Conference Paper / Review

ORGANIC CONTAMINANTS IN CROATIAN MUNICIPAL WASTEWATERS

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Municipal wastewaters are among the most important sources of waste materials released into the environment. In Croatia, this problem is especially pronounced since only 4.4 % of the total wastewaters are subject to complete mechanical and biological treatment. Beside a limited number of regulated organic contaminants, wastewaters contain an extremely high number of different potentially harmful organic compounds. Comprehensive analyses of Croatian wastewaters using mass spectrometric techniques (GC/MS, LC/MS) indicated the presence of a large number of different organic compounds with a predominance of two main groups of contaminants: petroleum hydrocarbons and detergent-derived surfactants. Recent investigations of specific organic contaminants in wastewater focused on the determination of so-called emerging contaminants, whose ecotoxicological relevance is based on new types of biological effects and for which water quality criteria have not yet been defined. The main goal of this paper is to make an overview of the present knowledge on the occurrence of different types of organic contaminants in Croatian municipal wastewaters, paying special attention to the emerging contaminants.

KEY WORDS: *emerging contaminants, novel contaminants, pharmaceuticals, regulated contaminants, surfactants, unregulated contaminants*

Wastewaters are among the main sources of environmental anthropogenic, organic and inorganic contaminants. Municipal wastewaters in Croatia are mainly of the mixed type since they include household and industrial wastewaters. Approximately 17 % of all industrial wastewaters go directly into the sewer system (1), which may significantly affect the total organic load of municipal wastewaters. Furthermore, only 4.4 % of the total municipal wastewaters receive a complete mechanical and biological treatment, while 88 % do not receive any treatment before they are released into the environment (1). This results in high organic load in Croatian receiving waters. The composition of the organic load is very complex and variable, which poses a great challenge to risk assessment and the use of modern wastewater treatment technologies. In addition to significant quantities of complex macromolecular organic matter, which usually dominate in the total organic load and in various types of collective contaminants such as total lipids, mineral oils, and detergents, wastewaters contain a large number of various specific organic contaminants. The variety and the quantity of organic contaminants have increased exponentially over the past few decades (Figure 1) (2). A significant percentage of these chemicals are used as detergents, personal care products, pharmaceuticals, plasticizers, flame retardants, and so on (Table 1) (3). However, their environmental quality criteria have not yet been regulated. There is a growing concern that such chemicals, frequently referred to as *novel* or *emerging* organic contaminants, may cause undesirable effects because of their continuous release into the environment. Some of these chemicals and/or their transformation products (such as hormones, phthalates, and alkylphenols) were found to act like

Table 1 *Overview of currently unregulated organic compounds (3)*

Types		Examples
Pharmaceuticals	Antimicrobials	Penicilins, tetracyclines, sulfonamides, macrolides, fluoroquinolones
	Analgesics/antiinflamatory drugs	Ibuprofen, diclofenac, naproxen, acetaminophen, acetysalycilic acid, propyphenazone
	Psyhiatric drugs	Diazepam, carbamazepine
	Blood-lipid regulating agents	Benzafibrate, clofibric acid, fenofibric acid, simvastatin
	B-blockers	Metoprolol, propanolol, timolol
	X-ray contrast agents	Diatriozate, iopamidol
	Steroids and hormones	β-estradiol, estrone, estriol, ethynil estradiol
Personal care products	Fragrances	Nitro, polycyclic and macrocyclic musks
	Sun-Screen agents	Benzophenone, camphor
	Insect repellents	N,N-diethyltoluamide
Antiseptics		Triclosane, chlorophene
Surfactants and surfactant metabolites		Alkylphenol polyethoxylates, alkylphenol carboxylates and dicarboxylates
Flame retardants		Tetrabromobisphenol A, hexabromocyclododecane (HCBD)
Industrial additives and agents		Chelating agents (EDTA), benzene and naphthalene sulphonates
Gasoline additives		Dialkyl ethers, methyl-tert-butyl ether (MTBE)

