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ORGANIC POLLUTION OF WATER AND HUMAN HEALTH

ZANIECZYSZCZENIA ORGANICZNE WÓD A ZDROWIE CZŁOWIEKA

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C. Data analysis/statistics
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D. Data interpretation
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Summary

The issue of human health should be considered in correlation with monitoring and protection of environment we live in, because of the increase of pollution of anthropogenic origin and the increase of health risk. Health risk caused by water pollutants with chemical compounds, including toxic micropollutants is not fully assessed, since chemical pollutants cause undesirable health effects after a long-term exposition.

Therefore, it is very important to choose the methodology of research for wider spectrum of pollution, especially organic, that can pose a threat to human health, and can be detected in environmental samples. On the basis of the review of existing eco-analytical research chromatographic methods in water analysis were selected, especially high-performance liquid chromatography (HPLC) and gas chromatography (GC) with mass detection in GC/MS, HPLC/MS techniques.

Non-target analysis revealed a high diversity in water chemical composition and a wider spectrum of organic contaminants comprising pharmaceuticals, technical additives, personal care products and pesticides. Some of the identified compounds are known as pollutants whereas some of these substances are so far unregistered contaminants. Although it was reported that the application of some of the identified compounds has been banned or restricted (e.g. lindane), the analyses showed that they can still be found in the environment. The study presented not only a comprehensive view on the state of pollution in studied waters, but also the eco-analytic methods and research results of the study may serve as the basis for widening the monitoring of environment.

Persistent organic pollution is a threat to human life to different degrees and it has not been yet fully examined. Therefore, in order to protect human health it is necessary to develop chemical trace analysis – eco analysis in complex monitoring and protection of environment we live in.

Keywords: organic pollution of water, eco analytics, human health

Streszczenie

Problematyka zdrowia człowieka powinna być rozpatrywana w korelacji z zagadnieniami monitoringu i ochrony środowiska, w którym żyjemy ze względu na wzrost zanieczyszczeń pochodzenia antropogenicznego, a tym samym wzrost ryzyka zdrowotnego. Ryzyko zdrowotne spowodowane zanieczyszczeniem wody związkami chemicznymi, w tym toksycznymi mikrozanieczyszczeniami, nie jest do końca zbadane, gdyż zanieczyszczenia chemiczne wywołują niepożądane skutki zdrowotne dopiero w wyniku długotrwałego działania.

Dlatego też tak ważny staje się wybór metodyki badań szerszego spektrum zanieczyszczeń, szczególnie organicznych, mogących stanowić zagrożenie dla zdrowia człowieka, występujących w próbkach środowiskowych. Na podstawie przeglądu badań ekoanalitycznych przybliżamy zastosowanie metod chromatograficznych w analizie wody, a w szczególności wysokosprawnej chromatografii cieczowej (HPLC) oraz chromatografii gazowej (GC) wraz z detekcją masową w technikach sprzężonych GC/MS, HPLC/MS.

Przedstawiona analiza niecelowana (non-target) ukazała szersze spektrum zanieczyszczeń organicznych, zawierające farmaceutyki, dodatki techniczne, produkty do pielęgnacji ciała oraz pestycydy. Niektóre z wymienionych związków są znane jako zanieczyszczenia, a część z nich to inne substancje niezarejestrowane jeszcze jako substancje zanieczyszczające. Mimo iż stwierdzono, że zastosowanie niektórych zidentyfikowanych związków zostało zakazane lub ograniczone (np. lindan) to analiza wykazała, że wciąż można je wykryć w środowisku. W pracy przedstawiono nie tylko wszechstronny pogląd na temat stanu zanieczyszczenia badanych wód ale zastosowane metody analityczne i wyniki badań mogą również służyć jako podstawa do rozszerzenia monitoringu stanu środowiska.

Trwałe zanieczyszczenia organiczne zagrażają zdrowiu ludzi w różnym stopniu i są jeszcze nie w pełni zbadane. W związku z powyższym w celu ochrony zdrowia człowieka należy rozwijać chemiczną analizę śladów - ekoanalitykę w kompleksowym monitoringu i ochronie środowiska, w którym żyjemy.

Słowa kluczowe: zanieczyszczenia organiczne wód, ekoanalityka, zdrowie człowieka

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Introduction

The issue of human health should be considered in correlation with monitoring and protection of environment we live in. Increase of organic contaminants of anthropogenic origin has a negative impact on human health and life. Complex monitoring and protection of natural environment are necessary.

