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EMERGING HAZARDOUS SUBSTANCES IN OUTDOOR AND INDOOR ENVIRONMENT. STATE OF THE ART. CURRENT AND PAST RESEARCH.

Abstract: The state of the art of contamination by hazardous emerging substances (HEMS) in the outdoor and indoor environment based on the original results of authors and key literature references is presented. History of the newly-recognized group of HEMS is described. The key physico-chemical characteristics of HEMS are emphesized, especially pseudoperzistency of HEMS, non monotonic dose response, chemical cocktails, irreversible binding to proteins, following by constants of partitioning and distribution and different forms of HEMS species in the aquatic environment (molecules, ions, cations and anions, and zwitter ions).

Within this study review, representative original results of HEMS detected in the river Danube in the vicinity of Novi Sad, waste water, air and human milk are compiled, gained by numerous international and national projects, more than 30 papers published in the SCI journals and 40 full length papers printed at international and national conferences. Based on concentration levels of HEMS, for the selected HEMS, risk assessment and RQ coefficients were calculated.

Key words: emerging substances, wastewater, Danube surface water, air, human milk, risk assessment

INTRODUCTION

State of the art and historical overview

The term of emerging substances of concern (ESOC) is introduced for the first time in 2004 in Florida Report [1]. According to Florida report, ESOC are categorized in 6 groups:

- Global organic contaminants;
- Pharmaceuticals and personal care products;
- Endocrine-modulating compounds;
- Nanoparticles;
- Industrial chemicals (new and recently recognized);
- Biological metabolites and toxins.

Global Organic Contaminants include polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and siloxanes. PBDEs and HBCDs are flame-retardant chemicals that are applied to a wide variety of everyday items such as clothing, upholstery, foam cushions, electronics, and automobile interiors. PBDEs do not chemically bind to the substrates to which they are applied, and so they are easily liberated. These moderately long-lived molecules are primarily released into the atmosphere, where they can be transported globally and readily bioaccumulate in biological tissues.

Pharmaceuticals and Personal Care Products (PPCPs) include all prescription and over-the-counter drugs,

diagnostic agents, dietary supplements, fragrances, soaps, conditioners, sunscreens, cosmetics, caffeine, and nicotine. PPCPs also include antibiotics used prophylactically to prevent disease in livestock production (feedlot) operations. This diverse category of ESOC includes many water-soluble compounds. The most common mechanism for their entry into the environment is through wastewater discharges (municipal and septic drainage), land application of sewage sludge and manure, and landfill leachate. Depending on the type of treatment employed and the specific chemicals involved, wastewater or drinking water facilities may or may not be effective at removing these compounds from the effluent or drinking water.

PPCPs compounds include:

- Analgetics (Acetaminophen/Paracetamol, Diclofenac, Ibuprofen, Ketoprofen, Naproxen)
- Antibiotics/Antimicrobials (Ciprofloxacin, Erythromycin, Sulfamethoxazole, Trimethoprim, Triclosan)
- Antihyperlipidemics (Benzafibrate, Clofibric acid, Gemfibrozil)
- Fragrances (Galaxolide, Tonalide)
- Other compounds (Bisphenol A, Caffeine, Carbamazepine)

Endocrine-Modulating Chemicals (EMCs) include natural and synthetic hormones, surfactants, pesticides, tributyltin, polychlorinated biphenyls (PCBs), and dioxins/furans. Estrogens are excreted by humans and

are readily degradable under aerobic conditions, but they degrade slowly under anaerobic conditions. Nanomaterials are natural and man-made structures, ranging in size from 1 nanometer (nm) to 100 nm, that are widely used in nanotherapeutic pharmaceuticals, drug delivery, cosmetics, personal care products, energy storage products, fabrics, lubricants, and even recreational equipment such as golf and tennis balls. Their use is already so ubiquitous that one would find it very difficult to avoid exposure to at least some form of nanomaterials. Due to their extremely small size, nanomaterials can pass through biological membranes and the blood/brain barrier.

Moldovan was [2] among the first researchers who published the screening and target analyzes of pharmaceutical and personal care products (PPCPs) in the Somes River (Transylvania), which is one of the main rivers in Romania and belongs to the Danubian basin, therefore the Somes River is tributary of Tisa River and Tisa River is tributary of Danube river. Moldovan identified and quantified in his research 15 target compounds using GC/MS methods after extraction of analytes by SPE.

