Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28565

275 (2022) 2–13
November

Determination of compounds of emerging concern in surface water from agricultural land

Edyta Kudlek*, Mariusz Dudziak

Faculty of Energy and Environmental Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland, Tel. +48 32 237-24-78; emails: edyta.kudlek@polsl.pl (E. Kudlek), mariusz.dudziak@polsl.pl (M. Dudziak)

Received 28 February 2022; Accepted 9 May 2022

ABSTRACT

Research undertaken on surface water quality indicated an increasing occurrence of anthropogenic contaminants. Those compounds can be harmful to the whole aquatic environment. The aim of the undertaken research was the identification of contaminants of emerging concern in small natural ponds located between arable fields in the Silesian Voivodeship. The samples were collected at the early stage of plant vegetation – spring period, and immediately before harvest – autumn season. The collected samples, after pre-treatment, were subjected to solid-phase extraction process and analysed with a gas chromatograph coupled with a mass detector. The analysis showed the presence of micropollutants from the group of pesticides, polycyclic aromatic hydrocarbons and industrial additives in the samples. Furthermore, trace amounts of zearalenone – a mycotoxin, were also confirmed in samples collected during the autumn season. The potentially harmful impact of the identified compounds was evaluated through toxicological analyses conducted on *Lemna minor* vascular plants and *Aliivibrio fischeri* saltwater bacteria. The obtained results indicated low toxicity towards plants of the water collected from points A, B and C, and a toxic character towards bacteria, regardless of the season.

Keywords: Surface water; Farmland; Pesticides; Zearalenone; Toxicity

1. Introduction

The literature indicated the increasing occurrence of contaminants in water that potentially can be harmful to the environment in the whole aquatic ecosystem [1]. The presences of those compounds in water reservoirs for potable reuse remain a health concern [2,3]. Compounds that are detected in the aquatic environment, which were not naturally present in it, and may have an impact on aquatic organisms are referred to as emerging contaminants or contaminants of emerging concern (CECs) [4]. The CECs group includes a wide range of micropollutants used for various applications. These compounds include pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), pesticides, food additives, flame retardants, and other industrial additives [5–7].

CECs may originate from many types of sources including agriculture, traffic networks, industries, or households, and enter water bodies through diverse paths [8]. Agriculture contributes in particular to the pollution of small water reservoirs which were located in the immediate vicinity of farmlands. The pollution is caused by the unsustainable and excessive use of pesticides, which are deposited in soil and are continuously carried through runoff leaching into water reservoirs [9]. Liess et al. [10] pointed out that regulatory acceptable concentration values of pesticides were exceeded in 81% of small streams in Germany. Hüesker and Lepenies [11] indicated that excessive pesticide use can lead to severe water quality problems in Europe and Beketov et al. [12] showed that intensive agricultural production reduces the

* Corresponding author.

Presented at the 2nd International Conference on Strategies Toward Green Deal Implementation – Water, Raw Materials and Energy (ICGreenDeal2021), 8–10 December 2021, Held Online by the Mineral and Energy Economy Research Institute, Polish Academy of Sciences

1944-3994/1944-3986

aquatic biodiversity. Monitoring campaign undertaken in different European countries indicate the presence of different types of pesticides in ponds, lakes, rivers and groundwater located near to agricultural land [13,14]. The presence of compounds in the aquatic environment that are forbidden for use is disturbing [13]. According to the guidelines given by the European Parliament, the concentration of a single pesticide in water intended for human consumption should not exceed 0.1 μg/dm^3, while the concentration for total pesticides cannot exceed 0.5 μg/dm^3 [15].

Kim and Zoh [16] indicate, that the concentration of pesticides and other types of CECs depends on their physico-chemical properties and bioavailability. Caliman and Gavrilescu [17] proposed a categorization of micropollutants generation and elimination based on physico-chemical properties, environmental factors, transport and retention, transformation, and accumulation. Also, the volatility, water solubility, stability of the chemical structure, and particulate distribution characteristics of contaminants decide about their dissolution in water [16].

The true picture of the water quality in a given water body is provided not only by the analysis of the basic physico-chemical parameters and the occurrence of micropollutant parent compounds but also by the analysis of their intermediaries. The intermediaries can be formed during the self-decomposition of parent compounds, the action of physico-chemical factors on water reservoirs (temperature, sunlight irradiation), interactions with natural organic matter (NOM), and metabolic processes of aquatic organisms [18]. It should be noted that some compounds do not decompose or only slightly decompose and accumulate in surface waters [19]. The comprehensive identification of intermediates in natural water samples is analytically challenging. This is caused by the trace levels of those compounds and the lack of analytical standards as well as instrumental sensitivity [20,21]. Meijer et al. [22], during the development of a CECs counting software, determined the presence of 69526 compounds with CAS number and 306279 different metabolites of these compounds which already occurring in the environment. Ecotoxicological tests, carried out on different indicator organisms, have confirmed the toxicity of a wide range of CECs occurring in water samples as a single compound or in compound mixtures [23]. Organic micropollutants not only harm individual organisms but also can affect higher levels of biological organization [24,25]. In addition, Halstead et al. [26] describe the response of aquatic mesocosm communities to mixtures of different chemicals. Bond et al. [27] pointed that advanced engineering solutions are required to remove CECs and their decomposition/transformation by-products. This is due to the fact that conventional water treatment processes, even if they are supported by chlorination, ozonation, or UV disinfection, were insufficient for the removal of persistent micropollutants [28]. It becomes necessary to optimize the field management, to stop the uncontrolled relies of chemicals into water bodies an minimize the risk of drinking water wells contamination [29,30]. The first step in the implementation of this assumptions is to identify the quality of water in water reservoirs supplying potential sources of drinking water.

The objective of the presented research was the analysis of water quality parameters and the identification of CECs in samples collected from natural ponds located between arable fields in the Silesian Voivodship, Poland. The samples were collected at the early stage of plant vegetation – spring period, and immediately before harvest – autumn season. The location of the studied ponds allows for the presumption of the presence of various plant protection agents and industrial admixtures in the collected water samples. To identify the CECs occurring in the ponds, the collected samples were pre-treated and subjected to solid-phase extraction (SPE). The quantitative and qualitative analysis was performed by the use of gas chromatography coupled with mass detection. To evaluate the potentially harmful action of the pond water, the samples were toxicologically analyzed by the use of vascular plants *Lemna minor* and saltwater bacteria *Aliivibrio fischeri* as indicator organisms

2. Material and methods

2.1. Study area and collection of samples

The objects of research were two ponds located near arable fields in the Silesian Voivodeship, Poland (Fig. 1). The ponds were fed mainly by groundwater and surface runoff from the surrounding farmlands. Additionally, pond I was from the west side fed by surface runoff from a fast traffic street (sampling place A), from the north side by runoff from arable fields with wheat (sampling place B), and the south side exposed to surface runoff from an industrial area operating in the area of road transport (sampling place C). Pond II was surrounded from the north side by a cornfield (sampling place D) and from the south side by a disused railway line located directly next to a mixed forest (sampling place E). Pond I had an area of about 500 m^2 and Pond II 200 m^2. The study has been carried out between the early stage of plant vegetation – spring period, and immediately before harvest – autumn season 2021. The temperature of the water during spring was between 12.0°C and 13.5°C, and during autumn between 14.2°C and 17.1°C. The sampling procedure was adapted from Ustaoğlu and Tepe [31] and performed according to standard methods [32]. Water samples were collected at a distance of 1 m from the shore from 10 cm depth from the surface at the sample places marked on Fig. 1. The samples were taken between 7 am and 8 am, only on rainless days, by holding the bottles upward and, immediately after sampling, transferred in a cooling box to the laboratory for analysis. The storing bottles were washed before sampling with a 1.5% HCl solution and rinsed with distilled water. Polyethylene bottles were used for the quantification of the basic physico-chemical properties of the water. While borosilicate glass bottles were used for the collection of samples to be analysed by chromatography. The sample bottles were labeled with the collection date and sampling point description.