Environmental Protection Inspectorate in Poland conducts regular monitoring of environment including surface water and groundwater monitoring. Basic physical and chemical parameters of water, content of inorganic compounds - especially compounds of carbon, nitrogen and hard metals are examined. The selected organic pollution such as pesticides or oil derivatives are also determined. At the same time, Chief Sanitary Inspectorate pervises the quality of water intended for human consumption for the whole country in terms of physical, chemical and microbiological properties. According to Central Statistical Office (GUS), Poland is one of the countries with poor water resources. Water used for collective supply of population in 2013 in 71.1% came from groundwater resources and in 28.9% from surface water resources. Big water suppliers in the biggest urban and industrial agglomerations usually use water from surface water resources. It may increase health risk caused by not evaluated water pollution. According to Health Ministry Regulation regarding the quality of water intended for human consumption, water is safe for health if it meets specific requirements. Exceeding parameters specified in the regulation requires every time evaluating the threat, assessing the risk of potential incidents dangerous to consumers' health and determining water's suitability for consumption [1,2].

The aim of work

The aim of the work is to present an overview of the research methodology for wider spectrum of water organic pollution possibly threatening human life on the basis of literature and the review of studies on water analyses.

Health risk caused by water pollution

Health risk caused by water pollutants with chemical compounds, including toxic micropollutants may not be fully assessed, since chemical pollutants cause undesirable health effects after a long-term exposition. An acceptable level of health risk caused by toxic micropollutants is reflected in probability (10^{-5}) of one additional death case in a specified population (100.000) during their whole life. Acceptable risk is an arbitrary decision taken relatively in the function of level of existing health, social, economic and environmental (biotic and abiotic) factors, dependent from civilization progress. This rule is the basis for recommendations, regulations and directives concerning the quality of drinking water [3-7].

Water, as a substrate of all life processes has a very important role in biosphere and a great influence on the life conditions of every living organism, especially human population. Surface water pollution is an important issue, since about half of people in our country use drinking water and water for consumption purposes from surface water resources [8,9]. Drinking water should have content profitable for human health (it shouldn't contain harmful substances) and should be safe in terms of microbiological properties. However, toxicological and epidemiological studies prove that natural water pollution is a real threat for water consumers. Among a few thousand of organic compounds identified as water pollutants, chemical plant protection products or drug residues (e.g. antibiotics residues) are an important tested group. Some groups of pesticides are compounds suspected of being carcinogenic or even being carcinogens, like e.g. lindane. Therefore, it becomes necessary to evaluate drinking water, especially water coming from resources fed by water from agricultural catchments and areas of animal production industry.

Eco analytics - chemical trace analysis in environment

The need for systematic environment control and *monitoring,* also water monitoring, challenges analysts in terms of finding new equipment and methodological solutions. Present classic analytical methods for determining the whole range of toxic substances in the environment at ever lower concentration levels are complemented with modern measuring instruments in terms of electrochemistry, spectroscopy, chromatography and electro migration techniques. Also comprehensive assessment of the state of environment components is enriched with microbiological analyses and sensor methods. Chemometry is a valuable method complementary to these determinations. It allows not only for error estimation (statistical analysis of results), but also for visualisation and modelling of processes and mechanisms. This is a fundament of intensively developing new direction in chemical trace analysis - eco analytics. Such comprehensive and interdisciplinary approach is connected with choosing and applying the proper method, selective method of samples preparing, choosing and applying the proper measurement technique and

estimating the results (validation) [12-15]. Nowadays, chromatography is the most popular analytical method. In combination with spectroscope methods it creates wide opportunities for analysing complicated mixtures, especially organic compounds. The most developed methods of identifying organic matter in environmental samples are chromatographic methods, especially high-performance liquid chromatography (HPLC) and gas chromatography (GC). They became popular in environmental samples analyses especially after mass detection and GC - MS. HPLC - MS techniques had been introduced. Gas chromatography with capillary columns can separate mixtures with hundreds of individuals, and mass spectrometer can identify the compound by registering spectrum. The majority of organic compounds of natural origin cannot be analysed with the use of chromatographic methods without chemical modification. With specially selected reactions it is possible to change simple organic compounds into suitable derivatives that meet the detection criteria of any chromatographic method. In GC analyses simple compounds are derivatized into suitable volatile derivatives, and in HPLC into suitable fluorogenic derivatives. Derivatization of analytes significantly influences the basic parameters of the chromatographic process, such as selectivity, resolution or the shape of chromatographic signal. Such wide use of advanced chromatographic methods in organic compounds analyses in tested environment samples comes from [12-16]:

- introducing modern detectors capable of sensitive, selective determination even of very complicated mixtures (mass spectrometer),
- introducing combined techniques (HPLC/MS/MS, GC/MS),
- ability to determine even traces of compounds in a very small sample (isolation, concentration, enrichment, lowering detection threshold),
- miniaturization and simplifying of analytical process.

Organic pollution of waters

A good example of eco analytical solutions might be using complementary target and non-target analysis of given environment samples as was presented in complex studies of state of pollution in Danube River and Sava River.

Many organic compounds have been identified in the Danube River, i.e., to date: alkylphenolic compounds, lipid series (n-alkanoic acids, n-alkanes, n-alkanols and sterols), pharmaceuticals (such as ibuprofen, diclofenac, sulphamethoxazole and carbamazepine), pesticides and their degradation products (e.g., bentazone, 2,4-D, mecoprop, atrazine, terbuthylazine and desethylterbutylazine), perfluorinated acids, and endocrine disrupting compounds (nonylphenol, NPE1C, bisphenol A and estrone) Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (OCPs), such as dichlorodiphenyltrichloroethane (DDT) and analogues, hexachlorocyclohexanes (HCHs) and hexachlorobenzene (HCB), were measured as well [18-21].

In the Sava River the following persistent organic pollutants were detected: polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), selected chlorinated pesticides and organo-tin compounds [22].

It has been reported that many organic compounds were found in Sava ground waters, such as oil derivatives: aliphatic hydrocarbons, aromatic hydrocarbons, PAHs, fatty acids, phenolic compounds, alkylsulphides, indoles, benzophenone, detergent-derived organic compounds, biodegradation products of nonylphenol polyethoxylates surfactants and EDTA [23].

In 2013 comprehensive analyses of water were conducted in order to assess the state of pollution of the Danube and Sava Rivers in the Belgrade region. Water samples were taken during two different sampling campaigns in January and February 2013 at five sampling locations along the Danube and the Sava Rivers in Serbia as presented on the map on figure 1 [17].

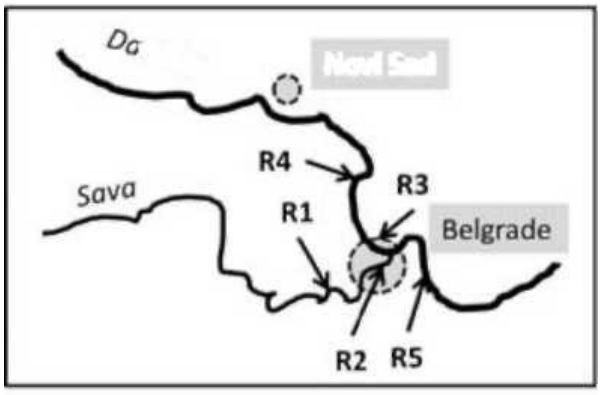

Figure 1. Map of the sampling locations[17].

For comprehensive analyses of tested water samples from Danube and Sava in Belgrad region, comparative studies were carried out; complimentary analytical approaches were used at different laboratories in Europe (Czech Republic, Slovenia, United Kingdom and Germany). The studies included basic physical and chemical parameters of water, inorganic water pollutants (such as carbon and nitrogen compounds), hard metals in sediments, eco toxicological tests, target analysis of organic pollution in water (such as hormones or neonicotinoids) and non-target analysis, which revealed wider spectrum of organic pollution including: pharmaceuticals, technical additives, plasticisers, personal care products, pesticides and residues of their degradation. The study, through identification and determination of traces of unknown organic compounds in the water presented a comprehensive view on the state of pollution of the Sava and Danube Rivers and became the base for setting up further monitoring programs [17].