Caffeine was detected in the range of 430 to 9700 ng/l. Galaxolide and Tonalide were detected around of 300 ng/l and 100 ng/l, respectively. Due to environmental stability Galaxolide and Tonalide were selected as suitable tracers for musk fragrance. The detected concentrations of pentoxifylline are 300 ng/l and 126 ng/l. The probable main source is the University Hospital of Cluj-Napoca, and untreated wastewater. acetylaminophenazone (AAP) formylaminophenazone (FAP) were detected in relative high quantity in every place. The AAP and FAP are metabolites of Metamizol (Noraminophenazone), a common analgesic and antipyretic drug. The Ibuprofen (NSAID) was detected in almost every sample of the effluent from Europe, which is probably a result of their high prescription extent and wide usage. In the UK effluents it was detected up to 1000 ng/l and in surface water from USA median values of 200 ng/l were reported. Carbamazepine is widely used as antiepileptic and is antidepressant drug and is known as a persistent substance. It has extremely low removal rate (fewer than 7 %) in WWTP and is an excellent tracer pharmaceutical agents substance for in environment. Carbamazepine was detected quantities of 65, 72 and 75 of ng/l. Diazepam is a psychiatric drug used as tranquillizer. In the WWTP effluent was found in the maximum quantity of 40 ng/l but in rivers was not detected above 30 ng/l.

Codeine is an analgesic often detected in surface water. It was detected in quantity of 54 ng/l, 40 ng/l and 27 ng/l. Cyclophosphamide is an antineoplastic drug frequently applied in cancer chemotherapy having a mutagenic action. It was found in 65 ng/l.

Triclosan is an antimicrobial agent found in many hand soaps (0.1 to 0.3%). In the Somes River triclosan

was found in concentration of 38 ng/l. Acetylsalicylic acid (Aspirin) is an analgesic and anti-inflammatory drug very frequently used in medical practice. It was sold in 2000 in quantities exceeding 1000 tons/ year in EU countries.

Our results, current and past research

The first detailed research of our group realized within NATO Project in wastewater and Danube surface water in the vicinity of Novi Sad. Within the NATO Project, based on determination of HEMS in the river Danube, we meet for the first time with NORMAN list of emerging substances [3], which was formed by NORMAN Project with the financial support of the European Commission within the 6th Framework EU According to NORMAN, substances are defined as substances that have been detected in the environment, but which are currently not included in routine monitoring programs at EU level and whose fate, behavior and (eco)toxicological effects are not well understood. Emerging substances were divided in categories/classes and sub-classes (Table 1). Examples from the NORMAN list of emerging substances are surfactants, flame retardants, pharmaceuticals and personal care products, gasoline additives and their degradation products, biocides, polar pesticides and their degradation products and various proven or suspected endocrine disrupting compounds (EDCs).

Table 1. Emerging substances by NORMAN

Category / class	Sub-class		
Algal toxins	Cyanotoxins		
Antifoaming agents	Antifoaming agents		
Antioxidants	Antioxidants		
Antifouling compounds	Antifouling compounds,		
	Organotin compounds		
Bio-terrorism/	Bio-terrorism/ sabotage		
sabotage agents	agents		
Complexing agents	Complexing agents		
	Aromatic sulphonates,		
	Alcohol ethoxylates (AEs),		
Detergents	,		
	Ethoxylates/carboxylates		
	of octyl/nonyl phenols		
Disinfection by-	Iodo-trihalomethanes,		
products (drinking	Bromoacids,, Other		
water)	disinfection by-products		
Plasticizers	Phthalates, Benzophenone		
T insticizers	derivatives		
	Brominated flame		
	retardants, Polybrominated		
Flame retardants	diphenylethers,		
	Organophosphates,		
	Chlorinated paraffins		
	Fragrances, Nitro musks,		
Fragrances	Macrocyclic musks,		
	Polycyclic musks		
Gasoline additives	Dialkyl ethers		
Industrial chemicals	Industrial chemicals		