endocrine disruptors (4), while continuous exposition to low levels of different antimicrobials is suspected to play a role in the formation of antibiotic-resistant bacterial strains (5). Identification and determination of many previously undetected organic anthropogenic compounds in wastewater, including a large number of pharmaceuticals, has progressed rapidly in recent years along with the development of new and improved analytical techniques. However, data on the occurrence and fate of individual organic contaminants in Croatian wastewaters are still rather limited. The main objective of this paper is to make an overview of the published data dealing with the occurrence of specific organic contaminants in municipal wastewaters of different Croatian cities. It will also present a few examples of ongoing research on organic contaminants derived from pharmaceutical products or detergents.

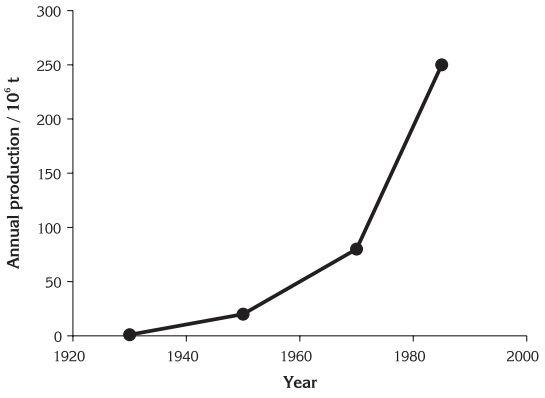

Figure 1 *Increase of global annual production of synthetic organic compounds (2)*

ORGANIC CONTAMINANTS REGULATED BY LAW

Regular surveys of wastewater organic load include only a limited number of group parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD_5), total organic carbon (TOC) as well as total and mineral oils. In addition, maximal permitted levels of total concentration of anionic, non-ionic and cationic detergents as well as several groups of so-called classical priority contaminants, including total aromatic hydrocarbons, halogenated hydrocarbons and organochlorine pesticides, are also regulated by law (6). These parameters are to be regularly monitored and the concentration levels reported to the authorities. However, these data usually receive only a very basic level of interpretation and are seldom published in public literature. Extensive literature search using the most popular databases, including the Web of Science and Current Contents, will show that relevant scientific publications dealing with organic contamination of Croatian wastewaters are extremely scarce. Only

a few papers relevant for this review were found in the proceedings of regular Yugoslav Conferences on Water Protection held between 1985 and 1991. *Jakovčić and Preka* (7) made an overview of different law-regulated parameters based on their multiannual determination in wastewaters released from various types of industries in the city of Zagreb, Croatia. The sewer systems in Croatia are mostly of the mixed type so that municipal wastewaters usually contain all the organic loads discharged by local industry. The concentration ranges of common organic pollution indicators, including COD, BOD_5, TOC, phenols, total oils and anionic surfactants, indicated that the highest contribution from the industrial wastewaters to the total wastewater organic load may be from chemical and paper industry. The concentration of anionic surfactants determined by the non-specific colorimetric method with methylene blue active substance (MBAS-method) was in the range of (0.1 to 100) mg L^{-1}. However, several extremes of up to 7200 mg L^{-1} were determined in the wastewaters from chemical industries. The concentration of phenols and total oils showed a very wide range of (0.003 to 20.7) mg L^{-1} and (2 to 8400) mg L^{-1}, respectively, depending on the sampling date and the type of industry.

Ahel and Vržina (8) investigated the influence of different types of municipal and industrial wastewaters of the city of Slavonski Brod on the contamination of the Sava River by mineral oils in 1984. The total oil concentration in municipal wastewaters determined by infrared spectroscopy, indicative of total extractable lipids, varied in a rather wide range of (0.9 to 1740) mg L^{-1}. However, most of the concentration values were below 50 mg L^{-1}. Mineral oil concentration [(0.1 to 23) mg L^{-1}] was generally less than 10 % of the total oils. The concentration of aromatic hydrocarbons as the most toxic fraction of mineral oils was even lower and rarely exceeded the lower μg L^{-1} range. Nevertheless, following a major spill from the adjacent petrochemical industry, the concentration of toluene, styrene, naphthalene and methylnaphthalene in the urban wastewaters of the city of Zagreb reached 20 μg L^{-1}, 250 μg L^{-1}, 9 μg L^{-1}, and 14 μg L^{-1}, respectively (9).

