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Original Research

Risk Assessment Approach for Prioritizing Danube Basin-Specific Pollutants: a Case Study in the Novi Sad Region

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Abstract

The aim of this work was to determine the most relevant pollutants in Danube surface water and wastewater in the city of Novi Sad, and to conduct a risk assessment approach on substances for the optimization of future monitoring programmes. According to the requirements of Serbian law, obligatory and operating monitoring was focused on physico-chemical and biological parameters while the expanded monitoring programmes have not been applied – often due to practical circumstances. Novi Sad, with a population of more than 300.000 inhabitants, does not have a wastewater treatment plant, and about 2 m^3 of wastewater is discharged directly to the Danube river every day. Screening analyses of the water within the Danube basin around city of Novi Sad included more than 300 different organic substances, while target analysis was conducted for all WFD pollutants. The methodology for generating the list of priority substances was applied for the first time in the Danubian region around the city of Novi Sad. By applying the prioritization procedure, 86 organic substances were determined in screening analyses and 27 substances obtained within target analyses were identified as the most relevant. In addition, seasonal variation analysis was conducted to determine the occurrence trends of specific compounds in different seasons.

Keywords: feco-toxicity, prioritization, screening and target analyses, water pollutants, water quality monitoring

Introduction

Water, as one of the most important parts of the environment, is essential for all living organisms. However, it can be easily contaminated and consequently represents a hazard. That is the reason why monitoring quality of water bodies has great importance.

In the European Union the Water Framework Directive (WFD), as the first joint legislation in this field, defines strategies against water pollution with the aim to achieve good (ecological and chemical) status of all water bodies within all member states and

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candidate countries. This legislation requires monitoring of priority and non-priority chemicals discharged in significant quantities [1].

Serbia has defined water quality monitoring parameters within its own Law on Water (Official Gazette of Republic of Serbia 30/10, 93/2012 and 101/2016). However, in the past, the monitoring was limited to physico-chemical parameters and analysis of inorganic compounds, while organics were completely neglected. Part of the legislation has been harmonized with EU legislation, but has so far not been fully implemented so far. Currently, monitoring the quality of surface water in Serbia is conducted by the Serbian Environmental Protection Agency (SEPA) and contains: (1) results of an examination of biological elements for evaluation of ecological status of surface water; (2) results of analysis of physico-chemical, chemical and microbiological parameters in surface water and groundwater; and (3) results of examination of the quality of sediment in rivers and accumulations. In 2015, the monitoring was enlarged and also included the majority of priority and priority-hazardous substances from 53 water bodies in Serbia. However, due to the technical limitations of the equipment and lack of expertise, we present analytical results on priority WFD substances, which in most of cases were below LOD and LOQ.

Additional monitoring of surface water for organic compounds in Serbia has been conducted through several international projects in past years. NATO Science for Peace Project ESP.EAP.SFPP 984087 included monitoring of wastewater, surface water and raw water used for production of drinking water in the City of Novi Sad, Serbia, 2012-2013. Obtained results from target [2] and non-target [3] analyses point out the presence of various organic compounds in aquatic matrices. Last Joint Danube Survey in 2013 [4, 5] monitored the quality of the Danube at 20 sampling locations in Serbia, including two locations upstream and downstream of Novi Sad.

On a national level there are several projects involving monitoring and analysis of organic compounds in water samples [6], however, they are mostly focused on certain types of industry [7] and agricultural activities. The results of other studies conducted in the Novi Sad region on caffeine and other emerging pollutants [8], pharmaceuticals [9], phthalates [10], OCPs [11] and other pollutants [12] point out on the need to define comprehensive and river-basin specific national monitoring programmes as well as to develop emergency response plans.

Even though, through non-target screening, information on various compounds can be obtained, it does not reveal information about the risk of these compounds to living organisms in surface water and consequently human health. This risk assessment is of significant importance, especially for Novi Sad, since the filtered surface water is used for the production of drinking water.

The prioritization techniques, as one of the effective ways for risk assessment, have evolved in the last 20 years, and since the adoption of the WFD it has become the obligatory procedure in the EU member states. Combined monitoring-based and modelling-based priority setting (COMMPS) procedure was the first European-wide prioritization exercise that resulted in the current list of priority substances [13].

The modelling-based approach did not allow for a quantitative assessment based on PEC/PNEC ratios [14]. A more recent study [15] has introduced a decision tree that first classifies chemicals into six categories, depending on the available information. The priority within each category is then evaluated based on the frequency of exceedance and the extent of exceedance of predicted no-effect concentrations (PNECs). These two indictors are based on maximum environmental concentrations (MEC) rather than the commonly used statistically based averages (predicted effect concentration, PEC).

The aim of this work was to determine the most relevant pollutants in Danube surface water that could represent a significant hazard for living organisms in surface water in the Novi Sad region, where untreated wastewater is directly discharged into the Danube in residential areas near the sources of raw water [16, 17]. In addition, the untreated landfill leachate from municipal landfill is indirectly discharged into the Danube surface water [18].

The prioritization approach was applied for the first time on target and non-target screening results from Serbia in order to develop a platform for selecting a river basin list of specific hazardous pollutants.

Experimental Procedures

Selection of Sampling Locations

Based on the location of the entire sewerage network in the City of Novi Sad, 9 sampling points have been selected for the campaigns. Four sites were located within municipal wastewater collectors (GC1', GC2', RO', RP'), including five in the Danube riverbed (RI, GC1'', GC2'', RO'', RP''). Information and location of sampling sites are given in Table 1 and in Fig. 1. Sampling site RI is located upstream of Novi Sad, before all discharge points, and it has been selected in order to assess the eco toxicological status of the Danube prior to any local urban impact. Analysis of wastewater from the sewerage system determined the level of contamination of municipal and industrial wastewater streams, which are discharged directly into the Danube without any treatment. Danube surface water has been sampled 100 m downstream of each discharge in order to assess the impact of wastewater streams on eco toxicological status of the river. The sewage system at sampling site RO' is located in the area of the water supply source and downstream close to the industrial part of the city

Table 1. GPS locations of sampling sites.