2.2. Analytical procedure

The collected water samples after the pretreatment conducted by their filtration through a glass microfiber filter (pore size – 0.45 μm) were subjected to the following physico-chemical analyses:

- pH and conductivity (CD) measurement;
- Turbidity measurement (TB);
- Total organic carbon (TOC) and inorganic carbon (IC) measurement;
- Analysis of the chemical oxygen demand (COD), biological oxygen demand (BOD_5);
- Analysis of the concentration of total nitrogen (TN), ammonium nitrogen (NH_4–N), nitrate nitrogen (NO_3–N), and phosphate (PO_4–P);
- Identification of CECs.

The laboratory pH meter/conductometer CPC-505 by Elmetron (Zabrze, Poland) was used to measure the pH and CD. While the TB of the samples was measured using the HI-93414-02 EPA Compliant Turbidity and Free & Total Chlorine Meter by HANNA Instruments (Woonsocket, USA). The TOC-L analyzer by Shimadzu Corporation (Kioto, Japan) estimated the IC and total carbon (TC) concentration based on the combustion catalytic oxidation method and non-dispersive infrared NDIR detection. The difference between the TC and IC allows the determination of the TOC value. The performed analyzes were compared to TC and IC calibration curves with a range from 0 to 100 mg/dm^3. The COD, BOD_5 as well as TN, NH_4–N, NO_3–N, and PO_4–P were measured by the UV-VIS Spectrophotometer Pharo 100 Spectroquant® by Merck KGaA (Darmstadt, Germany) based on Merck Brand Kits. The measuring range of the apparatus and the limit of detection (LOD) are given in Table 1. The identification of CECs was based on chromatographic analysis preceded by SPE. The SPE of the analytes was carried out by the use of two types of extraction cartridges: Supelclean™ ENVI-18 SPE tube and Supel™ Tox AflaZea tube. The analyzed volume of water samples was equal to 1 dm^3, which made it possible to determine compounds that are present in the samples in trace concentrations. Additionally,

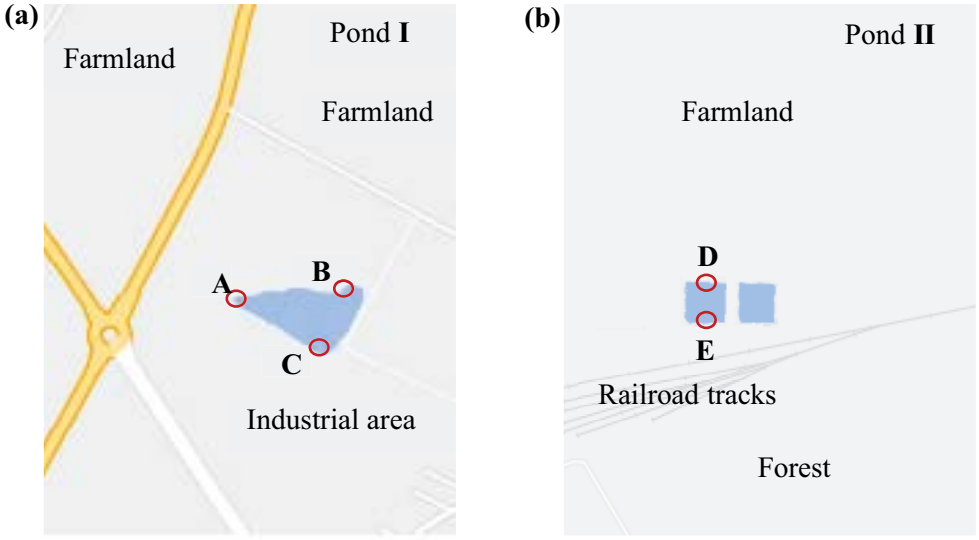

Fig. 1. Schematic representation of the location of studied water pond (a) I and (b) II (O – sampling point).

Table 1
Measuring range of the used analytical equipment their LOD

Equipment	Measured parameter	Measuring range, mg/dm^3	LOD
pH meter/conductometer	pH	–6,000 – 20,000	–
	CD	0.00 μS/cm – 1,999.9 mS/cm	–
Turbidity & Free and Total Chlorine Meter	TB	0.00 – 9.99 NTU	–
TOC-L analyzer	TOC	TC and IC calibration curves 0.01 – 100.00 mg/dm^3	0.01 mg/dm^3
	IC	Calibration curve 0.01 – 100.00 mg/dm^3	0.01 mg/dm^3
Spectrophotometer	COD	10.00 – 150.99 mg/dm^3	10.00 mg/dm^3
	BOD_5	0.50 – 3,000.00 mg/dm^3	0.50 mg/dm^3
	TN	0.50 – 15.00 mg/dm^3	0.50 mg/dm^3
	NH_4–N	0.01 – 2.00 mg/dm^3	0.01 mg/dm^3
	NO_3–N	0.50 – 25.00 mg/dm^3	0.50 mg/dm^3
	PO_4–P	0.05 – 5.00 mg/dm^3	0.05 mg/dm^3

the samples directed to the extraction performed by the Tox AflaZea tubes were acidified with hydrochloric acid (purity grade >99.8%). The details of the SPE are given in Table 2.

The SPE eluates were evaporated to dryness under a stream of nitrogen at 40°C. The dried residues were re-dissolved by adding 100 mm^3 of methanol and filtered through a 0.20 μm glass microfiber filter.

The chromatographic analysis of the extract was performed by the use of the GC-MS(EI) 7890B Gas Chromatograph by Agilent Technologies (Santa Clara, United States). The analytical tool was equipped with a capillary column SLB™ – 5 ms (30 m × 0.25 mm of 0.25 μm film thickness) by Sigma-Aldrich (Poznań, Poland). Helium 5.0 with a flow rate of 1.1 cm^3/min acts as the carrier gas for chromatographic analysis. The injection volume was 1 μL and was injected automatically with a speed of 3,000 mm^3/min. The injector temperature was set at 250°C. The oven temperature program of the GC oven was as follows: 80°C (6 min), 5°C/min up to 260°C, 20°C/min up to 300°C (2 min). The temperature of the ion trap and ion source was equal to 150°C and 230°C, respectively.

The identification of compounds occurring in the collected water samples was made based on their mass spectra obtained after chromatographic analysis carried out in the total ion current (TIC) mode. The range of monitored ion masses was set from 50 to 500 m/z. The mass spectra of picks noted at the obtained sample chromatograms were read with the MassHunter software and compared with the United States National Institute of Standards and Technology NIST v17 Mass Spectral Library. The quantitative analysis of the identified CECs concentrations was operated in the selected ion monitoring (SIM) mode, during which the representative ions of each compound were monitored. The identified compounds were presented in Table 3. The concentrations were calculated based on calibration curves for individual compounds. The standard solutions for calibration curves were prepared based on compound standards by Merck KGaA (Darmstadt, Germany). The LOD values for individual CECs are summarized in Table 3.

All glassware used during the experiment was washed with acid solutions, rinsed with distilled water, and dried in a drying oven for pure glassware. All used chemicals were of analytic grade and purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland) and Merck KGaA (Darmstadt, Germany).

One-way ANOVA variance of analyses was applied for the calculation of the mean minimum and maximum values of the parameter as well as their standard deviations. The one-way ANOVA allowed for the apportionment of significant difference ($p < 0.05$) between the measured parameter values in the sampling points. The Pearson Correlation Index (PCI) was used to determine the amount of relation between measured water quality parameters.

2.3. Toxicity tests

The toxicity of the collected water samples was estimated by two different biotests, that is, *Lemna* sp. Growth Inhibition Test and Microtox® test. The *Lemna* sp. Growth Inhibition Test uses as test organisms the freshwater vascular plants *Lemna minor*. The test procedure involves introducing two frond plants into the tested water samples and observing their morphological changes within 7 d. Only morphological changes in the number of plant fronds were observed in the studies. The water samples with the plants were stored at 25°C ± 1°C under constant exposure to 6,000 lux light. Plants from own culture were used for the research. Both the culture and the toxicity test itself were performed according to OECD Guideline 221.