Very few reports were published on other specific, highly toxic, priority contaminants in Croatian wastewaters. *Picer and Picer* (10) investigated the concentration of different chlorinated hydrocarbons in 44 wastewater samples in the city of Rijeka in 1979-1986. The concentration of DDT, dieldrin and polychlorinated biphenyls (PCBs) varied extremely: (<0.2 to 657) ng L^{-1}, (<0.1 to 179) ng L^{-1} and (<0.3 to 9116) ng L^{-1}, with respective median concentrations of 7.0 ng L^{-1}, 1.4 ng L^{-1} and 23.1 ng L^{-1}.

UNREGULATED ORGANIC CONTAMINANTS – QUALITATIVE CHARACTERISATION

Beside organic contaminants regulated by law, wastewaters contain numerous unregulated chemicals of different origin. Since the concentration levels and biological effects of individual organic compounds are very different, it is essential to provide their comprehensive characterisation using the best available techniques. Zagreb wastewaters which were profiled using gas chromatography coupled to mass spectrometry (GC/MS) contained a very large number of different organic compounds (11). The most prominent were oil-derived aliphatic and aromatic hydrocarbons, and several detergent-derived alkylbenzenes were also detected (Table 2). The main organic compounds in the polar fraction were soap-derived fatty acids and some biogenic sterols,

Table 2 *Overview of the main groups of organic contaminants determined in the wastewaters of the city of Zagreb by gas chromatography coupled to mass spectrometry (11)*

Compound type	Origin
Aliphatic hydrocarbons	Petroleum
Alicyclic hydrocarbons	Petroleum
Aromatic hydrocarbons	Petroleum, detergents
Polycyclic aromatic hydrocarbons	Petroleum
Chlorinated hydrocarbons	Solvents, water chlorination
Aliphatic carboxylic acids	Biosynthesis, soaps
Aromatic carboxylic acids	Chemical synthesis
Phthalates	Plasticizers
Sterols	Biosynthesis
Phenols	Chemical synthesis, non-ionic detergents

including coprostanol and cholesterol. In addition, several volatile chlorinated hydrocarbons and different types of phenols were found in detectable amounts. Even with the rather large number of individual organic contaminants detected by GC/MS, it should be pointed out that this technique successfully determines about 15 % of all extractable compounds, as it is suitable for the analyses of relatively volatile and thermostable compounds.

The development of new and improved analytical techniques, especially high-performance liquid chromatography coupled to mass spectrometry (LC/MS), enabled determination of many previously undetected organic anthropogenic compounds in different types of wastewaters (12). However, most data were obtained by specially designed, target-oriented LC/MS analyses, while LC/MS screening for unknown contaminants was rare, due to the lack of searchable mass spectra libraries needed for the identification of unknown peaks.

Preliminary qualitative LC/MS full scan (FS) analyses of the extracts of several different Croatian urban wastewaters indicated that different detergent- and soap-derived compounds were quantitatively the most important contaminants, while the concentrations of other compounds were too low to be detected in the total ion current scanning mode. The main class of anionic surfactants detected in all samples were linear alkylbenzene sulphonates (LAS) (Figure 2), while the main non-ionic surfactant species included linear alcoholethoxylates (LAEs) and nonylphenolpolyethoxylates (NPnEO) (Figure 3).