Target analysis of water

Target analysis of selected hormones and pesticides was applied in selected water samples. Initially, extraction was performed: hormones were isolated from the river water using SPE. SUPELCLEAN ENVI-18 SPE Tubes (6 ml, 1 g) that had been conditioned with 5 ml of n-hexane, 5 ml of ethyl acetate and 5 ml of methanol and washed with 10 ml of Milli-Q water. Then 400 ml of river water was loaded under moderate flow (3 ml/min). SPE cartridge was subsequently dried under vacuum for 20 min and then the hormones were eluted with 6 ml of a mixture of ethyl acetate and methanol (5:1). Extract was evaporated to dryness under gentle stream of nitrogen and reconstituted in small volume (100 µl) of methanol. This solution was filtered using LUT Syringe Filters PTFE, 13 mm, 0.45 µm [17]. The isolates received were analysed with HPLC-ESI-MS. An Agilent 1100 HPLC system with an Agilent 6320 spherical ion trap mass spectrometer and electrospray ionization was used. The hormones were separated on a Phenomenex Kinetex C_{18} column, 100 Å, 150×3 mm, 2.6 µm particle size (Coreshell type) at a temperature of 25°C using an acetonitrile (ACN)/water mixture at a flow of 0.25 ml/min (t_0: 40% ACN, t_{20}: 90% ACN). Nitrogen was used as the nebulising gas at a pressure of 25 psi, temperature and flow were 350°C and 10 l/min respectively. The ion trap scanning range was set from 50 to 800 u. Estradiol (α- and β-), estriol, estrone, diethylstilbestrol and ethinyl estradiol were detected in the negative ESI^-mode, and norethindrone and progesterone in the positive ESI^+ mode. The limit of quantification (LOQ) ranged from 0.03 to 0.5 ng/l and the limit of detection (LOD) was between 0.01 and 0.15 ng/l. The recoveries obtained for all target compounds, evaluated by using spiked real samples, were higher than 70% [17].

Then pesticides-neonicotinoids were analysed. Water samples of 1 l in volume were divided into two replicates and extracted using Strata C18-E columns polymeric sorbent (200 mg, 6 ml). Prior to extraction, the cartridges were activated with 5 ml of methanol and 5 ml of distilled water. After extraction, the samples were eluted with 5 ml of methanol. After evaporation of the solvent, the samples were dissolved in 0.5 ml of mobile phase and analysed using HPLC-DAD. Neonicotinoids were analysed with a Hewlett Packard 1100 Series chromatograph. The separation was achieved using a C8 column (250 mm×4.6 mm) with Chromasil 100 (5 µm) as the stationary phase. The column thermostat was maintained at 25°C. The injection volume was 75 µl. The eluents consisted of 30% acetonitrile and 70% acetic acid; the flow rate was 1 ml/min. The wavelength for thiamethoxam was 247 nm, for imidacloprid 250 nm and for clothianidin 260 nm. The retention time for thiamethoxam was 5.7 min, for imidacloprid 8.5 min and for clothianidin 7.4 min. For quantification purposes, calibration curves in the range from 0.1 to 100 mg/l were prepared. The LOD value for all the analysed neonicotinoids was 0.5 mg/l [17].

Quantitative analysis of eight selected hormones showed their presence in the test water samples and revealed no occurrence of the selected neonicotinoid insecticides [17].

As we can see, target analyses on their own do not show the real state of the pollution of tested waters, therefore it is important to introduce non-target analyses in order to see wider spectrum of organic pollution that can be a threat to human life.

Non-target analyses of water

Before non-target analyses sequential liquid/liquid extraction was performed. 2 dm^3 of water was extracted in three steps: the first one with 50 ml of n-pentane, the second one with dichloromethane and the third one with dichloromethane and 2 ml of concentrated hydrochloric acid that was pre-cleaned by intense extraction with n-hexane. Subsequently, the organic layers were separately dried by filtration over approximately 1 g of anhydrous granulated sodium sulphate (Merck, Germany). 50 µl of an internal standard solution containing d_{34} n-hexadecane, fluoroacetophenone and decafluorobenzophenone in n-hexane (the concentrations were 6.0, 7.2 and 6.9 ng/µl, respectively) was added to the first and second extracts. Acidic compounds in the third extract were methylated by

addition of a diazomethane solution. The methylated extract was purified by fractionation with dichloromethane and methanol (50:50, V/V) through silica-gel. In addition, 50 µl of the same internal standard was added to the purified third fraction as well. Before injection into the gas chromatograph (GC), all of the extracts were reduced to a volume of 50 µl at room temperature. For the gas chromatographic–mass spectrometric (GC–MS) analyses, the extracts were reduced to a volume of 20 µl at room temperature [17].