The Microtox® bioassay is based on the measurement of changes in the intensity of light emitted by bioluminescent saltwater bacteria *Aliivibrio fischeri* introduced to the tested samples. The bacteria were purchased in a freeze-dried form from Tigret Sp. z o.o. (Warszawa, Poland) immediately before the test, the freeze-dried bacteria were revitalized with the use of a reconstruction solution by Modern Water (London, United Kingdom). The test was carried out according to the Screening Test procedure of the MicrotoxOmni system, which supports the Microtox analyzer Model 500 by Modern Water (London, United Kingdom).

The obtained results measured as changes in the intensity of light emitted by Aliivibrio fischeri bacteria and changes in the number of fronts of individual plants in relation to the control sample were presented in a percentage value. A detailed description of the calculation was presented in [33]. This value showed the triggered toxicity effect and was interpreted based on a simplified four-class water sample toxicity classification presented in Table 4 [34,35].

Assignment errors marked on figures, which present the toxicity measurement results, were estimated based on the standard deviation for three repetitions of each test.

Table 2
SPE details for different extraction column types

Column type	Supelclean™ ENVI-18	Supel™ Tox AflaZea
Bed conditioning	5.0 cm^3 of acetonitrile; 5.0 cm^3 of methanol	5.0 cm^3 of methanol
Bed washing	5.0 cm^3 of deionized water	5.0 cm^3 methanol/water 10/90 (v/v)
Sample flow	1.0 cm^3/min	
Vacuum drying time after sample filtration	5.0 min	
Extract elution	1.5 cm^3 of methanol; 1.5 cm^3 of acetonitrile	3.0 cm^3 of methanol

Table 3
Identified organic micropollutants and their LOD

Identified compound	Molecular weight, g/mol	Monitored ions, m/z	Similarity to the data base mass spectra, %	LOD, ng/dm^3
Benzo[a]pyrene	252.31	113, 126, 224, 252	85	
Naphthalene	128.17	77, 102, 127, 128	95	
Nonylphenol	220.35	107, 121, 135, 149	73	
4-*tert*-octylphenol	206.32	96, 107, 133, 206	76	
2-Mercaptobenzothiazole	167.25	109, 123, 135, 167	71	
Diisodecyl phthalate	446.70	71, 141, 149, 307	78	
Triticonazole	317.80	83, 115, 235	74	
Prothioconazole	344.30	99, 180, 306, 342	82	
Beflubutamid	355.30	91, 176, 221, 355	73	
Benzothiazolone	151.19	96, 123, 151	91	
Zearalenone	318.36	149, 231, 283, 319	84	
1-Methyloxindole	147.17	91, 118, 147	70	
3,4-Difluorophenol	130.09	75, 81, 101, 130	86	
Phenol	94.11	65, 66, 94	95	

Table 4
Simplified water samples toxicity classification system [34,35]

Triggered effect (%)	Description	Water sample toxicity class
<25.00	Non toxic	I
25.00–50.00	Low toxic	II
50.01–75.00	Toxic	III
75.01–100	Highly toxic	IV

The error values for all tested samples did not exceed 5.0% for the *Lemna* sp. Growth Inhibition Test and 5.5% for the Microtox® bioassay.

3. Results and discussion

The mean of measured water quality parameters during the spring and autumn season are summarized in Table 5, respectively. It seems difficult to compare the quality of water taken from reservoirs located in the vicinity of various types of industry to samples from reservoirs surrounded mainly by arable fields. Each of the studied reservoirs will be exposed to a different type of pollution and requires an individual approach in proposing future methods of its protection or improving water quality. The one-way ANOVA results confirm this assumption and indicate a difference among parameters between the examined collection points of both ponds, which was not significant during one season ($p > 0.05$). Only in the case of the COD and BOD_5 concentration, measured in the autumn period, there was a significant difference between the values noted for sampling points A, B, and C to the samples taken from points D and E ($p < 0.05$). Therefore, it can be concluded that the location of the water reservoir influences the most, in this particular case, the COD value. On the other hand, the comparison of values of TB, TOC, IC, COD, BOD_5, TN, NH_4–N, NO_3–N, and PO_4–P between the spring and autumn seasons shows also a significant difference ($p < 0.05$). This is in line with the well-known changes in water quality in temperate zones during different seasons of the year.

The mean concentration of P–PO_4 in the water samples collected in the autumn season was higher than in the spring. The same correlation was also noted for the concentration of N_{og}, N–NH_4, N–NO_3 and TOC, IC, COD as well as BOD_5. Pietrzak [36] pointed that this may be due to seasonal changes in surface water supply caused groundwater amount. The water supply in Central Europe is usually large in the spring time, and smaller in summer due to the significant intensity of field evaporation [37]. The largest difference between the parameter values measured during the two seasons was noted for TB. The TB, which gives information on the clarity of the water was higher during the spring season and exceeded 6.54 NTU. It is related to the entry of clay, silt particles, organic matter and colloids into water ponds from surface runoff coming from the surrounding fields. Also, the presence of microscopic organisms can cause the increase of the TB value [38]. The pH and the CD did not change significantly between the spring and autumn season. It can be therefore concluded that the concentration of ionized species in the tested ponds was at a similar level during the sampling period.

The relationship of the measured water quality parameters during the spring and autumn season were calculated by Pearson Correlation Index and are presented in Table 6. The obtained results were interpreted based on the classification proposed by Liu et al. [39]. The correlation with values higher than 0.75 was described as strong and was noted, for example, between TB and CD, COD and BOD_5 as well as COD or BOD_5 and TB or CD for both spring and autumn season. A moderate correlation with values between 0.75–0.50 was observed for pH and NO_3–N or PO_4–P during both seasons. The pH and TOC as well as

Table 5
Physico-chemical parameter of the tested water samples collected during the spring and autumn season

