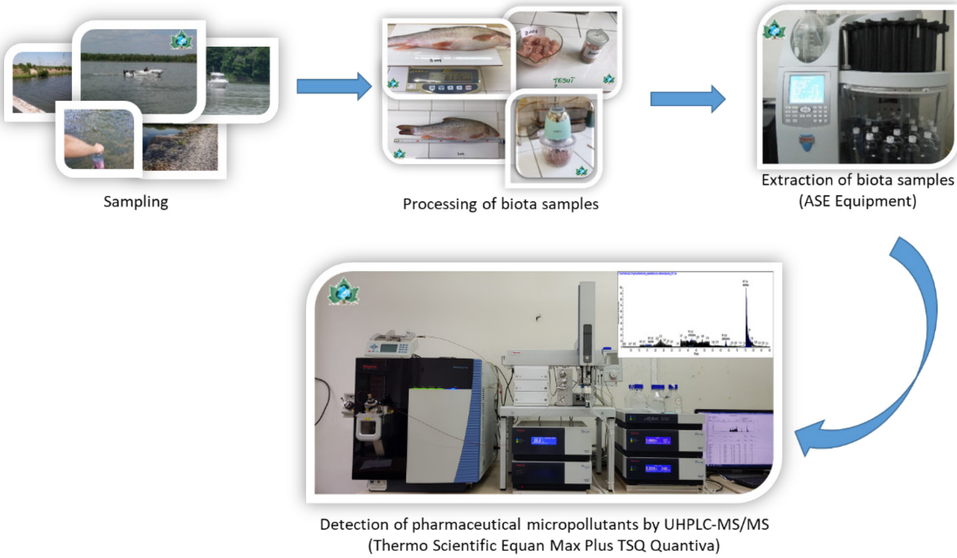

Fig. 2. Investigations on the presence of pharmaceutical residues in the aquatic environment

2.2.1 Chemical analysis of pharmaceutical micropollutants.

The identification of emerging pharmaceutical contaminants was performed using the Thermo Fisher Scientific™ EQuan MAX Plus™UltiMate 3000 SPE-online-UHPLC-MS/MS system coupled with the TSQ Quantiva triple quadrupole mass spectrometer. Methods developed for the detection of antibiotics, i.e. doxycycline, erythromycin, ampicillin, chloramphenicol, trimethoprim, metronidazole, ciprofloxacin, oxytetracycline, tetracycline, norfloxacin, colistine, chlorofloxacin, sulfamethoxazole, ofloxacin, amoxicillin, clarithromycin, oxacillin, azithromycin, anti-inflammatories and analgesics, i.e. diclofenac, ibuprofen, paracetamol, codeine, ketoprofen, the psychostimulants caffeine and β-blockers propranolol and metoprolol, meet the EU requirements for the detection limit, i.e. it has to be at least equal to the no-effect concentration estimate (PNEC) values in the corresponding matrix.

3 Results and Discussion

Method development for the detection of pharmaceutical micropollutants by UHPLC-MS/MS was carried out in accordance with the quantitative confirmation criteria described in Decision 2002/657/EC implementing Directive 96/23/EC concerning analytical methods and interpretation of results.

This study revealed a widespread prevalence of active pharmaceutical compounds in the aquatic environment. In surface water samples, 16 of the 26 compounds analysed were detected. The total concentration of pharmaceutical micropollutants detected in surface waters ranged from 5÷8570 ng/L with a mean value of 705 ng/L. The distribution of emerging pharmaceutical pollutants in aquatic environments is shown in Figure 3, Figure 4, Figure 5 and Figure 6.