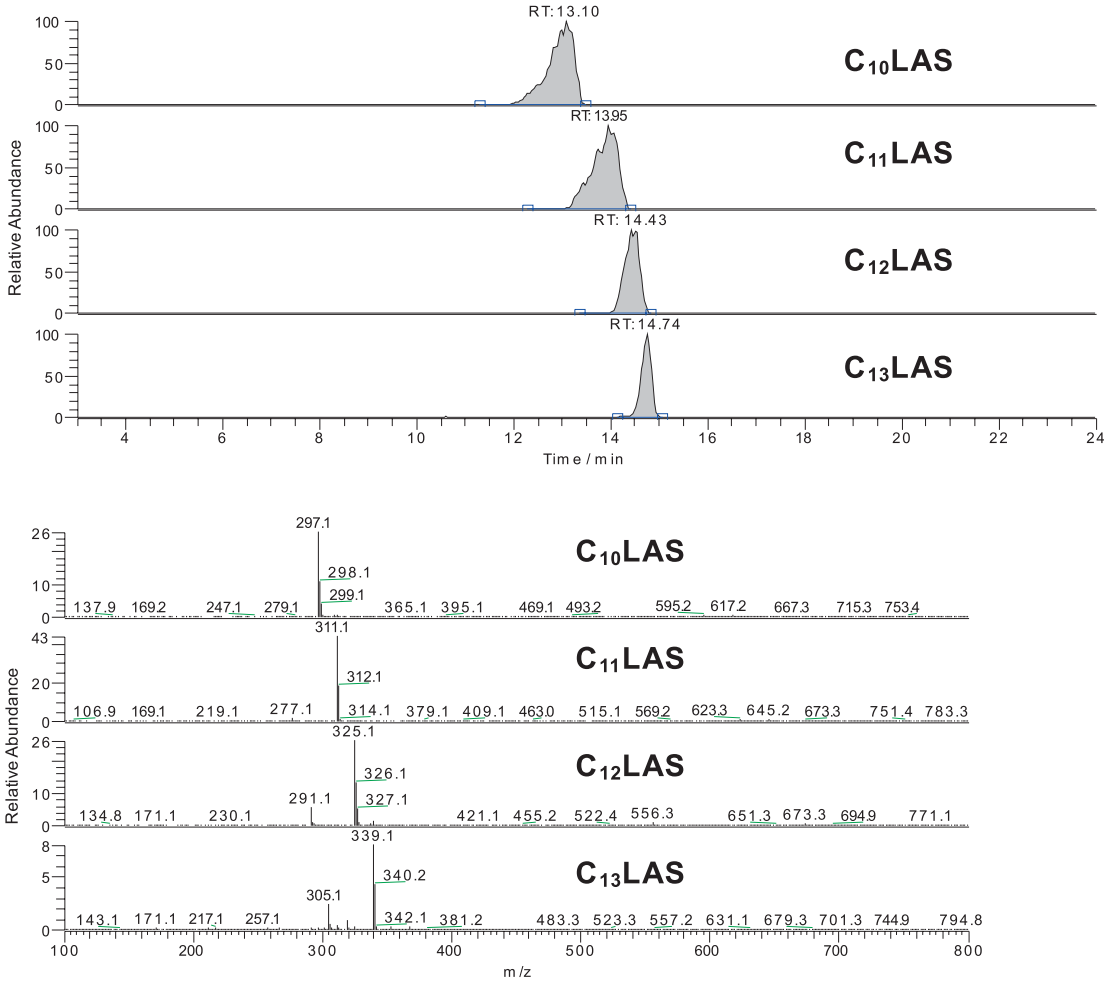

Figure 2 *Example of the full scan search of the urban wastewater extract performed by liquid chromatography coupled to mass spectrometry with electrospray ionisation in negative polarity mode (CnLAS = linear alkylbenzenesulphonates, n =10-13 carbon atoms in alkyl chain)*