Parameter	Collection point					Min.	Mean	Max.
	A	B	C	D	E			
				Spring season				
pH, –	6.62 ± 0.11	6.78 ± 0.16	6.85 ± 0.12	7.01 ± 0.03	7.05 ± 0.02	6.62 ± 0.11	6.86 ± 0.24	7.05 ± 0.02
CD, μS/cm	861.84 ± 12.35	866.12 ± 8.66	863.47 ± 5.07	745.66 ± 8.71	743.25 ± 9.02	743.25 ± 9.02	816.07 ± 72.82	866.12 ± 8.66
TB, NTU	6.51 ± 0.05	6.54 ± 0.04	6.45 ± 0.05	5.14 ± 0.03	5.11 ± 0.02	5.11 ± 0.02	5.95 ± 0.84	6.54 ± 0.05
TOC, mg/dm^3	10.19 ± 0.35	10.07 ± 0.29	10.15 ± 0.33	10.28 ± 0.45	10.34 ± 0.13	10.07 ± 0.29	10.21 ± 0.14	10.34 ± 0.13
IC, mg/dm^3	32.99 ± 0.27	33.15 ± 0.17	33.28 ± 0.23	38.63 ± 0.78	39.74 ± 0.56	32.99 ± 0.27	35.56 ± 4.18	39.74 ± 0.56
COD, mgO/dm^3	12.05 ± 0.38	11.98 ± 0.47	11.97 ± 0.17	10.54 ± 0.22	10.55 ± 0.11	10.54 ± 0.22	11.42 ± 0.88	12.05 ± 0.38
BOD_5, mgO/dm^3	2.45 ± 0.65	2.48 ± 0.58	2.47 ± 0.42	1.35 ± 0.08	1.23 ± 0.06	1.23 ± 0.06	2.00 ± 0.77	2.48 ± 0.58
TN, mg/dm^3	1.58 ± 0.12	1.56 ± 0.10	1.31 ± 0.11	1.45 ± 0.02	1.45 ± 0.01	1.31 ± 0.11	1.47 ± 0.16	1.58 ± 0.12
NH_4–N, mg/dm^3	0.25 ± 0.03	0.26 ± 0.02	0.30 ± 0.03	0.30 ± 0.01	0.31 ± 0.02	0.25 ± 0.03	0.28 ± 0.03	0.31 ± 0.02
NO_3–N, mg/dm^3	0.82 ± 0.02	0.80 ± 0.02	0.81 ± 0.01	0.85 ± 0.01	0.85 ± 0.01	0.80 ± 0.02	0.83 ± 0.02	0.85 ± 0.01
PO_4–P, mg/dm^3	0.20 ± 0.03	0.20 ± 0.02	0.18 ± 0.01	0.25 ± 0.03	0.21 ± 0.02	0.18 ± 0.01	0.21 ± 0.04	0.25 ± 0.03
				Autumn season				
pH, –	6.99 ± 0.05	6.98 ± 0.05	7.01 ± 0.02	7.08 ± 0.01	7.10 ± 0.01	6.98 ± 0.05	7.03 ± 0.07	7.10 ± 0.01
CD, μS/cm	868.36 ± 3.01	874.13 ± 2.46	869.73 ± 3.11	775.36 ± 13.40	798.55 ± 12.63	775.36 ± 13.40	837.23 ± 61.87	874.13 ± 2.46
TB, NTU	3.21 ± 0.03	3.20 ± 0.03	3.26 ± 0.02	2.51 ± 0.02	2.50 ± 0.01	2.5 ± 0.01	2.94 ± 0.44	3.26 ± 0.02
TOC, mg/dm^3	14.95 ± 0.13	14.87 ± 0.12	14.98 ± 0.09	15.05 ± 0.12	15.22 ± 0.09	14.87 ± 0.12	15.01 ± 0.21	15.22 ± 0.09
IC, mg/dm^3	53.47 ± 0.31	53.55 ± 0.27	53.46 ± 0.15	55.78 ± 0.14	55.98 ± 0.10	53.46 ± 0.15	54.45 ± 1.53	55.98 ± 0.10
COD, mgO/dm^3	14.59 ± 0.52	14.60 ± 0.55	14.67 ± 0.49	11.47 ± 0.04	11.52 ± 0.02	11.47 ± 0.04	13.37 ± 1.90	14.67 ± 0.49
BOD_5, mgO/dm^3	3.77 ± 0.17	3.79 ± 0.11	3.86 ± 0.12	1.69 ± 0.02	1.72 ± 0.02	1.69 ± 0.02	2.97 ± 1.28	3.86 ± 0.12
TN, mg/dm^3	2.83 ± 0.18	2.80 ± 0.16	2.43 ± 0.20	2.87 ± 0.04	2.82 ± 0.03	2.43 ± 0.20	2.75 ± 0.32	2.87 ± 0.04
NH_4–N, mg/dm^3	0.62 ± 0.05	0.65 ± 0.04	0.61 ± 0.02	0.72 ± 0.01	0.70 ± 0.01	0.61 ± 0.02	0.66 ± 0.06	0.72 ± 0.01
NO_3–N, mg/dm^3	1.44 ± 0.29	1.45 ± 0.25	0.96 ± 0.28	1.55 ± 0.10	1.72 ± 0.09	0.96 ± 0.28	1.42 ± 0.46	1.72 ± 0.09
PO_4–P, mg/dm^3	0.42 ± 0.09	0.52 ± 0.08	0.39 ± 0.07	0.60 ± 0.04	0.54 ± 0.03	0.39 ± 0.07	0.49 ± 0.11	0.60 ± 0.04

Table 6
Pearson correlation between physico-chemical parameters measured during the spring and autumn season

	pH	CD	TB	TOC	IC	COD	BOD_5	TN	NH_4–N	NO_3–N	PO_4–P
Spring season											
pH	1										
CD	–0.87	1									
TB	–0.89	0.99	1								
TOC	0.70	–0.90	0.99	1							
IC	0.89	–0.99	–0.90	0.90	1						
COD	–0.89	0.99	0.99	–0.88	–0.99	1					
BOD_5	–0.87	0.99	0.99	–0.91	–0.99	0.99	1				
TN	0.56	–0.84	–0.82	0.73	0.83	–0.83	–0.85	1			
NH_4–N	–0.94	0.98	0.98	–0.85	–0.99	0.98	0.98	–0.80	1		
NO_3–N	0.73	–0.96	–0.96	0.95	0.94	–0.94	–0.95	0.80	–0.33	1	
PO_4–P	0.53	–0.77	–0.75	0.56	0.70	–0.77	–0.74	0.79	–0.02	0.74	1
Autumn season											
pH	1										
CD	–0.94	1									
TB	–0.96	0.98	1								
TOC	0.93	–0.76	–0.83	1							
IC	0.97	–0.97	–0.99	0.85	1						
COD	–0.97	0.98	0.99	–0.83	–0.99	1					
BOD_5	–0.96	0.98	0.99	–0.83	–0.99	0.99	1				
TN	0.29	–0.48	–0.53	0.18	0.49	–0.50	–0.51	1			
NH_4–N	0.84	–0.94	–0.95	0.63	0.94	–0.95	–0.95	0.64	1		
NO_3–N	0.56	–0.62	–0.72	0.51	0.70	–0.69	–0.70	0.91	0.22	1	
PO_4–P	0.65	–0.80	–0.82	0.39	0.80	–0.81	–0.81	0.71	0.11	0.76	1

pH and TN also show a moderate correlation during the spring season. Moreover, the correlation between TN and TOC, and PO_4–P and TOC was only moderate during the spring season. During the autumn season, the correlation between this parameter was classified as weak (values between 0.50 and 0.30). A very weak correlation (0.11) was observed between PO_4–P and NH_4–N during the autumn season. This fact indicated that the concentration of PO_4–P did not reflect the NH_4–N concentration. Those two parameters are independent of each other. It may be related to the fact, that during autumn the plants have already absorbed nitrogen and phosphorus introduced by fertilizers [40,41]. Another reason for the negligible correlation between these parameters may be the use of fertilizers containing different composition of biogeneic compounds with different forms of bioavailability for plants in arable fields.

Negative values of the Pearson Correlation Index indicate an inverse relation between the parameters and show a decrease of a parameter by the increase in another parameter value. For example, a very high negative correlation has been noticed between IC or TOC and COD or BOD_5. A highly negative correlation of TOC and COD, BOD_5 was also noted by Mondal et al. [42]. The authors also pointed out that there is a hydrological relation between COD and BOD_5 which can affect the TOC and IC in a water ecosystem.

The GC-MS(EI) analysis allowed for the identification of 13 organic micropollutants in the tested water samples (Table 3) which can be classified as CECs. These compounds belong to the group of: polycyclic aromatic hydrocarbon – benzo[a]pyrene and naphthalene; industrial additives – nonylphenol, 4-*tert*-octylphenol, 2-mercaptobenzothiazole, diisodecyl phthalate and 1-methyloxindole; pesticides – triticonazole, prothioconazole, and beflubutamid; mycitoxins – zearalenone and compounds which can be possible decomposition by-products of other micropollutants – 3,4-difluorophenol and phenol. The presence of benzo[a]pyrene, naphthalene nonylphenol and 4-*tert*-octylphenol, which are on the list of priority substances [43], is particularly worrying. These substances can cause acute and chronic toxicity to aquatic organisms, accumulate in the ecosystem, lead to loss of habitats and biodiversity, and pose a threat to human health. European legislation [44], as well as, Polish Legislation [45] classifies benzo[a]pyrene and nonylphenol as priority hazardous substance in the field of water policy.