	6 1 6 11 6 1	
	Carbon fullerenes, Carbon	
	nanotubes, Carbon black,	
Nanoparticles	Silicon-based, Titanium	
	dioxyde, Aluminium	
	Oxide	
Perfluoroalkylated	Perfluoroalkylated	
substances and their	substances, Fluorotelomer	
transformation	alcohols,	
***************************************	Perfluorosulfonamido	
products	alcohols	
	Sun-screen agents, Insect	
Personal care products	repellents, Carriers,	
	Parabens (hydroxybenzoic	
	acid esters)	
	Polar pesticides and their	
	degradation products,	
	Other pesticides, New	
Pesticides	pesticides, Degradation	
	products of pesticides,	
	Antimicrobial agents	
Biocides	Biocides	
	Analgesic, Anorexic,,	
Pharmaceuticals	X-ray contrast media	
Trace metals and their	Trace metals and their	
compounds	compounds	
P	Benzotriazoles,	
Anticorrosives	Methylbenzotriazoles	
	(MBT), Tolyltriazoles	
	(TT)	
Wood preservatives	Phenols	
Jou preservatives	Drugs of abuse,	
Other	Benzothiazoles (BT),	
omei -	Nicotine metabolite	
	1 TOOTHIC HICKBOHIC	

In the Serbian language where the correct translation of EMS was requested, on the proposal of professor Milorad Miloradov and the members of our research group in accordance with the Serbian translation of priority and hazardous priority substances ("prioritetne i hazardno prioritetne supstance"), emerging substances were translated as "emergentne supstance". The first detailed description of HEMS as industrial emerging substances was published in Chemical

The unique physicochemical characteristics of HEMS

Industry, Miloradov et al. [4].

The dominant physicochemical characteristics very specific and unique for HEMS are: stable structure, low/non degradability, lipophilicity and hydrophilicity with log Kow in the range of -4.76 to 10.6, bioconcentration/bioaccumulation, biomagnification and protein interaction, toxicity, eco/toxicity, and acute but rather chronic effect (Table 2). Most of the molecules of HEMS are endocrine disruptors, with suspected teratogenic, mutagenic and carcinogenic consequences in low and sub low doses. Low doses effect and non-monotonic response in relation to dose are observed in the picomolar to nanomolar range.

HEMS are semivolatile, volatile and non-volatile compounds with different values of Henry constant, polar/nonpolar molecules, with short half-lives. In aquatic media HEMS could act as neutral, acidic or alkaline chemical species and exist in ionic or zwitter ionic states.

HEMS may cause negative environmental effects at very low concentrations. Mixtures of pharmaceutical compounds (chemical cocktails) may exert substantial effects even if individual compounds are present in low level concentrations. Effects of such continuous and long-term exposure on aquatic organisms and humans are of particular importance, because they may remain undetected until their cumulative level induce and trigger irreversible negative changes.

The most of HEMS/Pharmaceuticals are polar compounds, with the high persistence and as the consequences of these characteristic, they can become widespread throughout the aquatic environment and could affect water quality distant from the primary source. After their release to surface waters, photolysis may be the dominant degradation process which influences the fate of EmS in the surface water.

EmS are generally polar if their $\log K_{ow}$ are <4.5 and non or semi volatile (Henry coefficient, $K_{\rm H}$ <10⁻³ Pa m³ mol⁻¹). EmS are also relatively stable towards most chemical reactions in the aqueous environment.

Physicochemical properties of EmS (solubility, ad/absorbability, biodegradability, beside others) vary greatly depending on their different molecular number of structures, asymmetric C-atoms. stereochemistry, size and shape, hydrophobicity, charge, degree of ionization and other. For the most EmS, there is currently insufficient amount of the information about their potential toxicological consequences on ecosystem, particularly from longterm and low-level environmental exposure. The fate and the transport of EmS in natural aquatic media are unknown, especially in context mostly water/soil/sediment distribution and partitioning processes. These processes are in the intensive phase of research.

The main physical and chemical properties of EmS are characterized by some experimentally or mathematically derived constants of: protonation (Log pKa) which are in range of 9.6 – 2.5, octanol–water partition coefficient (Log Kow) and solubility (Sw) with the values from 10^6 mg L⁻¹ to 0.02 mg L⁻¹, sludge—water distribution coefficient Log Kd and some others constants.