GC–MS analysis was performed on a Finnigan Trace MS, ThermoQuest (Egelsbach, Germany) linked to a Carlo Erba, HRGC 5160 gas chromatograph equipped with a 25 m×0.22 mm ID×0.25 µm film BPX5 (SGE, Germany). The heating programme was 3 min. hold at 60°C, then 60°C to 300°C at a rate of 3°C/min and a 20 min hold at 300°C. The injection was performed via a split/splitless injector at 270°C; the splitless time was 60 s. The carrier gas was helium at a velocity was 2 cm/s and a source temperature of 200°C. The electron impact ionization mode (EI+, 70 eV), scanning from 35 to 500 Da at a rate of 1 s/dec and an inter-scan time of 0.1 s [17].

In order to identify organic compounds in selected water samples The EI^+-mass spectra were compared with spectra of reference compounds from mass spectral databases (NIST/EPA/NIH Mass Spectral Library NIST05, Wiley/NBS Registry of Mass Spectral Data, 7th electronic version) and their retention times were compared as well [17].

The identified organic pollution in selected water samples in different amounts in GC/MS non-target analysis is presented in table 1 [17].

Table 1. Organic pollution identified in water samples from five sampling locations along the Danube and the Sava Rivers in Serbia (+ present in small amounts, ++ present in high amounts) [17]

Compound	R1	R2	R3	R4	R5
Pharmaceuticals					
Carbamazepine	-	-	+	+	+
Personal care products					
Methylbenzophenone	+	+	+ +	+ +	+ +
4-Methoxy-2-ethylhexylcinnamate	+	+	+	+	+
N,N,N',N'-Tetraacetylethylene diamine, TAED	+	+ +	+ +	+ +	+ +
Galaxolide	+ +	+ +	+ +	+ +	+ +
Tonalide	+ +	+ +	+ +	+ +	+ +
Methyl dihydrojasmonate	+	+	+ +	+ +	+ +
a-Cadinol	+	+	+	+	+
Lilial	+	+	+	+	+
Technical additives, plasticizers					
2,6-Di-tert-butylhydroxytoluene	+ +	+ +	+	+ +	-
2,6-Di-tert-butyl-1,4-benzoquinone	+ +	+ +	+ +	+ +	+
2,2,4-Trimethyl-1,3-pentandiodiisobutyrate, TXIB	+ +	+ +	+ +	+ +	+ +
2-Ethylhexylbenzoate	+	+	+	+	+
1-Hydroxycyclohexyl phenyl ketone, Irgacure 184	+ +	+	+ +	+ +	+
N-Butylbenzenesulphonamide, NBBS	+	+	+	+ +	+
Benzothiazol	-	+	+	+ +	+ +
Diacetin	+	+ +	+ +	+ +	+ +
N,N-Dibutylformamide	+	+	+	+	+ +
2,4,7,9-Tetramethyl-5-decyne-4,7-diol, TMDD	+	+	+	+ +	+ +
Tris(2-chloroethyl)phosphate, TCEP	-	+	+	+ +	+
Tris(2-chloro-iso-propyl)-phosphate, TCPP	-	+	+	+ +	+
Tri-n-butylphosphate, TBP	+	+	+	+	+ +
Dimethylphthalate	+	+	+ +	+ +	+ +
Diethylphthalate	+ +	+ +	+ +	+ +	+ +
Diisobutylphthalate	+ +	+ +	+ +	+ +	+ +
2-Ethylhexylmethylphthalate	-	+	-	+	-