The concentrations estimated in samples collected during spring and autumn in the test ponds are summarized in Table 7. The presence of benzo[a]pyrene and naphthalene was only confirmed in samples collected from sampling point A. It was most exposed to surface runoff from the fast traffic street. The naphthalene concentration was

Table 7
Concentration of compounds in samples collected during the spring and autumn season given in ng/dm^3

Compound	Collection point					Min.	Mean	Max.
	A	B	C	D	E			
Spring season								
Benzo[a]pyrene	0.81 ± 0.12	<LOD	<LOD	<LOD	<LOD	0.81 ± 0.12	0.81 ± 0.12	0.81 ± 0.12
Naphthalene	0.24 ± 0.10	<LOD	<LOD	<LOD	<LOD	0.24 ± 0.10	0.24 ± 0.10	0.24 ± 0.10
Nonylphenol	3.42 ± 0.21	<LOD	8.64 ± 0.42	<LOD	0.32 ± 0.11	0.32 ± 0.11	4.13 ± 4.51	8.64 ± 0.42
4-*tert*-octylphenol	18.64 ± 0.92	12.50 ± 0.41	23.61 ± 0.32	1.52 ± 0.22	2.11 ± 0.12	1.52 ± 0.22	11.68 ± 11.93	23.61 ± 0.32
2-Mercaptobenzothiazole	7.54 ± 0.21	<LOD	8.50 ± 0.31	<LOD	<LOD	7.54 ± 0.21	8.02 ± 0.48	8.50 ± 0.31
Diisodecyl phthalate	31.01 ± 1.30	28.14 ± 1.05	35.44 ± 2.54	11.62 ± 0.53	11.32 ± 0.39	11.32 ± 0.39	23.51 ± 12.19	35.44 ± 2.54
Triticonazole	–	–	–	8.23 ± 0.09	7.12 ± 0.08	7.12 ± 0.08	7.68 ± 0.56	8.23 ± 0.09
Prothioconazole	0.23 ± 0.11	0.12 ± 0.10	0.20 ± 0.10	0.10 ± 0.12	0.12 ± 0.11	0.10 ± 0.12	0.15 ± 0.08	0.23 ± 0.11
Beflubutamid	28.70 ± 1.81	33.31 ± 1.62	18.72 ± 0.90	16.70 ± 0.49	12.62 ± 0.78	12.62 ± 0.78	22.01 ± 11.30	33.31 ± 1.62
Zearalenone	<LOD	<LOD	<LOD	<LOD	<LOD	–	–	–
1-Methyloxindole	0.10 ± 0.08	<LOD	0.21 ± 0.08	<LOD	<LOD	0.10 ± 0.08	0.16 ± 0.06	0.21 ± 0.08
3,4-Difluorophenol	0.94 ± 0.22	1.62 ± 0.30	0.20 ± 0.11	<LOD	<LOD	0.20 ± 0.11	0.92 ± 0.72	1.62 ± 0.30
Phenol	41.62 ± 5.72	37.11 ± 4.53	45.70 ± 2.61	18.40 ± 0.71	20.73 ± 1.41	18.40 ± 0.71	32.71 ± 14.31	45.70 ± 2.61
Autumn season								
Benzo[a]pyrene	0.60 ± 0.11	<LOD	<LOD	<LOD	<LOD	0.60 ± 0.11	0.60 ± 0.11	0.60 ± 0.11
Naphthalene	0.20 ± 0.12	<LOD	<LOD	<LOD	<LOD	0.20 ± 0.12	0.20 ± 0.12	0.20 ± 0.12
Nonylphenol	1.22 ± 0.10	<LOD	2.11 ± 0.30	<LOD	<LOD	1.22 ± 0.10	1.67 ± 0.47	2.11 ± 0.30
4-*tert*-octylphenol	9.11 ± 0.72	5.60 ± 0.31	11.82 ± 0.72	<LOD	<LOD	5.60 ± 0.31	8.84 ± 3.24	11.82 ± 0.72
2-Mercaptobenzothiazole	7.80 ± 0.33	<LOD	8.32 ± 0.23	<LOD	<LOD	7.80 ± 0.33	8.06 ± 0.26	8.32 ± 0.23
Diisodecyl phthalate	51.71 ± 7.64	45.93 ± 8.33	69.91 ± 6.71	16.72 ± 0.94	16.54 ± 0.81	16.54 ± 0.81	40.16 ± 29.74	69.91 ± 6.71
Triticonazole	<LOD	<LOD	<LOD	<LOD	<LOD	–	–	–
Prothioconazole	0.23 ± 0.10	0.10 ± 0.11	0.21 ± 0.10	0.11 ± 0.10	0.12 ± 0.13	0.11 ± 0.10	0.15 ± 0.05	0.21 ± 0.10
Beflubutamid	19.72 ± 1.01	28.31 ± 0.90	12.90 ± 1.22	10.62 ± 0.43	9.51 ± 0.52	9.51 ± 0.52	16.21 ± 12.09	28.31 ± 0.90
Zearalenone	<LOD	<LOD	<LOD	0.20 ± 0.11	0.11 ± 0.11	0.11 ± 0.11	0.16 ± 0.06	0.20 ± 0.11
1-Methyloxindole	<LOD	<LOD	<LOD	<LOD	<LOD	–	–	–
3,4-Difluorophenol	0.52 ± 0.12	0.92 ± 0.30	<LOD	<LOD	<LOD	0.52 ± 0.12	0.72 ± 0.22	0.92 ± 0.30
Phenol	63.63 ± 4.45	55.52 ± 3.83	59.44 ± 3.61	32.52 ± 2.50	38.20 ± 3.20	32.52 ± 2.50	49.86 ± 17.36	63.63 ± 4.45

lower than the benzo[a]pyrene, and did not exceed 0.24 ng/dm^3. The concentration of both substances was lower than the environmental quality standards given by the Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy [44] (concentration of benzo[a]pyrene < 0,05 μg/dm^3 and naphthalene < 1.2 μg/dm^3). Kluska [46] reported that the benzo[a]pyrene concentration in river water in Poland ranged from 4.6 to 15.6 ng/dm^3 and is higher during the spring season than during summer and autumn. He also pointed out that the average concentration of polycyclic aromatic hydrocarbons during the winter season reached the value of 184 ng/dm^3, while during autumn it decreased to 81 ng/dm^3.

The concentration of nonylphenol and 4-*tert*-octylphenol was higher during the spring season than during autumn. However, the determined concentrations did not exceed the environmental quality standards for inland surface waters given by the Directive 2008/105/EC [44]. This could be related to the decomposition of this phenolic compound by sunlight and metabolic processes of microorganisms [47,48]. The decomposition of a compound with a phenolic group can be also confirmed by the increasing concentration of phenol in water. For example, the mean concentration of phenol in samples collected during spring was about 33 ng/dm^3 and during autumn did not exceed 50 ng/dm^3. The concentration of phenol was the highest among other identified CECs concentrations. It may be related to the presence of other compounds in the tested aqueous samples, the identification of which was not possible with the selected analytical technique. The second-highest concentration, especially in samples collected from points A and C were noted for the plasticizer diisodecyl phthalate. The concentration of this compound, in all tested samples, was higher during the autumn season than during spring.

Special attention should be paid to 2-mercaptobenzothiazole, which belongs to the group of benzothiazoles. This compound is used in sulfur vulcanization of rubber and as an additive to oil-based hydraulic fluids used [49] and is listed as a high production volume chemical [50]. The presence of this compound was reported not only in surface water but also in drinking water [51]. In the

presented study 2-mercaptobenzothiazole was detected only in the sample collection points A and C. Its concentration was stable during the spring and autumn season and ranged from about 7.5 to 8.5 ng/dm^3. Ni et al. [52] during the examination of riverine runoff of the Pearl River Delta noted average concentrations of these compound ranging from 24 to 87 ng/dm^3. The presence of compounds belonging to benzothiazoles can cause genotoxicity, cytotoxicity, carcinogenicity and modulation of the thyroid hormone [28,53–55]. However, Whittaker et al. [56] set the allowable concentration of 2-mercaptobenzothiazole in drinking water at 60 ng/dm^3.

The presence of low concentrations of 3,4-difluorophenol in samples collected from pond I can be the result of the decomposition of beflubutamid, which also has F atoms in their chemical structure. The presence of 1-methyloxindole may also be related to its formation during the decomposition of 2-mercaptobenzothiazole.