The unique and specific physicochemical characteristic of EmS are:

- Low doses occurrence and effects ppm, ppb, and lower
- Non Monotonic Dose Response, NMDR
- Pseudo persistency / persistency, short half live, t1/2
- Stability low / non degradability

- Hydro/lipophilicity (LogKow=- 4.76 10.6)
- Bioconcentration / bioaccumulation / biomagnification
- Irreversible binding and interaction with the proteins
- Toxicity with hazardous and chronic effects
- Endocrine modulating/disruption, with teratogenic and carcinogenic consequences within the low/sub low doses
- Volatile, non or semi volatile compounds
- Water/lipid soluble molecules (0.06-3.1 104 mg L-1)
- Polar/nonpolar molecules
- Neutral, acidic or basic aquatic media
- Ionic-cationic, anionic or zwitter ionic charge status in the water system
- Chemical cocktails
- Size in nano scale range
- Poorly sorbed to solid phase (sediments, soil, adsorbents) depending on pH and type and class of EmS
- WWTP processes partially remove EmS from wastewater.

Table 2. Examples of some pharmaceutical constants

Examples	рКа	LogKow	Sw	log <i>Kd</i>
Aspirin	3.5	1.13	5295	n.d.
Diclofenac	4.15	4.51	4.52	1.2
Ibuprofen	4.51	3.90	41	0.9
Naproxen	4.2	3.18	144.9	1.1
Ciprofloxacin	6.38	0.4	1.2 *10 ⁴	4.3
Doxycycline	3.5/ 7.7/9. 5	-0.02	312.9	nd
Penicillin V	-2.79	1.87	101.1	nd
Sulfamethoxazole	-5.7	0.89	3942	2.7
Tetracycline	3.3/7. 7/9.7	-1.30	3877	3.9
Trimethoprim	-7.2	0.91	2334	2.3
Enalapril	nd	2.45	34.88	nd
Carbamazepine	-13.9	2.45	17.66	0.1

Our results gained within international projects

Some provocative results of the research of HEMS in wastewater and surface water in the literature resources were the challenges for exploring emerging substances focused on pharmaceuticals and PPCP in our research activities within international Projects, NATO and NETREL TEMPUS; and national project financed by Ministry of Education, Science and Technological Development, Provincial Government and city of Novi Sad.

The research activities were divided on screening and target analysis [5]. Four screening and two target analyses were performed. In screening analyses, more than 300 organic and inorganic substances were detected. Approximately 100-150 compounds have been found in specific sampling points of wastewater

and Danube River. In table 3, the results of the screening analysis of wastewater from the collector RP and Danube surface water, 100 m downstream of the discharge, are summarized. Compounds Benzothiazole, 2-(methylthio)-, phthalates 1,2benzenedicarboxylic acid, diethyl ester and 1,2benzenedicarboxylic acid, dibutyl ester and Cholest-5en-3-ol (3 beta)- are detected in both samples. Polycyclic aromatic hydrocarbon Anthracene, fragrance Dihydro methyl jasmonate, personal care product 2-propenoic acid, 3-(4-methoxyphenyl)-, 2ethylhexyl ester and β-Sitosterol are detected only in the Danube water.

Based on the results of screening analyses 69 compounds were selected for target analyses. Among 69 compounds selected for target analysis, 29 were above limit of detection (LOD) in surface water, wastewater and raw water samples collected on 11 sampling sites. PAHs, 8 PCBs, phthalates and organochlorine pesticides were measured above LOD and their concentrations varied from very low, about 1 ng/L for PCB congeners to 2170 ng/L for phthalate (di-(ethylhexyl)-phthalate).

Table 3. Results of screening analysis of wastewater from the collector RP and Danube water, 100 m downstream of the discharge