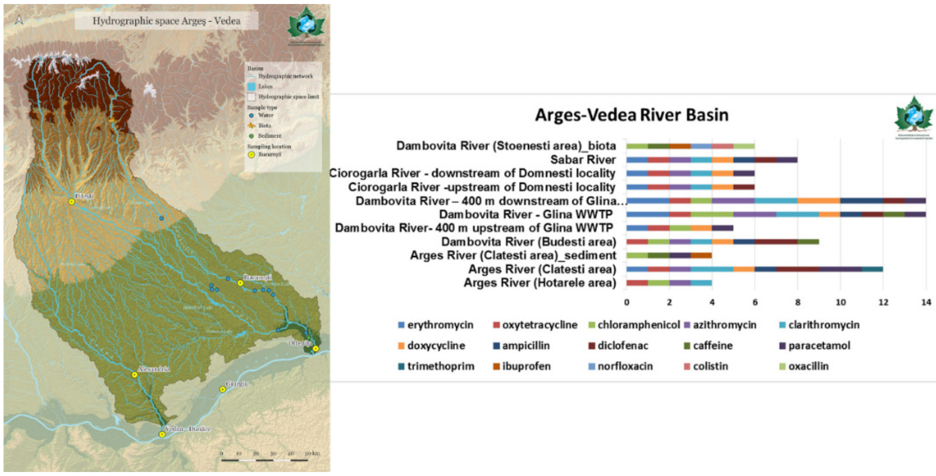

Fig. 3. Distribution of emerging pharmaceutical pollutants in aquatic environments from the areas Arges-Vedea river basin

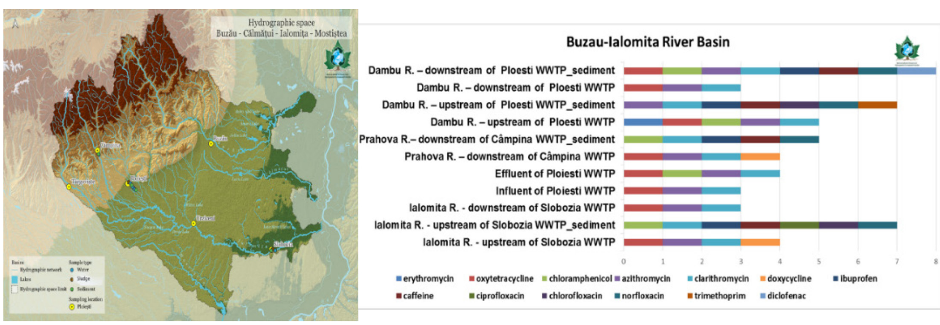

Fig. 4. Distribution of emerging pharmaceutical pollutants in aquatic environments from the areas Buzau-Ialomita river basin

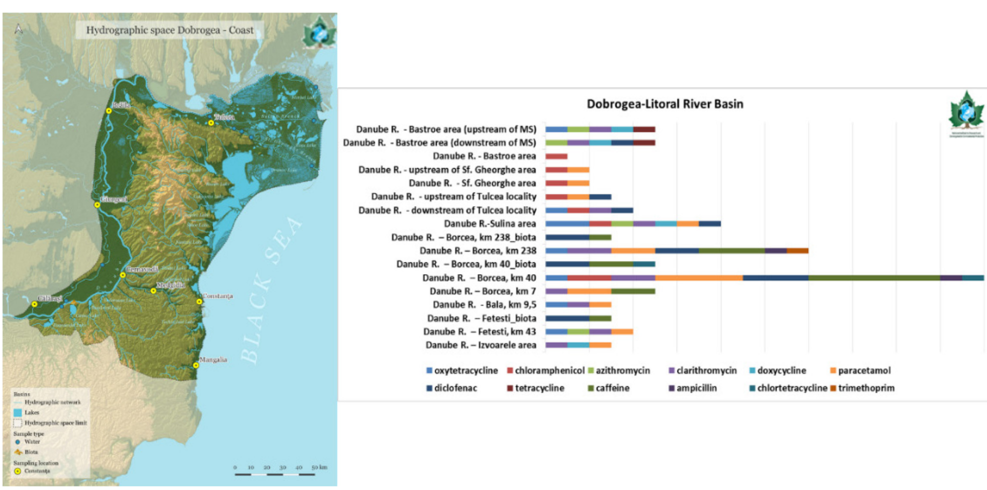

Fig. 5. Distribution of emerging pharmaceutical pollutants in aquatic environments from the areas Dobrogea-Litoral river basin