The occurrence of fungicides, herbicides, and insecticides is related to the use of pesticides to plants grown in fields located in the immediate vicinity of the studied water reservoirs. Triticonazole was only detected in samples D and E during the spring season, and its concentration did not exceed 8.23 ng/dm^3. This compound is used for the protection of maize seeds from decomposition by fungi [57]. The concentration of prothioconazole, which is also a fungicide used in cereals growing [58], was at a constant level during all sample collection periods and ranged from 0.10 to 0.23 ng/dm^3. Higher concentrations were noted in the case of beflubutamid an amide herbicide. The concentration of this compound ranged from 12.62 to 33.31 ng/dm^3 during spring and from 9.51 to 28.31 ng/dm^3 during autumn. Tasumi et al. [59] pointed out that this herbicide is degraded relatively quickly (DT_{50} = 5.4 d), therefore its concentrations that reach the water ponds could be much higher after its application on the field. The summary concentration of the identified pesticides did not exceed the threshold concentration of pesticides in water that can be a source of drinking water for humans [15].

In samples D and E, collected from the pond surrounded by maize cornfields, during the autumn season trace concentration of zearalenone were found. This compound is a non-steroidal estrogen mycotoxin [60] produced by fungi of the genus *Fusarium* [61]. Mally et al. [62] reported that it is especially produced in temperate and warmer climates. The source of zearalenone can therefore be fungal-infected maize crops. Examples of corncobs that were infected by fungi (type of fungus was not specified in the study) and found in the field located near the tested pond II during the harvest are shown in Fig. 2. The concentration of this CECs did not exceed 0.20 ng/dm^3. The content of compounds belonging to the group of mycotoxins in the water environment varies from 0 to 60 ng/dm^3 [63,64]. Gromadzka et al. [65] pointed out that the concentration of zearalenone in surface water in Poland did not exceed 44 ng/dm^3.

The conducted toxicity test showed a low toxicity (>25% and <50%) of samples collected from point A, B, and C against vascular plants *Lemna minor*, and a toxic nature of the water against *Aliivibrio fischeri* bacteria, regardless of the season of the year (Fig. 3). Whereas samples collected from points D and E were non-toxic to (<25%) *Lemna minor* plants, and low toxic to the indicator bacteria. Thus, the test results confirm the quality differences between the samples taken from reservoirs I and II. The reduction of the toxic effect was also noted in the samples taken in the autumn compared to the samples taken in the spring. This may indicate a stronger decomposition of toxic compounds under the influence of solar radiation and the metabolic processes of microorganisms occurring in water reservoirs in the autumn. Observations of the tested water ponds at the sampling places also showed the absence of higher organisms such as fish. This indicates a poor quality of water, which was demonstrated by the results of the chromatographic analysis and the performed toxicological analyzes.

4. Conclusions

The results obtained during the conducted studies indicated that values of water quality parameters were higher during the autumn season than during spring. This indicates the dependence of pond water quality on the volume of surface runoff, which depends on the frequency of

Fig. 2. Examples of corncobs found in the field located near the tested pond II.

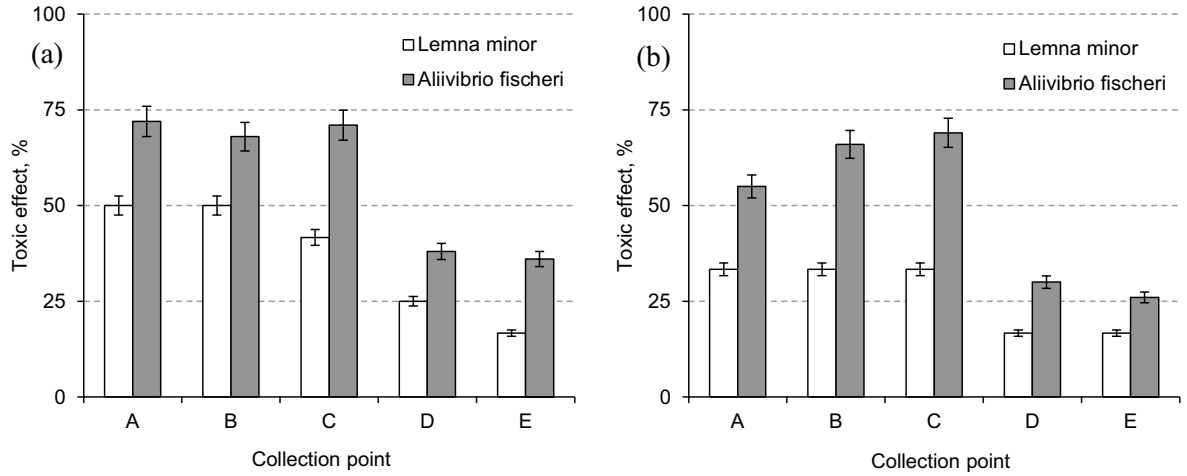

Fig. 3. Mean toxicity of water samples collected during (a) spring and (b) autumn season.

precipitation. Therefore it can be assumed, that the pollution of water bodies with undesirable compounds from the surrounding usable areas is greatest during rainy seasons. The GC-MS(EI) analysis showed the presence of organic micropollutants from the group of pesticides, PAH, and industrial additives in all collected samples. This indicates that not only the surrounding farmland can be a source of water pollution, but also surface runoff from areas covered by the transport industry. Even when these areas seem to be adequately protected against leakage of pollutants into the environment. The identified compounds can be classified as CECs due to their toxic or potentially toxic nature towards living organisms, including humans. The concentrations of those compounds varied with the season of the year. The variation was especially pronounced in the case of pesticides. This was related to their seasonal introduction to farmlands and the frequency of rainfall. The presence of trace amounts of zearalenone – a nonsteroidal estrogenic mycotoxin was also confirmed in samples collected during the autumn season from the pond located near corn crop fields. The conducted toxicological analysis of pond I indicated low toxicity of the water towards vascular plants and a toxic character towards bacteria, regardless of the season. While the water from pond II was non-toxic for the test organism during the whole time of the experiment. The conclusions of the research show that the use of plant protection products in arable fields contributes to the release of these substances into the aquatic environment, and at the same time does not provide the crops with adequate protection against pathogens. The proof of which is the presence of zearalenone in the tested water samples. Recognition of the sources of the deteriorating water quality in water reservoirs will allow for the search for effective solutions for their protection.

Acknowledgments

This work was supported by Ministry of Science and Higher Education Republic of Poland within statutory funds, BKM-679/RIE4/2022.