Phenol, 2-(1,1-	Wastewater and	
dimethylethyl)-	Danube water	
Phenol, 2,4-bis-(1,1-	Wastewater and	
dimethylethyl)-	Danube water	
Pentadecane	Wastewater and	
Pentadecane	Danube water	
Undecanoic acid, 10-methyl-, methyl ester	Danube water	
1.2 hanzanadiaanhavylia	Wastewater and	
1,2-benzenedicarboxylic acid, diethyl ester	Danube water	
aciu, uletilyi ester	NORMAN list	
Benzothiazole, 2-	Wastewater and	
(methylthio)-	Danube water	
(methyltino)-	NORMAN list	
Hexadecane	Wastewater and	
Ticxadecane	Danube water	
Dihydro methyl jasmonate	Danube water	
Diffyti o methyf jasmonate	NORMAN list	
Phenanthrene-D-10	Wastewater and	
Thenantinene-D-10	Danube water	
	Danube water	
Anthracene	WFD hazardous	
	priority substance	
Heptadecane, 3-methyl-	Danube water	
1-naphthalenol, 5,6,7,8-		
tetrahydro-2,5-dimethyl-8-(1-	Wastewater	
methylethyl)-		
phenol, 4-(1-methyl-1-	Wastewater and	
phenylethyl)-	Danube water	
1,2-benzenedicarboxylic acid,	Wastewater	
bis(2-methylpropyl) ester		

7-Acetyl-6-ethyl-1,1,4,4- tetramethyltetralin	Wastewater
3,7,11,15-Tetramethyl-2- hexadecen-1-ol	Wastewater
1,2-benzenedicarboxylic acid, dibutyl ester	Wastewater and Danube water NORMAN list
2-propenoic acid, 3-(4- methoxyphenyl)-, 2- ethylhexyl ester	Danube water NORMAN list
Cholest-5-en-3-ol (3 beta)-	Wastewater and Danube water NORMAN list
β-Sitosterol	Danube water NORMAN list

The most of the detected compounds (fluoranthene, pentachlorobenzene, anthracene, trifluralin hexachlorocyclohexane, octylphenols, endosulfan, dieldrin and endrin are included in the list of Priority Substances and Certain Other Pollutants according to Annex II of Directive 2008/105/EC. Eight EPA PCB congeners, dieldrin and endrin belong to the Annex A of the Stockholm convention, DDT is included in Annex B of the Stockholm convention, hexachlorocyclohexane gamma (Lindane) belongs to the list of nine new chemicals of the Stockholm convention, while di-n-butyl phthalate was included as plasticizer in the list of NORMAN emerging substances, therefore special attention should be focused to those compounds.

Within the sampling campaigns of Danube river water and wastewater discharged directly into Danube, organochlorine pesticides were detected in the highest concentrations, especially in the wastewater, indicating pollution from agricultural activities, households and farms in the vicinity of the sampling point RO' (Table 4). These pesticides were determined in concentrations more than ten times higher than annual average values in European Union countries. Although DDT was banned in Serbia since 1972, determination of DDT in high concentrations could be the reason of concern. In the recent time, high concentrations of DDT in environmental samples were also mentioned in other literature, although in EU countries concentrations showed decreasing trend. This could be the evidence of uncontrolled usage of DDT in European countries. p,p'-DDD (Rhothane), metabolite of DDT, the most lipophilic with the lowest value of K_{OW} of 4.73 within the metabolites of DDT, was detected in almost all samples with extremely high values at sampling sites RO' and GC1", which confirms historical contamination, but also recent contamination inputted upstream of the city of Novi Sad. According to the concentration ratio of p,p'-DDD and p,p'-DDT at sampling points with the highest concentrations, RO' and GC1", the values of 1.24 and 1.29 indicated historical contamination with these chemicals. Comparing results for DDT metabolites in surface water of Danube, we could

conclude that they were in correspondence with the results of the quality of surface water of Serbian Environmental Agency in 2011.

Table 4. Results of target analysis of wastewater from the collectors GC1, GC2, RO and RP in the vicinity of Novi Sad (in ng/L)

Compound	GC1'	GC2'	RO'	RP'
Dieldrin	<10	<10	70	<10
Endrin	<10	<10	20	<10
Chlorpyrifos				
(Chlorpyrifos-	< 30	< 30	40	< 30
ethyl)				
Endosulfan alpha	<5	<5	60	<5
Endosulfan beta	<5	<5	80	<5
p,p`-DDD	230	240	620	220
p,p`-DDE	80	80	110	80
p,p`-DDT	260	<10	500	<10

p,p'-DDD is so similar to p,p'-DDT and is a metabolite of p,p'-DDT. p,p'-DDD is the solid substance and has been used as pesticide for agricultural use. Also, technical mixture of DDT which has been used in agricultural purposes, contains up to 30% of p,p'-DDD. Increased concentration of Rhothane could be the consequence of uncontrolled usage of this chemical as pesticide in East European countries.