Benzylbutylphthalate	+	+	+	+	+
Bis(2-ethylhexyl)phthalate, DEHP	+ +	+ +	-	+ +	+ +
Pesticides					
Acetochlor	-	-	-	-	-
Uvazol 236	-	+	+	+	+
Desethylterbutylazine	+ +	+ +	+	+	-
Lindane, HCH	-	-	-	+	-
Food constituents					
Caffeine	+	+ +	+ +	+ +	+ +
Vitamin E	+	+	+	+	+
Natural products					
Dipropyl disulphide, 1-(n-Propyldisulphanyl)propane	+ +	+	+ +	+	+
Dipropyl trisulphide, l-(n-Propylsulfanyldisulfanylpropane)	+	+	+	+	+
Non-specific (unknown application)					
2-Nitro-4-methylphenol	-	+	-	+	+
2-Nitrophenol	+	+	+	+	+
2-Phenoxyethanol	-	+	+	+	+ +
2,6-Di-tert-butyl-4-nitrophenol	-	+	+	+	+
N-Benzylformamide	+	+	+	+	+ +
3-Chloroacetophenone	+	-	+ +	+	-
Fluorenone	-	+	-	+	+
Antraquinone	+	+	-	+	-

The majority of the identified contaminants were of anthropogenic origin. Many of them have been reported formerly as river pollutants, e.g. carbamazepine, which is frequently used as an antiepileptic or psychotropic drug [17,24].

A higher diversity as compared to the pharmaceuticals was evident for residues from personal care products: fragrances, washing agents, or ingredients in cosmetics. For example, galaxolide (4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta- [g]isochromene) and tonalide (1-(3,5,5,6,8,8-hexamethyl-6,7-dihydronaphthalen-2-yl) ethanone) are known synthetic fragrances and have been frequently detected in the environment, since they are emitted from domestic sewage and therefore they enter natural waters [17, 25].

Also large quantities of Irgacure 184 were found in all test water samples while the toxicity of this substance has not been fully assessed. Also toxicological properties of N-butylbenzenesulphonamide (NBBS) have not been evaluated although NBBS is a known neurotoxin [17].

Pesticides are a very well-known group of water pollutants. Acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)-acetamide) is a constituent of a variety of commercial herbicides (e.g., TripleFlex®), but its use is restricted because of its high toxicity. Acetochlor is one of the most frequently detected herbicide in natural waters. According to toxicology data it is dangerous for human's eyes, digestive and respiratory systems [17].

Another detected substance was lindane (the γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane). It was produced industrially until the late 1980s when it was banned because of the high toxicity. However, it can still be detected in the environment, which poses a threat to human health because of its suspected carcinogenicity [17, 26].

In summary, a high threat is posed by well-studied pesticides, such as: DDT, methoxychlor, toxaphene, lindane, because they are suspected to have carcinogenic properties or even to be carcinogenic. When it comes to organic compounds used for production in chemical industry, benzene or vinyl chloride are cancirogenes. Persistent organic pollutants (POPs) poses a threat to human health and environment. They cause especially neurotoxicity and endocrine disrupting, which are not fully examined [26-29].

Conclusions

Increase of organic contaminants of anthropogenic origin has a negative impact on human health and life. Complex monitoring and protection of natural environment are necessary. Therefore it is very important to choose the methodology of research for wider spectrum of pollution, especially organic, that can pose a threat to human

health, and can be detected in environmental samples. On the basis of the review of existing eco analytical research chromatographic methods in water analysis were selected, especially high-performance liquid chromatography (HPLC) and gas chromatography (GC) with mass detection in GC/MS, HPLC/MS techniques.

The chromatographic studies of selected organic pollution in water samples are extended with non-target analysis which aimed at identifying specific organic pollution in the two rivers and obtaining an overview on the emission sources affecting the state of pollution in the river systems. Non-target analysis revealed a high diversity in water chemical composition and a wider spectrum of organic contaminants comprising pharmaceuticals, technical additives, plasticizers, personal care products and pesticides. Some of the identified compounds are known as pollutants whereas some of these substances are so far unregistered contaminants. Although it was reported that the application of some of the identified compounds has been banned or restricted (e.g., TCEP, TCPP, lindane and acetochlor), this analysis showed that they can still be found in the environment. The study presented not only a comprehensive view on the state of pollution in studied waters, but also the eco analytic methods and research results of the study may serve as the basis for widening the monitoring of environment. Most importantly, it revealed that various chemical analyses of the selected contaminants may lead to different water quality assessments. In particular, the confrontation of target and non-target analyses indicates to potential misinterpretation in analyses of the real state of pollution by using restricted, target analytical approaches [17, 27].

Persistent organic pollution is a threat to human life to different degrees which have not been yet fully examined [26-30]. Therefore in order to protect human health it is necessary to develop chemical trace analysis – eco analysis in complex monitoring and protection of environment we live in.

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