No.	Location	Code	Northern latitude	Eastern longitude
1	Cepelin	GC1″	45°15’5.40”N	19°51’22.53”E
2	Beogradski kej	GC2″	45°15’43.03”N	19°51’27.09”E
3	Ratno ostrvo	RO″	45°15’13.39”N	19°54’38.48”E
4	Rokov potok	RP″	45°15’0.47”N	19°54’11.33”E
5	Collector Cepelin	GC1′	45°15’3,704”N	19°51’18,329”E
6	Collector Beogradski kej	GC2′	45°15’44.19”N	19°51’22.16”E
7	Discharge Ratno ostrvo	RO′	45°15’22.95”N	19°54’39.94”E
8	Collector Rokov potok	RP′	45°14’56.65”N	19°53’43.673”E
9	Ribarac	RI	45°13’54.25”N	19°50’44.62”E

with an Oil Refinery, thermoelectric and heat generating plant.

RP’ is located on the other bank of the river in agricultural area and in the vicinity of a plant for production of diagnostic reagents, laboratory chemicals and solvents. Sampling sites GC1’’ and GC2’’ are located on the stretch near or under three bridges, indicating the water runoff from the bridges as a possible source of Danube surface water pollution.

Sampling was scheduled during winter, summer and autumn in order to compare pollution during different seasons and connect them with typical agricultural, industrial and human activities.

Description of Screening and Target Analysis Methods

Stir bar sorptive extraction (SBSE) and liquid-to-liquid extraction was applied for preparation of samples, while GC-TOF-MS was used for screening analyses. The extraction method and analytical approach are fully described in the paper by Milic et al. [3].

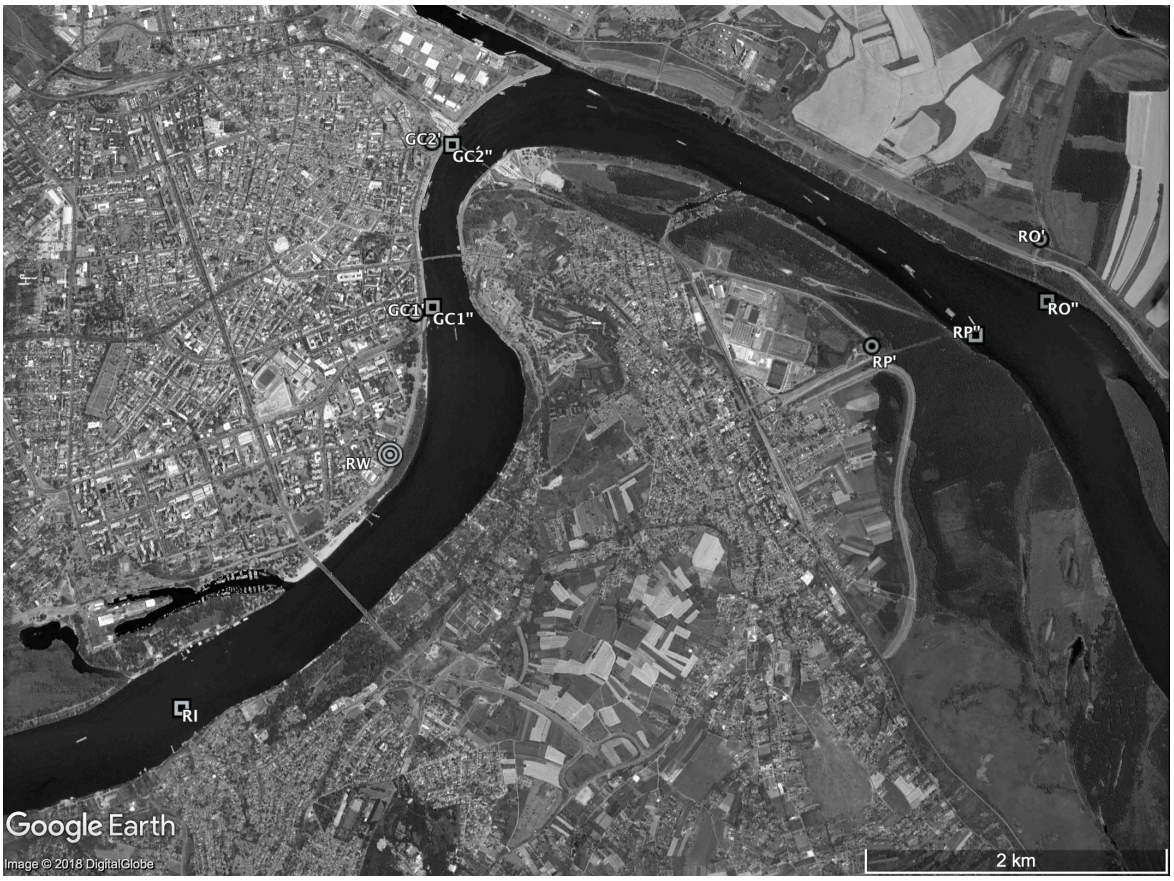

Fig. 1. Location of sampling sites within the city of Novi Sad.

Miloradov and cooperates [2] explained that the procedures used for quantitative analyses of selected compounds (WFD pollutants - ISO 6468, VOCs - ISO 10301, tributyltin compounds - DIN EN 17025, and Simazine, Atrazine, Isoproturon, Diuron and hormones - modified ISO 11369).

Quantification of Concentration Values from Screening Analysis

The screening analysis was performed to identify as many pollutants in wastewater and surface water as possible, which would extend the list of the relevant pollutants for Novi Sad. The results obtained within the screening analysis were quantified by comparison of the signal of an unknown compound to the signal generated by the known concentration of an internal standard. This method provides only rough estimation of the actual concentration, but this error usually varies within one order of magnitude, which is well within the range of uncertainty associated with the eco-toxicological predictions.