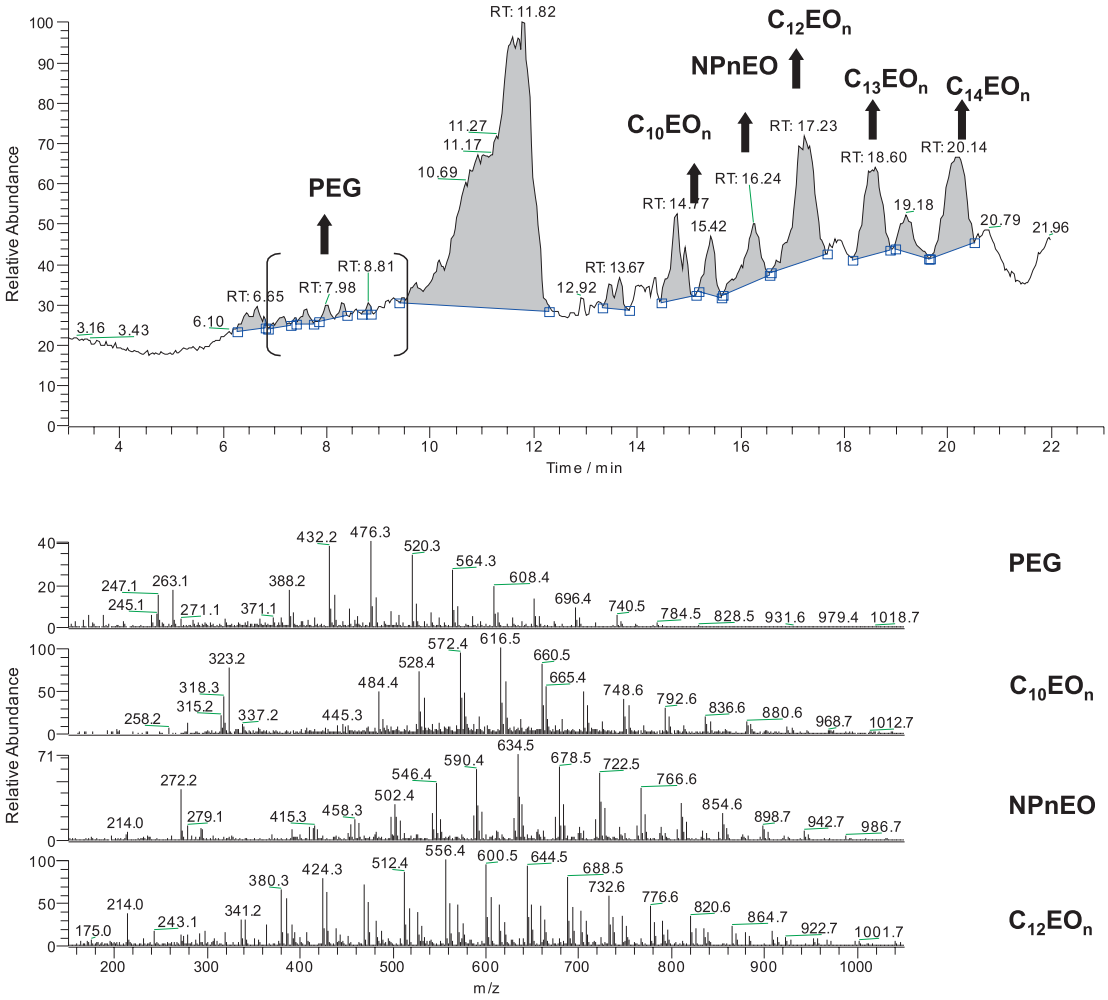

Figure 3 *Example of the full scan search of the urban wastewater extract performed by liquid chromatography coupled to mass spectrometry with electrospray ionisation in positive polarity mode (PEG = polyethylene glycol, CnEO = linear alcoholethoxylates with 10-14 carbon atoms in alkyl chain, NPnEO = nonylphenolpolyethoxylates)*

UNREGULATED ORGANIC CONTAMINANTS – QUANTITATIVE DETERMINATION

Surfactants

Maximal permissible concentration of total non-ionic surfactants in wastewater is regulated by law (6) as a group parameter indicating the presence of several types of non-ionic surfactants. However, from the ecotoxicological point of view, alkylphenolpolyethoxylates (APnEO) are the most critical group of non-ionic surfactants, since some of their stable degradation products exhibit high acute and chronic toxicity (13) as well as a weak estrogenic activity in fish (4).