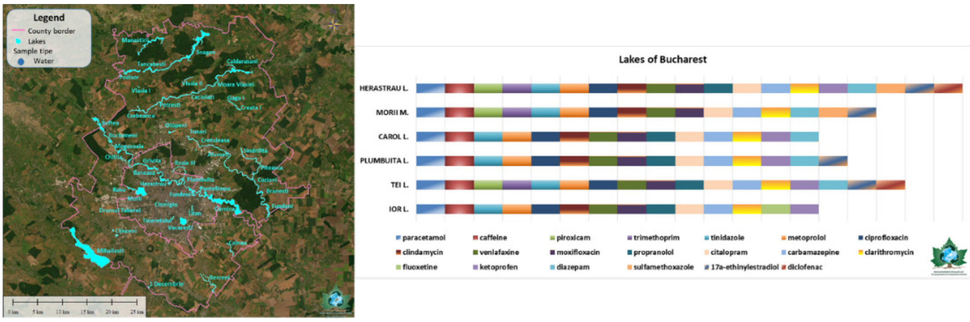

Fig. 6. Distribution of emerging pharmaceutical pollutants in aquatic environments from the lakes of Bucharest

Several pharmaceutical compounds were also identified in sediments between 4 and 8 of the 26 analysed, with a total concentration of 24.8 ng/g in the Dambu R. area - downstream of WWTP of Ploiesti. Up to 7 pharmaceutical compounds were identified in biota samples, with a total concentration of 18.21 ng/g in the biota (fish) sample in the Danube R. – Borcea area, km 40. The most frequently detected were clarithromycin from the antibiotic class and diclofenac from the non-steroidal anti-inflammatory drug (NSAID) class which were quantified in 57.5% and 68% of the surface water samples respectively, and paracetamol was identified with a frequency of 78%.

Among the pharmaceutical micropollutants identified in the Arges-Vedea river basin, paracetamol was detected most frequently, with a frequency of 69% and antibiotics with a frequency of 65.52%, in the Dobrogea-Litoral basin paracetamol was detected with a frequency of 74.2% and antibiotics with a frequency of 54.84%, while antibiotics were detected in all surface water samples and paracetamol with a frequency of 80% in the Buzau-Ialomita river basin.

Preliminary research on the presence of emerging pharmaceutical contaminants in Lakes Plumbuita, Carol, Morii, Alexandru Ioan Cuza (IOR), Herastrau, and Tei has revealed, as shown in Figure 6, the frequent presence of some substances like paracetamol, tinidazole, carbamazepine, moxifloxacin, clarithromycin, and caffeine.

The presence of pharmaceuticals in the area of the investigated hydrographic basins is mainly due to the consumption for medical purposes by the population of these areas as well as due to the inadequate disposal of expired or unused medicines due to a limited control in their management. Another major source of disposal of pharmaceutical products in the investigated areas is represented by agricultural and zootechnical waste, since in intensive animal breeding farms they are fed with feed containing drugs.

4 Conclusion

This study presents the quantification and distribution of emerging pharmaceutical pollutants in surface water, sediments and biota at the level of three river basins in Romania, namely Arges-Vedea, Buzau-Ialomita and Dobrogea-Litoral as well as the Danube River. Also, preliminary investigations were carried out regarding the contamination of lakes with active pharmaceutical ingredients (APIs) the metropolitan area of the municipality of Bucharest. The results obtained highlight the frequent presence of pharmaceutical micropollutants such as antibiotics, paracetamol and diclofenac in the studied areas, and further investigations on the presence and risk assessment of pharmaceuticals in aquatic ecosystems are needed.

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