Determining Eco-Toxicity Values

The quantitative structure-activity relationships (QSAR) approach was used to predict the toxicity of selected identified organic pollutants based on their chemical structure. In the classical approach, toxicity of compounds is expressed as the minimal concentration that is toxic for living organisms at three different trophic levels (e.g., with fish, algae and *Daphnia magna*). The QSAR approach is based on the prediction of critical effect concentrations (PNEC – predicted no-effect concentration). PNEC value represents the concentration predicted to cause no effect on an organism.

Around 300 compounds, identified from three screening and two target analyses, have been selected for eco-toxicity assessment. Determining PNEC values was conducted by renowned external company with significant experience in this field.

The most accurate were PNEC values already defined in the existing EU legislation: Directive 2011/876/EC, Directive 2008/105/EC and Water Framework Directive 2000/60/EC.

Compounds that do not have PNEC values defined in the legislation were identified in the ecotoxicity databases: AQUIRE and ETOX. Values for remaining compounds were determined using the QSAR approach.

Prioritization Procedure

For defining a list of major pollutants a prioritization approach was applied based on a comparison of the compounds' measured exposure levels, referred as predicted environmental concentration (PEC) and ecological safety threshold, or predicted no-effect concentration (PNEC) [19]. All compounds with the PEC/PNEC risk ratio above 1 [20] were regarded as relevant and were ranked based on the ratio.

Results and Discussion

Identifying Environmental Pressures

Sampling campaigns of wastewater and Danube surface water in Novi Sad were conducted in winter, spring/summer and autumn periods. The distribution of sampling campaigns to different seasons should cover all industrial and domestic activities over the whole year. In winter, the most expected compounds were those coming from increased residential heating, incomplete combustion of oil, etc. In spring, summer and autumn the most commonly expected pollutants could be pesticides and fertilizers due to significant agricultural activity in this area [21] and the absence of a wastewater treatment plant and chemical compounds coming directly from household waste (e.g., cosmetics, fragrances, detergents, sun protection agents, washing powders, pharmaceuticals and the wide use of a large variety of products, etc.). Detection of alkanes was anticipated on localities downstream from the Novi Sad oil refinery. The destruction of the Novi Sad oil refinery during the 1999 NATO Campaign caused a spill of more than 70,000 tons of crude oil, of which more than 5,500 tons were discharged directly into the Danube. As a result, Danube sediment was heavily polluted with PAHs and other oil derivatives (UNEP report: The Kosovo Conflict, Consequences for the Environment and Human Settlements, 1999, ISBN 92-807-1801-1), and still represents one of the major sources of pollution of the surface water and a threat to the quality of raw water used for the production of drinking water.

Prioritization Approach

The screening analysis was conducted on all 34 samples. Phthalates, PAHs, glycols and derivatives, caffeine, bisphenol A, terpenes and fatty acids were the most frequently occurring compounds in the wastewater and the Danube surface water near the Novi Sad location. Dibutyl phthalate, diethyl phthalate, dioctyl phthalate, and bisphenol A which are on the NORMAN list of emerging substances and di(2-ethylhexyl) phthalate [22], which is on the list of WFD priority substances, were detected in all the examined samples [3]. Phthalates are used as plasticizers, industrial and lubricating oils, defoaming agents, cosmetics and insect repellents, thus indicating pollution of anthropogenic origin. Terpenes could occur in cosmetics, care products, and home cleaning products, and originate directly from household waste. The sources of the detected fatty acids in the aquatic media are mainly from degradation processes of petroleum hydrocarbons or animal and vegetable fats.

Based on the screening analysis results, 151 organic compounds were selected for the two target analyses of

Table 2. List of compounds – screening analysis.