Seasonal variations of caffeine and antibiotic concentrations were investigated along the selected sites of the Danube. The obtained results confirmed the presence of caffeine at four sampling points, near the wastewater discharges. The mean caffeine concentrations for summer, autumn, winter and spring were 24.78 ng/L, 26.83 ng/L, 24.61 ng/L, and 86.29 ng/L, respectively. The analysed antibiotics (sulfamethoxazole, chloramphenicol and tiamuline) were under the limit of detection in all tested samples taken from the Danube [6].

Seasonal variations of bisphenol A (BPA, IUPAC: 4,4'-(propane-2,2--diyl)diphenol) were investigated in the Danube River along the Novi Sad bank, Serbia. The obtained results confirmed the presence of BPA above the limit of quantification (6 ng L⁻¹) in 22 out of 32 the water samples at all eight sampling sites. The BPA concentration varied from <6 to 693 ng L⁻¹. The mean BPA concentration for summer (220 ng L⁻¹) significantly differed from those obtained for autumn (39 ng L⁻¹), winter (6 ng L⁻¹) and spring (41 ng L⁻¹) [7].

Three groups of POPs - DDT, HCH and PCBs were monitored in early human milk for 27 years (1982-2009), as a measure of environmental pollution in the same geographic region (South Bačka, Voyvodina, Serbia). Concetrations of DDT and HCH had general decreasing trend from 1982 to 2009. However, the concentrations of both groups of compounds showed small rises in 1994. Concentrations of PCBs had general decreasing trend from 1982 to 2009 - smooth and steep only till 1994 and with two small peaks in

2003 and 2009. The latest estimated daily intake of DDT and HCH was well below the EU upper limit for pesticides in food intended for infants and small children. Although the estimated daily intake of PCBs was far below the upper limit for daily milk products in Serbia, its increase in 2003 and 2009 is a clear indication of environmental influx of these compounds after the 1994 measurements. The likely explanation for such POP profiles in South Bačka could have been a series of negative environmental impacts escalating in 1999, after which four hot spots were identified in Serbia (Novi Sad, Pančevo, Bor and Kragujevac) by UNEP. The results of this monitoring showed that although a long standing environmental presence of POPs has a decreasing trend, their occasional output in the environment may cause bioaccumulation and biomagnification in human organisms which already start in the neonatal age through mother-child transfer via human milk [8].

Table 5. Concentrations of pesticide residues and PCBs (µg/kg w.w.) in human milk samples. The values are mean, SD and range.

Pollutants	Year of human milk collection			
measured	(number of samples)			
	1982	1004 (n=14)	2006	
	(n=26)	1994 (n=14)	(n=16)	
	89.34 ±	19.76 ±	6.02±	
ΣDDT	45.54	15.01	14.22	
2 001	16.09 –	0.00 -	0.00 -	
	207.43	61.20	64.57	
	69.39 ±	18.28 ±	2.52 ±	
nn' DDE	33.79	14.51	1.42	
p,p'-DDE	11.96 –	0.00 -	0.00 -	
	139.24	57.70	3.53	
	20.01 ±	1.44 ±	4.61 ±	
p,p'-DDT	15.94	1.15	10.37	
p,p -DD1	4.13 -	0.00 -	0.00 -	
	68.19	3.50	46.60	
DDE:DDT	3.5:1	13:1	0.5:1	
ΣΗCΗ	3.19 ±	7.54 ±	$0.60 \pm$	
	3.42	5.08	0.23	
	0.14 -	0.00 -	0.00 -	
	16.01	22.70	0.79	
α-НСН	0.46 ±	1.51 ±	0.35 ±	
	0.48	2.26	0.26	
	0.00 - 1.91	0.00 -	0 .00–	
		8.10	0.79	

The selected results presented in Table 5 evidently illustrate current and past research of persistent, hazardous emerging substances from 1982 to 2009 period in biological material – human milk.

For the risk evaluation the main task is to examine stressor-response relationship. Method for risk assessment is based on calculation of risk quotient (RQ) via MEC and PEC, measured environmental concentration and predicted environmental concentration, respectively, and PNEC values

(predicted no-effect concentration) for every persistent and HEMS chemicals. The obtained results of the risk assessment calculation lead to the conclusion that the metal cations on three locations of Danube surface water posse a significant risk to the aquatic environment and human health, especially for cations of chromium, lead and cadmium.