References

[1] I.B. Gomes, J.-Y. Maillard, L.C. Simões, M. Simões, Emerging contaminants affect the microbiome of water systems—strategies for their mitigation, npj Clean Water, 3 (2020) 39, doi: 10.1038/s41545-020-00086-y.
[2] T. Merle, D.R.U. Knappe, W. Pronk, B. Vogler, J. Hollender, U. von Gunten, Assessment of the breakthrough of micropollutants in full-scale granular activated carbon adsorbers by rapid small-scale column tests and a novel pilot-scale sampling approach, Environ. Sci. Water Res. Technol., 6 (2020) 2742–2751.
[3] A. Alsbaiee, B.J. Smith, L.L. Xiao, Y.H. Ling, D.E. Helbling, W.R. Dichtel, Rapid removal of organic micropollutants from water by a porous β-cyclodextrin polymer, Nature, 529 (2016) 190–194.
[4] A.K. Sarmah, Advances in Chemical Pollution, Environmental Management and Protection, Vol. 7, Elsevier, Cambridge, 2021.
[5] S.D. Richardson, S.Y. Kimura, Water analysis: emerging contaminants and current issues, Anal. Chem., 88 (2016) 546–582.
[6] F.T. Lange, M. Scheurer, H.-J. Brauch, Artificial sweeteners—a recently recognized class of emerging environmental contaminants: a review, Anal. Bioanal. Chem., 403 (2012) 2503–2518.
[7] C.J. Houtman, Emerging contaminants in surface waters and their relevance for the production of drinking water in Europe, J. Integr. Environ. Sci., 7 (2010) 271–295.
[8] C. Stamm, K. Räsänen, F.J. Burdon, F. Altermatt, J. Jokela, A. Joss, M. Ackermann, R.I.L. Eggen, Unravelling the impacts of micropollutants in aquatic ecosystems: interdisciplinary studies at the interface of large-scale ecology, Adv. Ecol. Res., 55 (2016) 183–223.
[9] H. Zia, N.R. Harris, G.V. Merrett, M. Rivers, N. Coles, The impact of agricultural activities on water quality: a case for collaborative catchment-scale management using integrated wireless sensor networks, Comput. Electron. Agric., 96 (2013) 126–138.
[10] M. Liess, L. Liebmann, P. Vormeier, O. Weisner, R. Altenburger, D. Borchardt, W. Brack, A. Chatzinotas, B. Escher, K. Foit, R. Gunold, S. Henz, K.L. Hitzfeld, M. Schmitt-Jansen, N. Kamjunke, O. Kaske, S. Knillmann, M. Krauss, E. Küster, M. Link, M. Lück, M. Möder, A. Müller, A. Paschke, R.B. Schäfer, A. Schneeweiss, V.C. Schreiner, T. Schulze, G. Schüürmann, W. von Tümpling, M. Weitere, J. Wogram, T. Reemtsma, Pesticides are the dominant stressors for vulnerable insects in lowland streams, Water Res., 201 (2021) 117262, doi: 10.1016/j.watres.2021.117262.
[11] F. Hüesker, R. Lepenies, Why does pesticide pollution in water persist?, Environ. Sci. Policy, 128 (2022) 185–193.

[12] M.A. Beketov, B.J. Kefford, R.B. Schäfer, M. Liess, Pesticides reduce regional biodiversity of stream invertebrates, Proc. Natl. Acad. Sci. U.S.A., 110 (2013) 11039–11043.
[13] L. Guzzella, F. Pozzoni, G. Giuliano, Herbicide contamination of surficial groundwater in Northern Italy, Environ. Pollut., 142 (2006) 344–353.
[14] N. Baran, N. Surdyk, C. Auterives, Pesticides in groundwater at a national scale (France): impact of regulations, molecular properties, uses, hydrogeology and climatic conditions, Sci. Total Environ., 791 (2021) 148137, doi: 10.1016/j.scitotenv.2021.148137.
[15] Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the Quality of Water Intended for Human Consumption (Recast) (Text with EEA Relevance), Official Journal of the European Union, European Union.
[16] M.-K. Kim, K.-D. Zoh, Occurrence and removals of micropollutants in water environment, Environ. Eng. Res., 21 (2016) 319–332.
[17] F.A. Caliman, M. Gavrilescu, Pharmaceuticals, personal care products and endocrine disrupting agents in the environment – a review,. CLEAN–Soil Air Water, 37 (2009) 277–303.
[18] S.C. Monteiro, A.B.A. Boxall, Occurrence and fate of human pharmaceuticals in the environment, Rev. Environ. Contam. Toxicol., 202 (2010) 53–154.
[19] J.L. Zhou, Z.L. Zhang, E. Banks, D. Grover, J.Q. Jiang, Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water, J. Hazard. Mater., 166 (2009) 655–661.
[20] J. Jiang, J. Han, X. Zhang, Nonhalogenated aromatic DBPs in drinking water chlorination: a gap between NOM and halogenated aromatic DBPs, Environ. Sci. Technol., 54 (2020) 1646–1656.
[21] J. Han, X. Zhang, Evaluating the comparative toxicity of DBP mixtures from different disinfection scenarios: a new approach by combining freeze-drying or rotoevaporation with a marine polychaete bioassay, Environ. Sci. Technol., 52 (2018) 10552–10561.
[22] J. Meijer, M. Lamoree, T. Hamers, J.-P. Antignac, S. Hutinet, L. Debrauwer, A. Covaci, C. Huber, M. Krauss, D.I. Walker, E.L. Schymanski, R. Vermeulen, J. Vlaanderen, An annotation database for chemicals of emerging concern in exposome research, Environ. Int., 152 (2021) 106511, doi: 10.1016/j.envint.2021.106511.
[23] R.N. Carvalho, A. Arukwe, S. Ait-Aissa, A. Bado-Nilles, S. Balzamo, A. Baun, S. Belkin, L. Blaha, F. Brion, D. Conti, N. Creusot, Y. Essig, V.E.V. Ferrero, V. Flander-Putrle, M. Fürhacker, R. Grillari-Voglauer, C. Hogstrand, A. Jonáš, J.B. Kharlyngdoh, R. Loos, A.-K. Lundebye, C. Modig, P.-E. Olsson, S. Pillai, N. Polak, M. Potalivo, W. Sanchez, A. Schifferli, K. Schirmer, S. Sforzini, S.R. Stürzenbaum, L. Søfteland, V. Turk, A. Viarengo, I. Werner, S. Yagur-Kroll, R. Zounková, T. Lettieri, Mixtures of chemical pollutants at European legislation safety concentrations: how safe are they?, Toxicol. Sci., 141 (2014) 218–233.
[24] M. Heynen, J. Fick, M. Jonsson, J. Klaminder, T. Brodin, Effect of bioconcentration and trophic transfer on realized exposure to oxazepam in 2 predators, the dragonfly larvae (*Aeshna grandis*) and the Eurasian perch (*Perca fluviatilis*), Environ. Toxicol. Chem., 35 (2016) 930–937.
[25] F.J. Burdon, M. Reyes, A.C. Alder, A. Joss, C. Ort, K. Räsänen, J. Jokela, R.I.L. Eggen, C. Stamm, Environmental context and disturbance influence differing trait-mediated community responses to wastewater pollution in streams, Ecol. Evol., 6 (2016) 3923–3939.
[26] N.T. Halstead, T.A. McMahon, S.A. Johnson, T.R. Raffel, J.M. Romansic, P.W. Crumrine, J.R. Rohr, Community ecology theory predicts the effects of agrochemical mixtures on aquatic biodiversity and ecosystem properties, Ecol. Lett., 17 (2014) 932–941.
[27] T. Bond, W. Chu, U. von Gunten, M.J. Farré, Themed issue on drinking water oxidation and disinfection processes, Environ. Sci. Water Res. Technol., 6 (2020) 2252–2256.
[28] C. Liao, U.-J. Kim, K. Kannan, A review of environmental occurrence, fate, exposure, and toxicity of benzothiazoles, Environ. Sci. Technol., 52 (2018) 5007–5026.
[29] Y. Cousquer, A. Pryet, C. Delbart, R. Valois, A. Dupuy, Adaptive optimization of a vulnerable well field, Hydrogeol. J., 27 (2019) 1673–1681.
[30] M. Janža, Optimization of well field management to mitigate groundwater contamination using a simulation model and evolutionary algorithm, Sci. Total Environ., 807 (2022) 150811, doi: 10.1016/j.scitotenv.2021.150811.
[31] F. Ustaoğlu, Y. Tepe, Water quality and sediment contamination assessment of Pazarsuyu Stream, Turkey using multivariate statistical methods and pollution indicators, Int. Soil Water Conserv. Res., 7 (2019) 47–56.
[32] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater. Standard Methods, American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), Washington, D.C., 2012.
[33] E. Kudlek, Formation of micropollutant decomposition by-products during oxidation processes supported by natural sunlight, Desal. Water Treat., 186 (2020) 361–372.
[34] C. Mahugo Santana, Z. Sosa Ferrera, M.E. Torres Padrón, J.J. Santana Rodríguez, Methodologies for the extraction of phenolic compounds from environmental samples: new approaches, Molecules, 14 (2009) 298–320.
[35] J. Bohdziewicz, M. Dudziak, G. Kamińska, E. Kudlek, Chromatographic determination and toxicological potential evaluation of selected micropollutants in aquatic environment – analytical problems, Desal. Water Treat., 57 (2016) 1361–1369.
[36] S. Pietrzak, Phosphates in ground waters under grasslands in Poland, Woda Środ. Obsz. Wiej. T., 15 (2015) 89–100 (in Polish).
[37] S. Hänsel, Z. Ustrnul, E. Łupikasza, P. Skalak, Assessing seasonal drought variations and trends over Central Europe, Adv. Water Resour., 127 (2019) 53–75.
[38] E. Popek, Sampling and Analysis of Environmental Chemical Pollutants, 2nd ed., Elsevier, Amsterdam, Netherlands, 2018.
[39] C.W. Liu, K.H. Lin, Y.M. Kuo, Application of factor analysis in the assessment of groundwater quality in a Blackfoot disease area in Taiwan, Sci. Total Environ., 313 (2003) 77–89.
[40] T. Stathers, J. Low, R. Mwanga, T. Carey, M. McEwan, S. David, R. Gibson, S. Namanda, M. McEwan, J. Malinga, R. Ackatia-Armah, M. Benjamin, H. Katcher, J. Blakenship, M. Andrade, S. Agili, J. Njoku, K. Sindi, G. Mulongo, S. Tumwegamire, A. Njoku, E. Abidin, A. Mbabu, J. Mkumbira, K. Ogero, S. Rajendran, J. Okello, A. Bechoff, D. Ndyetabula, F. Grant, J. Maru, H. Munyua, N. Mudege, T. Muzhingi, Everything You Ever Wanted to Know About Sweetpotato: Reaching Agents of Change ToT Manual, International Potato Center, Lima, Perú, 2018.
[41] C. Grant, D. Flaten, D. Tomasiewicz, S. Sheppard, The importance of early season phosphorus nutrition, Can. J. Plant Sci., 81 (2001) 211–224.
[42] S. Mondal, A.K. Mukherjee, T. Senapati, S. Haque, A.R. Ghosh, Interrelationship Between TOC, IC, TC and DO, BOD, COD of Water in Regard to Stratification of an Abandoned OCP at Raniganj Coal Field Area, Burdwan, West Bengal, 1st International Congress of Applied Ichthyology & Aquatic Environment, Volos, Greece, 2014, pp. 25–29.
[43] Regulation of the Ministry of Maritime Economy and Inland Navigation of 1 March 2019 on the List of Priority Substances, Journal of Laws of 2019, (Item 528).
[44] Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on Environmental Quality Standards in the Field of Water Policy, Official Journal of the European Union, L 348/84.
[45] Act of 20 July 2017 – Water Law (Journal of Laws 2017, Item 1566 as Amended).
[46] M. Kluska, Dynamics of changes in the concentration of polycyclic aromatic hydrocarbons in selected Polish surface water, Ochr. Śr. Zasobów Nat., 31 (2020) 11–17.
[47] M. Foszpańczyk, E. Drozdek, M. Gmurek, S. Ledakowicz, Toxicity of aqueous mixture of phenol and chlorophenols upon