InChIKey	CAS	Compound name / NIST library	Lowest PNEC ng/l	Max concentration	MC/PNEC
BIADSXOKHZFLSN-RMCJHQKMSA-N	473-03-0	Ambrein	0,0000024	100,59	42802953,7
HMSWAIKSFDFLKN-UHFFFAOYSA-N	630-01-3	Hexacosane	0,00022	781,56	3627715,4
YKNWIILGEFFOPE-UHFFFAOYSA-N	629-99-2	Pentacosane	0,00054	956,51	1779488,1
POOSGDOYLQNASK-UHFFFAOYSA-N	646-31-1	Tetracosane	0,0013	662,10	494513,4
BJQWYEJQWHSSCJ-UHFFFAOYSA-N	593-49-7	Heptacosane	0,000086	38,16	442598,7
HOWGUJZVBDQJKV-UHFFFAOYSA-N	629-97-0	Docosane	0,0083	590,54	71455,4
OSJUENOXPFOHLF-UHFFFAOYSA-N	6418-47-9	Heneicosane, 3-methyl-	0,012	364,63	30312,9
CCXNGHAFWSFYNV-UHFFFAOYSA-N	25117-37-7	Heneicosane, 5-methyl-	0,012	208,55	17378,9
FNAZRRHPUDJQCJ-UHFFFAOYSA-N	629-94-7	Heneicosane	0,020	230,91	11280,1
KZJWDPNRJALLNS-FBZNIEFRSA-N	83-47-6	Stigmast-5-en-3-ol	0,059	402,05	6849,3
LQERIDTXQFOHKA-UHFFFAOYSA-N	629-92-5	Nonadecane	0,125	732,75	5869,0
RZJRJXONCZWCBN-UHFFFAOYSA-N	593-45-3	Octadecane	0,307	1227,21	3997,9
NHLUYCJZUXOUBX-UHFFFAOYSA-N	27400-77-7	Nonadecene	0,388	1222,93	3154,8
MLKZKPUBHSWMNA-UHFFFAOYSA-N	1560-84-5	Eicosane, 2-methyl-	0,122	338,25	2781,6
NYRRMADCQLTNBX-UHFFFAOYSA-N	6418-45-7	Nonadecane, 3-methyl-	0,297	437,10	1473,9
QIQXTHQIDYTFRH-UHFFFAOYSA-N	57-11-4	Octadecanoic acid	1,318	1094,29	830,2
HVYWMOMLDIMFJA-DPAQBDIFSA-N	57-88-5	Cholesterol	0,536	424,50	791,9
XUGNVMKQXJXZCD-UHFFFAOYSA-N	142-91-6	Isopropyl palmitate	2,520	1859,61	738,0
FHIVAFMUCKRCQO-UHFFFAOYSA-N	333-41-5	Diazinone	0,200	146,06	730,3
KZJWDPNRJALLNS-VJSFXXLFSA-N	83-46-5	beta-Sitosterol	0,059	40,14	683,8
NDJKXXJCMXVBJW-UHFFFAOYSA-N	629-78-7	Heptadecane	1,072	725,81	677,0
BFAGLVWBOUDHBS-UHFFFAOYSA-N	54833-23-7	Eicosane, 10-methyl-	0,128	54,55	425,9
BGHCVCJVXZWKCC-UHFFFAOYSA-N	629-59-4	Tetradecane	2,913	1096,47	376,4
ULBTUVJTXULMLP-UHFFFAOYSA-N	123-95-5	Octadecanoic acid, butyl ester	0,210	74,63	355,4
IPCSVZSSVZVIGE-UHFFFAOYSA-N	57-10-3	Hexadecanoic acid	9,622	3273,90	340,2
YCOZIPAWZNQLMR-UHFFFAOYSA-N	629-62-9	Pentadecane	1,550	425,89	274,8
ADOBXTDBFNCOBN-UHFFFAOYSA-N	6765-39-5	Heptadecene	1,977	420,11	212,5
ZQPPMHVWECSIRJ-KTKRTIGZSA-N	112-80-1	9-octadecenoic acid	17,636	3317,34	188,1
CCCMONHAUSKTEQ-UHFFFAOYSA-N	112-88-9	Octadecene	0,867	131,15	151,3
OYHQOLUKZRVURQ-HZJYTTRNSA-N	60-33-3	9,12-octadecadienoic acid	24,692	3713,77	150,4
DCAYPVUWAIABOU-UHFFFAOYSA-N	544-76-3	Hexadecane	8,100	1160,33	143,3
PESKGJQREUXSRR-JDIFZLMISA-N	601-53-6	Cholestan-3-one	4,243	436,49	102,9
QYIXCDOBOSTCEI-QCYZZNICSA-N	80-97-7	Cholestanol	12,260	1215,18	99,1
HPDKJRSKBCPMIY-UHFFFAOYSA-N	6418-44-6	Heptadecane, 3-methyl-	1,578	155,83	98,7
GLYJVQDYLFAUFC-UHFFFAOYSA-N	111-06-8	Hexadecanoic acid, butyl ester	0,738	66,82	90,5
VLPFTAMPNXLGLX-UHFFFAOYSA-N	538-23-8	Glycerol tricaprylate	1,323	111,51	84,3
LGJMUZUPVCAVPU-KZXGMYDKSA-N	19466-47-8	Stigmastanol	3,156	251,97	79,8
RYYVLZVUVIJVGH-UHFFFAOYSA-N	58-08-2	Caffeine	100,000	4600,14	46,0

Table 2. Continued.

ORFWYUFLWUWSFM-UHFFFAOYSA-N	646-13-9	Octadecanoic acid, 2-methyl-propyl ester	0,356	15,63	43,9
YYELLDKEOUKVIQ-UHFFFAOYSA-N	3055-98-9	Octaethylene glycol monodo-decyl ether	32,227	1130,50	35,1
TUNFSRHWOTWDNC-UHFFFAOYSA-N	544-63-8	Tetradecanoic acid	69,405	2057,13	29,7
HFDVRLIODXPAHB-UHFFFAOYSA-N	1120-36-1	1-tetradecene	22,873	494,59	21,6
WWPCLIMUTNKTDY-UHFFFAOYSA-N	6418-43-5	Hexadecane, 3-methyl-	3,678	75,94	20,7
NQAVPKIJZCHUNS-UHFFFAOYSA-N	1795-18-2	Cyclohexane, tetradecyl-	0,778	13,89	17,9
BOTWFXYSPFMFNR-PYDDKJGSSA-N	150-86-7	Phytol	7,061	112,95	16,0
IZWSFJTYBVKZNK-UHFFFAOYSA-N	14933-08-5	3-(N,N-dimethyllaurylammo-nio)propanesulfonate	381,210	5718,55	15,0
SECPZKHBENQXJG-FPLPWBNLSA-N	373-49-9	9-hexadecenoic acid	93,829	1274,56	13,6
FLIACVVOZYBSBS-UHFFFAOYSA-N	112-39-0	Hexadecanoic acid, methyl ester	11,611	154,81	13,3
HPEUJPJOZXNMSJ-UHFFFAOYSA-N	112-61-8	Octadecanoic acid, methyl ester	1,830	18,79	10,3
OJIBJRXMHVZPLV-UHFFFAOYSA-N	110-34-9	Hexadecanoic acid, 2-methyl-propyl ester	1,900	19,38	10,2
LAPRIVJANDLWOK-UHFFFAOYSA-N	3055-95-6	Pentaethylene glycol monodo-decyl ether	164,980	1477,17	8,9
SNRUBQQJIBEYMU-UHFFFAOYSA-N	112-40-3	Dodecane	25,564	211,53	8,3
NKJOXAZJBOMXID-UHFFFAOYSA-N	629-82-3	Octane, 1,1'-oxybis-	19,440	158,87	8,2
SIKJAQJRHWYJAI-UHFFFAOYSA-N	120-72-9	1h-indole	1000,000	7153,71	7,2
VCHDBLPQYJAQSQ-KYJUHHDHSA-N	27554-26-3	1,2-benzenedicarboxylic acid, diisooctyl ester	140,000	878,56	6,3
ARYTXMNEANMLMU-OZEQXKMUSA-N	6538-02-9	Ergostanol	5,622	33,33	5,9
JGMYDQCXGIMHLL-WAYWQWQTSA-N	2416-20-8	Hexadecenoic acid, (11)-	160,010	821,70	5,1
POULHZVOKOAJMA-UHFFFAOYSA-N	143-07-7	Dodecanoic acid	1339,800	6606,79	4,9
WPMWEFXCIYCJSA-UHFFFAOYSA-N	5274-68-0	Tetraethylene glycol monodo-decyl ether	293,200	1406,21	4,8
IIYFAKIEWZDVMP-UHFFFAOYSA-N	629-50-5	Tridecane	27,839	122,06	4,4
NYOXRYYXRWJDKP-GYKMGIIDSA-N	601-57-0	Cholest-4-en-3-one	5,153	21,80	4,2
BTFJIXJJCSYFAL-UHFFFAOYSA-N	629-96-9	1-eicosanol	0,992	3,91	3,9
JWMFYGXQPXQEEM-GCOKGBOCSA-N	641-85-0	Allopregnane	3,000	11,69	3,9
AFFLGGQVNFXPEV-UHFFFAOYSA-N	872-05-9	1-decene	558,300	2158,58	3,9
LEACJMVNYZDSKR-UHFFFAOYSA-N	5333-42-6	1-dodecanol, 2-octyl-	1,675	6,28	3,8
NEHDRDVHPTWWFG-UHFFFAOYSA-N	123-79-5	Hexanedioic acid, dioctyl ester	4,290	14,78	3,4
BOTWFXYSPFMFNR-HMMYKYKNSA-N	102608-53-7	3,7,11,15-tetramethyl-2-hexa-decen-1-ol	7,060	23,39	3,3
JXNPEDYJTDQORS-UHFFFAOYSA-N	1577-52-2	9,12-octadecadien-1-ol	10,818	30,10	2,8
GHVNFZFCNZKVNT-UHFFFAOYSA-N	334-48-5	Decanoic acid	2188,800	5336,87	2,4
DOIRQSBPFJWKBE-UHFFFAOYSA-N	84-74-2	1,2-benzenedicarboxylic acid, dibutyl ester	600,000	1267,81	2,1
YNPNZTXNASCQKK-UHFFFAOYSA-N	85-01-8	Phenanthrene	30,000	62,61	2,1
FKMHSNTVILORFA-UHFFFAOYSA-N	3055-94-5	Triethylene glycol monodo-decyl ether	553,650	1150,44	2,1