The first detailed investigation of the occurrence and fate of non-ionic surfactants of the APnEO type in Croatian urban wastewaters was performed in the late 1980s and early 1990s (14-18). All quantitative determinations were performed using high-performance liquid-chromatography with both normal-phase (oligomer distribution) and reversed-phase systems (homologue distribution). The main alkylphenolic species were of the nonylphenolpolyethoxylate (NPnEO) type, while their octylphenolic analogues were not determined at significant levels. The concentration levels were in accordance with the concentration of these compounds reported for several other western European countries (19), which indicated a widespread use of NPnEO-containing detergents during the investigated period (Figure 4). The oligomer distribution in all studies was characterised by a maximum at NP10EO, which

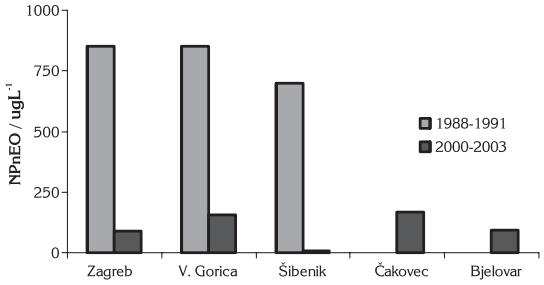

Figure 4 *Concentration of nonylphenolpolyethoxylates (NPnEO) in Croatian municipal wastewaters over two periods of time*

indicated heavy-duty detergents as the dominant source of NPnEO in the investigated area.

Ahel et al. (14) studied APnEO and their transformation products in the wastewater treatment plant (WWTP) of Velika Gorica. The highest NPnEO concentration was determined in raw wastewaters [(210 to 1390) μg L^{-1}], while the concentration levels varied in the range of (346 to 5540) μg L^{-1} and (10 to 150) μg L^{-1} in the primary and secondary effluent, respectively. Concentrations of several types of lipophylic NPnEO transformation products, including nonylphenol (NP), nonylphenolmonoethoxylate (NP1EO) and nonylphenoldiethoxylate (NP2EO), were also determined at different stages of wastewater treatment process. The concentrations of these compounds in untreated wastewater [NP: (11 to 31) μg L^{-1}; NP1EO: (8 to 40) μg L^{-1}; NP2EO: (<0.3 to 10) μg L^{-1}] did not differ much from those in the secondary effluent (SE) [NP: (3 to 24) μg L^{-1}; NP1EO: (2 to 64) μg L^{-1}; NP2EO: (<0.3 to 40) μg L^{-1}]. However, the contribution of these compounds to the total alkylphenolic species concentration was much higher in SE than in raw wastewater (RW). NP sludge mass fraction [(80 to 480) μg g^{-1}] was rather high, while the presence of NP1EO [(32 to 950) μg g^{-1}] and NP2EO [(2 to 920) μg g^{-1}] in the sludge indicated an incomplete fermentation during the anaerobic stabilisation of the sludge.

The concentration of alkylphenolic compounds in the wastewaters of the city of Zagreb (16) was rather similar to those reported for RW of the city of Velika Gorica. NPnEO concentration was in the range of (213 to 1185) μg L^{-1}, while the concentration range of NP, NP1EO and NP2EO was (0.6 to 20.7) μg L^{-1}, (0.9 to 19.5) μg L^{-1}, and (0.3 to 8.4) μg L^{-1}, respectively. Based on the average concentration of APnEO of 600 mg m^{-3} and an average wastewater flow rate of 5 m^3 s^{-1}, the daily input of APnEO into the Sava River via wastewaters was estimated at about 260 kg.