The paper of Radonic et al. [9] presents the assessment of emission sources and health risk of 16 PAHs in the city of Novi Sad, Serbia, with developed oil, food, chemical and cement industry. The carcinogenic potency of studied PAHs, expressed as the sum BaPeq, ranged from 0.25 ng/m³ for best-case scenario (i.e. minimum exposure to PAHs) to 49.54 ng/m³ for worst-case scenario (maximum exposure). During the heating season, carcinogenic potency was over 8 times higher comparing to non-heating season.

Within indoor research activities the results of determination of cancerogenic emerging substance formaldehyde is abstracted in this study review. The presence of formaldehyde with concentration levels significantly higher than maximum allowed concentration (MAC) of formaldehyde in Serbia is 0.1 mg·m⁻³. The highest formaldehyde concentration value of 19.80 ppm in all three campaigns has been detected in the preparation room during the process of extraction of anatomical specimens from formalin as part of getting ready for the classes [10].

CONCLUSION

Hazardous emerging substances were recognized as old chemicals but new contaminants for the first time in wastewater and surface water, but later in air and soil. In this study review, the general state of art of HEMS based on selected literature references as well as of our original results were underlined with the dominant and unique physicochemical characteristics of HEMS, exclusively pseudopersistency of HEMS, non-monotonic dose response, chemical cocktails, irreversible binding to proteins, following by constants of partitioning and distribution and different forms of HEMS species in the aquatic environment (molecules, ions, cations and anions, and zwitter ions). The concentration levels of HEMS were resulted from our international and national projects and scientific research papers. In this study, in outdoor and indoor environment, concentration levels of HEMS in waste water, surface water, indoor air and human milk were emphasised. A brief review of risk assessment and risk quotient of some selected HEMS is described and calculated.

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Emeritus Mirjana Miloradov is full professor with high experiences in the educational and research field of inorganic, bioorganic and environmental chemical engineering. The recent activities were focused on the applied physicochemical principles in environmental



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Professor Mirjana published 5 monographs, numerous textbook materials in Serbian and English languages with co-authors. She was a mentor for more than 50 MSc and 30 PhD theses. Prof. Emeritus Mirjana Miloradov was the Director of Centre for Interdisciplinary Studies for Environmental Engineering at University of Novi Sad for more than 10 years.

EMERGENTNE HAZARDNE SUPSTANCE U ŽIVOTNOJ I RADNOJ SREDINI. STANJE U OBLASTI NAUKE. TEKUĆA I PRETHODNA ISTRAŽIVANJA.

Mirjana Vojinović Miloradov, Ivana Mihajlović

Rezime: U preglednom radu predstavljeno je stanje u oblasti kontaminacije hazardnim emergentnim supstancama (HEMS) u životnoj i radnoj sredini bazirano na originalnim rezultatima autora i ključnim literaturnim referencama. Opisan je istorijski prikaz novoprepoznate grupe HEMS-a. Ključne fizičko-hemijske karakteristike HEMS-a su istaknute, pseudoperzistencija HEMS-a, ne-monotoni dozni odgovor, hemijski kokteli, ireverzibilno vezivanje HEMS za proteine, ilustrovane konstantama raspodele i distribucije u različitim hemijskim specijama HEMS u vodenoj sredini(molekuli, joni, katjoni i anjoni, i zwiter joni).

U prikazu istraživačkih aktivnosti kompilovani su reprezentativni originalni rezultati detektovanih HEMS-a u reci Dunav u okolini Novog Sada, otpadnoj vodi, vazduhu i humanom mleku realizovani u okviru brojnih međunarodnih i nacionalnih projekata i saopšteni u više od 30 radova objavljenih u časopisima SCI liste i 40 radova štampanih u celini na međunarodnim i nacionalnim konferencijama. Na osnovu određenih koncentracionih nivoa HEMS, za selektovane grupe HEMS-a urađene su analize procene rizika i izračunati RQ koeficijenti.

Ključne reči: emergentne supstance, otpadna voda, površinska voda Dunava, vazduh, humano mleko, procena rizika