Table 2. Continued.

DWHIUNMOTRUVPG-UHFFFAOYSA-N	3055-97-8	Heptaethylene glycol mono-dodecyl ether	71,998	146,76	2,0
KSEZPRJUTHMFGZ-UHFFFAOYSA-N	88-29-9	7-acetyl-6-ethyl-1,1,4,4-tetramethyl tetralin	514,010	1023,74	2,0
AXISYYRBXTVTFY-UHFFFAOYSA-N	110-27-0	Tetradecanoic acid, 1-methyl-ethyl ester	20,621	36,83	1,8
CSHWQDPOILHKBI-UHFFFAOYSA-N	198-55-0	Perylene	24,510	40,80	1,7
AAOYEEWVNUXGDK-UHFFFAOYSA-N	3208-26-2	9-phenyl-1-nonanol	259,680	430,33	1,7
YQLRKXVEALTVCZ-UHFFFAOYSA-N	28556-81-2	2,6-dimethylphenyl isocyanate	2215,400	3076,65	1,4
MGLDCXPLYOWQRP-UHFFFAOYSA-N	1191-85-1	5,8,11,14-eicosatetraynoic acid	84,667	116,69	1,4
UIKROCXWUNQSPJ-VIFPVBQESA-N	486-56-6	2-pyrrolidinone, 1-methyl-5-(3-pyridinyl)-	660,320	907,02	1,4
VQOXUMQBYILCKR-UHFFFAOYSA-N	2437-56-1	1-tridecene	52,886	60,47	1,1
TXVHTIQJNYSSKO-UHFFFAOYSA-N	192-97-2	Benzo[e]pyrene	17,974	20,47	1,1
ZTMZUYHXZPUDRF-UHFFFAOYSA-N	82304-66-3	7,9-di-tert-butyl-1-oxaspi-ro[4.5]deca-6,9-diene-2,8-dione	365,680	416,11	1,1
HHZIOLLKZWLCOX-MDZDMXLPSA-N	13481-95-3	10-octadecenoic acid, methyl ester	8,860	9,79	1,1
LLEMOWNGBBNAJR-UHFFFAOYSA-N	90-43-7	[1,1'-biphenyl]-2-ol	360,000	389,82	1,1
BGRWYDHXPHLNKA-UHFFFAOYSA-N	10543-57-4	N,N,N',N'-tetraacetylethylen-ediamine	1294,800	1397,06	1,1

the wastewater and surface water samples. The obtained results indicate that the attention should focus on priority pollutants such as octylphenols, di-(ethylhexyl)-phthalate, DDT, endosulfan, dieldrin, endrin, and some heavy toxic metal ions. Concentration levels of all selected compounds exceeded proposed annual average environmental quality standard (AA EQS) values [2]. Octylphenols are commercially added to a number of products (paints, adhesives, plastics and cosmetics), and thus their presence in water samples indicates pollution from household waste.

The results of both quantified screening and target analysis, as well as eco-toxicity data for detected compounds, were used in order to compile the list of the most relevant pollutants for Novi Sad. The prioritization approach based on the occurrence and predicted toxicity data has been applied. The main decision criterium was the exceedance of predicted no-effect concentrations (PNEC) for all organic compounds monitored in the wastewater and surface water samples. Values below LoQ were not included in the prioritization approach. The indicator for ranking of compounds shows the exceedance of the compound's concentration respective to the corresponding PNEC value. It was obtained through the ratio of maximum concentration (MC) and the PNEC value of each analyzed compound. The MC/PNEC ratio was used to rank the compounds. Only pollutants with a ratio above 1 were considered. Obtained PNEC values relate only to surface water compounds and may be applied to wastewater pollutants if the dilution factor is applied. Since this research had only three sampling campaigns, and therefore an insufficient number of samples, the dilution factor for wastewater compounds has been disregarded since it would lead to the elimination of certain pollutants that might be relevant in the future.