The input of APnEO and their lipophylic transformation products into the Šibenik Harbour was determined by analysing wastewaters from all major outlets of the city of Šibenik in the period 1990-1991 (17, 18). The concentration of NPnEO in untreated municipal wastewaters varied from 70 μg L^{-1} to 2960 μg L^{-1}. A relatively high percentage (6 to 60) % of NPnEO was associated with wastewater suspended solids and rather different oligomer patterns were detected in the dissolved and particulate phase. The concentration of NP, NP1EO and NP2EO in municipal wastewaters varied within the ranges of (<0.5 to 419) μg L^{-1}, (<0.5 to 35) μg L^{-1}, and (<0.5 to 54) μg L^{-1}, respectively, representing only a minor fraction of the total surfactant-derived nonylphenolic compounds.

The most recent investigations (20-22) performed in several Croatian municipalities show that these compounds are still widely present in municipal wastewaters. However, their concentration is generally lower than before (17, 18) and rarely exceeds 100 μg L^{-1}. Such decrease is probably a result of legal and voluntary restrictions on the use of NPnEO in laundry detergents, introduced in Western Europe in the late 1980s. It is likely that this change had an impact on the Croatian detergent manufacturers, whose laundry detergents, according to our analyses of some typical products on the market, ceased to contain NPnEO.

The maximal permissible levels of the total anionic surfactants in wastewaters and recipients are regulated by law (6), while their regular monitoring is performed using the non-specific colorimetric MBAS method which does not distinguish contributions of individual classes of surfactants. In particular, it is important to get information on the occurrence and fate of linear alkylbenzenesulphonates (LAS) as the most popular detergent-derived anionic surfactants. *Terzić and Ahel* (23, 24) investigated the input and behaviour of LAS in the stratified Krka River estuary. Individual LAS homologues in municipal wastewaters of the city of Šibenik were analysed using reversed-phase high-performance liquid chromatography with spectrofluorimetric detection. The investigated wastewaters contained LAS homologues with alkyl-chain lengths from C_{10}-C_{13} at total concentrations ranging from 285 μg L^{-1} to 1040 μg L^{-1}, while the total LAS input via wastewaters into the Šibenik Harbour was estimated at 12.6 kg per day. A relatively large fraction [(11 to 59) %] of total LAS was found in the particulate phase, which was significantly enriched by

the more lipophylic, higher LAS homologues (C_{12}, C_{13}). Rather high concentrations of LAS [(1 to 10) mg L^{-1}] determined very recently in the wastewaters of several Croatian municipalities confirmed these surfactants as among the most important anthropogenic contaminants in urban wastewaters (21, 22). The elimination efficiency of these compounds was very high (up to 99 %) only in WWTPs with biological treatment, while mechanical treatment did not significantly reduce total LAS load in the wastewaters.

Pharmaceutical compounds

The first comprehensive survey of pharmaceuticals in wastewaters was performed by *Ternes et al*. (25). The studies initiated in Germany were followed by many other in various European countries, making pharmaceutical compounds one of the most popular class of emerging contaminants in the past few years. The first study, dealing with the occurrence of pharmaceutical compounds in Croatian municipal wastewaters, was published by *Jeličić and Ahel* (26). The authors investigated the distribution and behaviour of selected pharmaceuticals, including analgesics of the phenazone type and caffeine in RW and sewage effluents from several Croatian treatment plants. All the determinations were performed by GC/MS. The most abundant phenazone compound was propyphenazone, whose concentration in RW varied in the range of (<0.1 to 1.0) μg L^{-1}, while the concentration of all other measured analgesics was below 0.05 μg L^{-1}. The concentration of caffeine in RW was relatively uniform and much higher (up to 100 μg L^{-1}), indicating that the main source of this compound in the wastewaters were not pharmaceuticals, but most probably coffee, tea and cola drinks. The elimination efficiency of caffeine after biological treatment in WWTPs was rather high [(95 to 99) %], compared to propyphenazone whose elimination was modest in all WWTPs (<44 %).