photosensitized oxidation initiated by sunlight or vis-lamp, Environ. Sci. Pollut. Res. Int., 25 (2018) 34968–34975.
[48] W.W. Anku, M.A. Mamo, P.P. Govender, Phenolic Compounds in Water: Sources, Reactivity, Toxicity and Treatment Methods, M. Soto-Hernandez, M. Palma-Tenango, M. del Rosario Garcia-Mateos, Eds., Phenolic Compounds – Natural Sources, Importance and Applications, IntechOpen, London, United Kingdom, 2017.
[49] G. Luongo, R. Avagyan, R. Hongyu, C. Östman, The washout effect during laundry on benzothiazole, benzotriazole, quinoline, and their derivatives in clothing textiles, Environ. Sci. Pollut. Res., 23 (2016) 2537–2548.
[50] P. Jiang, J. Qiu, Y. Gao, M.I. Stefan, X.-F. Li, Nontargeted identification and predicted toxicity of new by-products generated from UV treatment of water containing micropollutant 2-mercaptobenzothiazole, Water Res., 118 (2020) 116542, doi: 10.1016/j.watres.2020.116542.
[51] N. Esmaile, S. Mofavvaz, S. Shabaneh, M.R. Sohrabi, B. Torabi, A simple colorimetric method using gold nanoparticles for the detection of 2-mercaptobenzothiazole in aqueous solutions, soil and rubber, Int. J. Environ. Anal. Chem., 8 (2020) 1–12, doi: 10.1080/03067319.2020.1779241.
[52] H.-G. Ni, F.-H. Lu, X.-L. Luo, H.-Y. Tian, E.Y. Zeng, Occurrence, phase distribution, and mass loadings of benzothiazoles in riverine runoff of the Pearl River Delta, China, Environ. Sci. Technol., 42 (2008) 1892–1897.
[53] L. Wang, J.J. Zhang, H.W. Sun, Q.X. Zhou, Widespread occurrence of benzotriazoles and benzothiazoles in tap water: influencing factors and contribution to human exposure, Environ. Sci. Technol., 50 (2016) 2709–2717.
[54] E. Fries, Determination of benzothiazole in untreated wastewater using polar-phase stir bar sorptive extraction and gas chromatography–mass spectrometry, Anal. Chim. Acta, 689 (2011) 65–68.
[55] R. Avagyan, I. Sadiktsis, C. Bergvall, R. Westerholm, Tire tread wear particles in ambient air—a previously unknown source of human exposure to the biocide 2-mercaptobenzothiazole, Environ. Sci. Pollut. Res., 21 (2014) 11580–11586.
[56] M.H. Whittaker, A.M. Gebhart, T.C. Miller, F. Hammer, Human health risk assessment of 2-mercaptobenzothiazole in drinking water, Toxicol. Ind. Health, 20 (2004) 149–163.
[57] M.P. Charnay, C. Verge, E. Barriuso, Influence of soil type and water content on release of triticonazole from coated maize seed, Pest Manage. Sci., 56 (2000) 249–256.
[58] H. Lin, B. Dong, J. Hu, Residue and intake risk assessment of prothioconazole and its metabolite prothioconazole-desthio in wheat field, Environ. Monit. Assess., 189 (2017) 236, doi: 10.1007/s10661-017-5943-1.
[59] E. Tasumi, S. Kanazawa, S. Fukuda, Degradation of a herbicide, beflubutamid, in upland soils and isolation of its degrading microbes, Soil Sci. Plant, 53 (2007) 236–245.
[60] I.A. Tsakmakidis, A.G. Lymberopoulos, C. Alexopoulos, C.M. Boscos, S.C. Kyriakis, In vitro effect of zearalenone and α-zearalenol on boar sperm characteristics and acrosome reaction, Reprod. Domest. Anim., 41 (2006) 394–401.
[61] M.S. Mostrom, Zearalenone, R. Gupta, Ed., Veterinary Toxicology: Basic and Clinical Principles, Academic Press, Cambridge, MA, USA, 2012.
[62] A. Mally, M. Solfrizzo, G.H. Degen, Biomonitoring of the mycotoxin zearalenone: current state-of-the art and application to human exposure assessment, Arch. Toxicol., 90 (2016) 1281–1292.
[63] M. Dudziak, Analysis of zearalenone in aqueous environment using GC-MS, Pol. J. Environ. Stud., 20 (2011) 231–235.
[64] N. Hartmann, M. Erbs, F.E. Wettstein, R.P. Schwarzenbach, T.D. Bucheli, Quantification of estrogenic mycotoxins at the ng/L level in aqueous environmental samples using deuterated internal standards, J. Chromatogr. A, 1138 (2007) 132–140.
[65] K. Gromadzka, A. Waśkiewicz, P. Goliński, J. Świetlik, Occurrence of estrogenic mycotoxin – zearalenone in aqueous environmental samples with various NOM content, Water Res., 43 (2009) 1051, doi: 10.1016/j.watres.2008.11.042.