The Selection of Relevant Pollutants from Screening and Target Analyses

Table 2 shows the list of the compounds observed within three screening analyses on 11 locations in the samples of wastewater and Danube surface water and ranks the compounds according to the exceedance of lowest PNEC. Additionally, Table 3 presents the ranked list of compounds detected in two screening analyses in Novi Sad.

Only relevant pollutants with the MC/PNEC ratio above 1 are presented in both tables.

Tables 2 and 3 show that the most hazardous group of compounds in the Novi Sad are linear and branched alkanes, which is not surprising due to the vicinity of the oil refinery. Other important groups of compounds include hormones, pesticides (Heptachlor, DDT and DDD), industrial chemicals, and PAHs. The presence of pesticides indicates pollution from agricultural activities, households and farms in the vicinity of the Danube surface water. PAHs, primarily generated from

Table 3. List of compounds – target analysis.

InChIKey	CAS	Compound name / NIST library	Lowest PNEC ng/l	Max concentration	MC/PNEC
FRCCEHPWNOQAEU-UHFFFAOYSA-N	76-44-8	Heptachlor	0,0002	420	2100000,0
ZXFXBSWRVIQKOD-UHFFFAOYSA-N	1024-57-3	Heptachlor epoxide	0,0002	50	250000,0
DXBHBZVCASKNBY-UHFFFAOYSA-N	56-55-3	Benz(a)anthracene	1,8	210	116,7
GVEPBJHOBDJJJI-UHFFFAOYSA-N	206-44-0	Fluoranthene	6,3	510	81,0
YVGGHNCTFXOJCH-UHFFFAOYSA-N	50-29-3	DDT-4,4’	10	500	50,0
RDYMFSUJUZBWLH-UHFFFAOYSA-N	115-29-7	Endosulfan-alpha	5	230	46,0
OTMOUPHCTWPNSL-UHFFFAOYSA-N	5598-15-2	Chlorpyrifos	1	40	40,0
DFBKLUNHFCTMDC-PICURKEMSA-N	60-57-1	Dieldrin	10	270	27,0
AHJKRLASYNVKDZ-UHFFFAOYSA-N	72-54-8	DDD-4,4’	25	620	24,8
BBEAQIROQSPTKN-UHFFFAOYSA-N	129-00-0	Pyrene	20	490	24,5
YNPNZTXNASCQKK-UHFFFAOYSA-N	85-01-8	Phenanthrene	30	360	12,0
DTMRKGRREZAYAP-UHFFFAOYSA-N	35694-08-7	PCB-194	0,2	1,2	6,0
JLYXXMFPNIAWKQ-GNIYUCBRSA-N	58-89-9	Hexachlorocyclohexane-gamma	5,5	30	5,5
NTDQQZYCCIDJRK-UHFFFAOYSA-N	1806-26-4	Octylphenol	100	540	5,4
CKAPSXZOOQJIBF-UHFFFAOYSA-N	118-74-1	Hexachlorobenzene	10	50	5,0
UCNVFOCBFJOQAL-UHFFFAOYSA-N	72-55-9	DDE-4,4’	25	110	4,4
HEDRZPFGACZZDS-UHFFFAOYSA-N	67-66-3	Trichloromethane	2500	9720	3,9
SNQQPOLDUKLAAF-UHFFFAOYSA-N	84852-15-3	Nonylphenol	300	1150	3,8
IGFHQQFPSIBGKE-UHFFFAOYSA-N	104-40-5	4-nonylphenol	300	1140	3,8
DOIRQSBPFJWKBE-UHFFFAOYSA-N	84-74-2	1,2-benzenedicarboxylic acid, dibutyl ester	600	2150	3,6
MWPLVEDNUUSJAV-UHFFFAOYSA-N	120-12-7	Anthracene	100	280	2,8
BJQHLKABXJIVAM-UHFFFAOYSA-N	117-81-7	Di(2-ethylhexyl)phthalate (DEHP)	1300	2630	2,0
NIHNNTQXNPWCJQ-UHFFFAOYSA-N	86-73-7	Fluorene	100	140	1,4
WDECIBYCCFPHNR-UHFFFAOYSA-N	218-01-9	Chrysene	100	130	1,3
ISAVYTVYFVQUDY-UHFFFAOYSA-N	140-66-9	4-(1,1,3,3-tetramethylbutyl)-phenol	100	110	1,1
YXFVVABEGXRONW-UHFFFAOYSA-N	108-88-3	Toluene	4300	4410	1,0
ZSDSQXJSNMTJDA-UHFFFAOYSA-N	1582-09-8	Trifluralin	30	30	1,0

combustion processes, could be transported by wind from the thermal plant, oil refinery and small farms and through atmospheric deposition processes end up in surface water.

The highest exceedance of PNEC for compounds detected in screening analyses, was obtained for Ambrein, as the result of its very low value of PNEC (2.35E-6 ng/l), even though it was detected only in one wastewater sample in the concentration of 100.59 ng/l. Ambrein is a fragrant substance used in the perfume industry. It was not detected in Danube surface water due to its low concentration level at the discharge and the dilution factor. Stigmast-5-en-3-ol is one of several phytosterols (plant sterols) with the basic cholestane structure. Phytosterols are isolated from vegetable oils or from by-product of wood pulp manufacture. A high extent of exceedance of almost 7000 was observed, since Stigmast-5-en-3-ol was detected in high concentrations in four wastewater samples. It was not detected in Danube surface water due to biological degradation processes and the dilution factor. Diazinone is a nonsystemic organophosphate insecticide currently

Table 4. List of compounds in terms of seasonal variation – screening analyses.