The most recent comprehensive study of the occurrence of different antimicrobial compounds in Croatian wastewaters was performed within the framework of an EU-funded research project "Reduction of Environmental Risks, Posed by Emerging Contaminants, through Advanced Treatment of Municipal and Industrial Wastes – EMCO" (27). Sampling was performed at 17 locations, encompassing all major Croatian cities, and could be regarded representative of different Croatian regions. The study was performed using highly specific analytical techniques, including tandem liquid chromatography/mass spectrometry with electrospray ionisation (LC/ESI/MS/MS) and gas chromatography-mass spectrometry (GC/MS), and encompassed a large number of individual compounds. The first preliminary results were reported in the Proceedings of the 1st EMCO workshop held in Dubrovnik (22, 28). The results indicate that the concentrations of the investigated compounds were rather similar to those determined in some other parts of western Europe (29, 30). The most abundant sulphonamide antimicrobial was sulfamethoxazole [(0.3 to 2.0) μg L^{-1}]; norfloxacin [(0.01 to 3.0) μg L^{-1}] and ciprofloxacin [(0.01 to 2.6) μg L^{-1}] were the most abundant fluoroquinolones, while azithromycin [(0.02 to 1) μg L^{-1}] and erythromycin were the most prominent macrolide antibiotics in Croatian wastewaters (22). *Gros et al*. (28) reported the presence of 30 pharmaceutical compounds, including antibiotics, antiphlogistics, lipid regulators, psychiatric drugs, antiulcer agents antibiotics and β-blockers in the same samples. The most abundant groups of pharmaceutical compounds in all samples were antiinflammatories and analgesics, especially acetaminophen, which was detected at a high μg L^{-1} level.

Acknowledgements

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Sažetak

ORGANSKA ZAGAĐIVALA U KOMUNALNIM OTPADNIM VODAMA REPUBLIKE HRVATSKE

Komunalne otpadne vode jedan su od najvažnijih oblika unošenja otpadnih tvari u okoliš. U Republici Hrvatskoj taj je problem posebno izražen jer se od ukupne količine otpadnih voda obrađuje samo 12 %, od čega samo 37 % prolazi cjeloviti postupak mehaničkog i biološkog pročišćavanja. Redovito praćenje organskog opterećenja, koje se putem otpadnih voda unosi u prirodne vode, obuhvaća samo manji broj skupnih pokazatelja, kao što su kemijska potrošnja kisika (KPK), biološka potrošnja kisika (BPK), ukupni organski ugljik (TOC) te ukupna i mineralna ulja, hlapljivi fenoli i ukupni tenzidi. Zakonom su propisane i maksimalno dopuštene vrijednosti manjeg broj spojeva iz skupine prioritetnih zagađivala (npr. halogenirani ugljikovodici, ukupni aromatski ugljikovodici), dok su broj i raznovrsnost različitih organskih spojeva u otpadnoj vodi izuzetno veliki. Sveobuhvatne pretrage hrvatskih komunalnih voda masenospektroskopskim tehnikama upozorile su na prisutnost velikog broja specifičnih organskih zagađivala, od kojih su najzastupljeniji naftni ugljikovodici te različiti organski sastojci podrijetlom iz detergenata i sredstava za čišćenje. U novije se vrijeme sve više ističe važnost istraživanja novih tipova zagađivala, čije unošenje u okoliš nije zakonom regulirano, a njihovo štetno djelovanje na okoliš počiva na biološkim mehanizmima koji su tek odnedavno objavljeni u znanstvenoj literaturi. Vrlo istaknuti predstavnici takvog tipa zagađivala su antropogeni spojevi s endokrinim djelovanjem i farmaceutski spojevi. U ovom je radu načinjen pregled postojećeg znanja o pojavljivanju različitih organskih zagađivala u otpadnim vodama hrvatskih gradova, s posebnim naglaskom na rezultate dobivene visokospecifičnim tehnikama.

KLJUČNE RIJEČI: *aromatski ugljikovodici, farmaceutski spojevi, halogenirani ugljikovodici, novi tipovi zagađivala, prioritetna zagađivala, tenzidi*

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