Compound name	Winter Max ratio	Compound name	Summer Max ratio	Compound name	Autumn Max ratio
Ambrein	42802954	Hexacosane	3627715	Heptacosane	442599
Stigmast-5-en-3-ol	6849	Pentacosane	1779488	Hexacosane	337665
Octadecanoic acid	830	Tetracosane	494513	Pentacosane	205682
Cholesterol	792	Docosane	71455	Tetracosane	134916
Diazinone	730	Heneicosane, 3-methyl-	30313	Docosane	26203
beta-Sitosterol	684	Heneicosane, 5-methyl-	17379	Heneicosane	9230
Hexadecanoic acid	340	Heneicosane	11280	Heneicosane, 3-methyl-	1867
Pentadecane	243	Nonadecane	5869	Nonadecane	505
9-octadecenoic acid	188	Octadecane	3998	Eicosane, 10-methyl-	426
9,12-octadecadienoic acid	150	Nonadecene	3155	Eicosane, 2-methyl-	154
Cholestan-3-one	103	Eicosane, 2-methyl-	2782	Octadecane	110
Cholestanol	99	Nonadecane, 3-methyl-	1474	Heptadecane	20
Stigmastanol	80	Stigmast-5-en-3-ol	771	Cyclohexane, tetradecyl-	18
Heptadecane	65	Isopropyl palmitate	738	Octadecanoic acid	16
Hexadecane	47	Heptadecane	677	Nonadecane, 3-methyl-	12
Caffeine	46	Tetradecane	376	Hexadecanoic acid	5
Octaethylene glycol monododecyl ether	35	Octadecanoic acid, butyl ester	355	1-eicosanol	4
Tetradecanoic acid	30	Pentadecane	275	Allopregnane	4
3-(N,N-dimethyllaurylammonio) propanesulfonate	15	Heptadecene	213	1-dodecanol, 2-octyl-	4
9-hexadecenoic acid	14	Octadecene	151	Hexanedioic acid, dioctyl ester	3
Isopropyl palmitate	13	Hexadecane	143	Pentadecane	3
Octadecanoic acid, methyl ester	10	Cholesterol	128	9-octadecenoic acid	2
Pentaethylene glycol monododecyl ether	9	Heptadecane, 3-methyl-	99	Hexadecane	2
1h-indole	7	Hexadecanoic acid, butyl ester	91		
Ergostanol	6	Glycerol tricaprylate	84		
Tetradecane	5	Octadecanoic acid, 2-methylpropyl ester	44		
Hexadecenoic acid, (11)-	5	1-tetradecene	22		
Dodecanoic acid	5	Hexadecane, 3-methyl-	21		
Tetraethylene glycol monododecyl ether	5	Phytol	16		
Cholest-4-en-3-one	4	Hexadecanoic acid, methyl ester	13		
1-decene	4	Hexadecanoic acid, 2-methylpropyl ester	10		
1,2-benzenedicarboxylic acid, di-isooctyl ester	3	Dodecane	8		

Table 4. Continued.

9,12-octadecadien-1-ol	3	Octane, 1,1'-oxybis-	8		
Hexadecanoic acid, methyl ester	3	1,2-benzenedicarboxylic acid, diisooctyl ester	6		
Decanoic acid	2	Tridecane	4		
1-tetradecene	2	3,7,11,15-tetramethyl-2-hexadecen-1-ol	3		
Triethylene glycol monododecyl ether	2	1,2-benzenedicarboxylic acid, dibutyl ester	2		
Heptaethylene glycol monododecyl ether	2	Phenanthrene	2		
7-acetyl-6-ethyl-1,1,4,4-tetramethyl tetralin	2	Tetradecanoic acid, 1-methylethyl ester	2		
1,2-benzenedicarboxylic acid, dibutyl ester	2				
Perylene	2				
9-phenyl-1-nonanol	2				
2,6-dimethylphenyl isocyanate	1				
5,8,11,14-eicosatetraynoic acid	1				
2-pyrrolidinone, 1-methyl-5-(3-pyridinyl)-	1				
1-tridecene	1				
Benzo[e]pyrene	1				
7,9-di-tert-butyl-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione	1				
10-octadecenoic acid, methyl ester	1				
[1,1'-biphenyl]-2-ol	1				
N,N,N',N'-tetraacetylethylenediamine	1				

used in agriculture due to the ban of DDT. It was detected in wastewater samples with the maximum concentration of 146.06 ng/l. Diazinone is relatively stable under standard ambient temperature and pressure. As a consequence, it was not detected in Danube water samples even though its exceedance of PNEC is very high. Benzo(a)anthracene and Fluoranthene, belonging to the group of PAHs, have similar values of MC/PNEC ratio, and were only detected in wastewater samples. Due to their low solubility in water and high potential to sorb sediments, their concentration levels in Danube surface water were very low. Other compounds such as: Cholestan-3-one, Stigmastanol, Dodecane, and others, which were detected only in wastewater samples collected at discharges, have much smaller MC/PNEC ratios. Due to the dilution factor, they were not measured in Danube surface water samples. Compounds with high exceedance detected only in Danube surface water samples, such as Heptachlor epoxide, Octadecene and Chlorpyrifos, occurred in water due to several factors: upstream Danubian countries, soil runoff, atmospheric deposition, and chemical reactions in aquatic environment.

Within the target analyses, MC of 27 organic compounds exceeded the predicted no effect concentrations (PNEC). The highest exceedance (2.100.000 times) was noted for Heptachlor, a commonly used insecticide, and consequently Heptachlor epoxide (250.000 times), which is a degradation product of Heptachlor formed by plants, animals and even humans after exposure to Hepatchlor. The third most relevant pollutant by target analyses is Benz(a)anthracene, with the MC/PNEC ratio of 116,67. MC of Fluorene and Anthracene were 1.4 and 2.8 times higher than PNEC of 0.1 μg/L. The value of PNEC for Phenantrene is 0.03 μg/L and MC is 12 times higher than PNEC, while for fluoranthene PNEC of 0.0063 μg/L was 81 times lower than MC. All above-mentioned PAHs were detected at 3 of 11 sampling sites. Dibutylphthalate

Table 5. List of compounds in terms of seasonal variation – target analyses.

Compound	Max ratio Summer	Compound	Max ratio Autumn
Heptachlor	2100000	Benzo(a)anthracene	117
Heptachlor epoxide	250000	Fluoranthene	81
DDT-4,4’	50	Pyrene	25
Endosulfan-alpha	46	Phenanthrene	12
Chlorpyrifos	40	Octylphenol	5
Dieldrin	27	Pentachlorobenzene	5
DDD-4,4’	25	Trichloromethane	4
PCB-194	6	Nonylphenol	4
Pentachlorobenzene	6	4-nonylphenol	4
Hexachlorocyclohexane-gamma	5	1,2-benzenedicarboxylic acid, dibutyl ester	4
Hexachlorobenzene	5	Anthracene	5
DDE-4,4’	4	Di(2-ethylhexyl)phthalate (DEHP)	2
Di(2-ethylhexyl)phthalate (DEHP)	2	Fluorene	1
Phenanthrene	1	Chrysene	1
		4-(1,1,3,3-tetramethylbutyl)-phenol	1
		Toluene	1

was detected in all 11 samples above PNEC of 0.6 μg/L, while MC was 3.6 times higher than PNEC. The value of PNEC for DEHP is 1.3 μg/L, which is 2 times lower than MC. Nonylphenols were detected at all sampling sites above PNEC of 0.021 μg/L. MC of octylphenols was 5.4 higher than PNEC (0.1 μg/L). For (4-(1,1′,3,3′-tetramethylbutyl)-phenol environmental concentration exceeded PNEC of 0.1 μg/L in only one water sample. Nonylphenols are produced in large volumes, and used in consumer laundry detergents, latex paints and lawn care products, thus they could originate from the household waste.

Seasonal Variation of Relevant Substances

The effects of climate change and different conditions in different seasons, such as temperature and precipitation, can have a significant effect on surface water quality. The increase of temperature can boost chemical reactions, while precipitation invokes surface runoff, thus increasing the concentration of a number of pollutants in water, such as pesticides, various microorganisms, etc. Since during the sampling campaigns the only difference in temperature was noted, it was not possible to take into consideration the impact of precipitation on the concentration levels of pollutants.

Tables 4 and 5 rank the pollutants observed within the screening and target analyses according to the season when they were detected (winter, summer and autumn). For all compounds presented in the following tables, CAS and InChIKey can be found in Tables 2 and 3.

Screening analysis results for summer and autumn seasons show increased concentration levels of alkanes (especially Hexacosane, Heptacosane, Pentacosane, Tetracosane, Docosane, Heneicosane, etc), possibly as a consequence of oil refinery activities in the part of the Danube prior to RP’ and Sever IV’ discharge locations. With the exception of Pentadecane, Heptadecane and Hexadecane (which are present in all seasons), in winter period alkanes were not detected in high concentrations in examined samples, unlike summer and autumn, most probably due to lower solubility in cold water. Significant compounds in winter include the following hormones with very high concentration levels: Stigamast-5-en-3-ol, Cholesterol, beta-Sitosterol, Cholestan-3-one, Cholestanol and Stigmastanol, which appear with MC/PNEC ratio ranging from 80-6849. In summer season only Stigmast-5-en-3-ol and Cholesterol are present, while in autumn no hormones (with the exception of Allopregnane used for medical treatment in dermatology) were detected in significant concentration levels. Hormones indicate human or animal fecal pollution, hence the presence of bacteria could also be expected in polluted water. Hexadecanoic acid and Pentadecaonic acid have been observed in all three seasons, but particularly in winter, with the MC/PNEC ratio 4 times higher than in summer, and more than 80 times higher than in autumn. Caffeine (pharmaceutical, diuretic), as a good indicator for human refuse, is another compound detected with

a significant ratio, but only in winter period, as is the pesticide Diazinon, with an MC/PNEC ratio of 730, due to its use as ear tags for cattle and as an insecticide. Pesticides and caffeine were not present in summer and autumn.

Contrary to the screening analysis, results obtained by target analysis show that during the autumn period PAHs were the most relevant compounds detected in wastewater and surface water in the Novi Sad area, while in summer mostly pesticides were indicated as the most relevant, which is expected due to high agricultural activity [23].

Conclusions

Conducted screening analyses resulted in the preliminary list of 300 compounds of concern in the Danube basin in Novi Sad area. Additional target analyses were focused on 69 compounds (WFD pollutants), of which 29 had values above LoD. All compounds were subjected to eco-toxicity analyses, which resulted in the derivation of PNEC values.

The combined results from screening and target analyses and eco-toxicity study were used for calculating prioritization ratio, and the list of the most relevant pollutants has been developed. The list contains 86 compounds detected within screening analyses and 27 compounds determined in target analyses, and it is the first list in the Balkan region, established by the approach adopted in the EU. The most hazardous group of compounds in Novi Sad are linear and branched alkanes, followed by hormones, pesticides, industrial chemicals, and PAHs.

Seasonal variation analysis confirmed that certain compounds occur independently in the season (e.g., hormones, alkanes), while other compounds such as pesticides (summer), and PAHs (autumn) are present only during particular seasons. The future research within seasonal variations will be focused on the impact of particular environmental factors (temperature, precipitation, etc.) on the pollutants' concentration levels and their PEC/PNEC ratio.

In compliance with WFD requirements, a prioritization approach should be applied every 4 years and, accordingly, monitoring programmes should be developed to include newly identified relevant pollutants.

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Conflict of Interest

The authors declare no conflict of interest.

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