Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29836

305 (2023) 217–226
September

Analysis of organic and inorganic compounds in rainwater from the highway and its treatment in membrane processes

Anna Marszałek*, Mariusz Dudziak, Edyta Kudlek

Silesian University of Technology, Department of Energy and Environmental Engineering, Konarskiego 18, 44-100 Gliwice, Poland, email: anna.marszalek@polsl.pl (A. Marszałek)

Received 3 February 2023; Accepted 2 August 2023

ABSTRACT

Municipal stormwater is a common source of organic and inorganic pollutants. Rainwater pollution from the streets can be affected by traffic, that is, wear and tear of tyres, brake linings, engines and vehicle bodies. The main objective of the research was to determine the type of pollutants present in rainwater from the highway, and then the possibility of their removal in membrane processes. A number of analyses were performed to determine the concentration of organic and inorganic pollutants and toxicity tests and microbiological studies were performed. Rainwater contained heavy metals in the amount as follows: nickel 0.41 mg/dm^3, zinc 5 mg/dm^3, lead 0.52 mg/dm^3. In rainwater, both typically industrial compounds (biphenyls, polycyclic saturated hydrocarbons, aromatic hydrocarbons, phenols and bisphenol A), naturally occurring compounds and components of plant protection products were determined. Rainwater toxicity was expressed as percentage inhibition of *Vibrio fischeri* luminescence after 5 and 15 min of incubation and based on the growth of the freshwater vascular plant *Lemna minor*. Water showed toxicity to *V. fischeri* at 27.52% (5 min) vs. *L. minor* at 33%. In the ultrafiltration process, the retention coefficient of organic compounds, that is, TOC and phenol, was respectively 9% and 79%, while in the case of heavy metals, the following values were obtained: Ni(II) 75%, Pb(II) 67%, Zn(II) 98%, and octadecane was reduced by more than 81%. In the nanofiltration process, the retention coefficient was higher and was at the TOC level 100%, phenol 90%, Ni(II) 82%, Pb(II) 67%, Zn(II) 98%, and the octadecane was reduced by more than 85%.

Keywords: Rainwater; Ultrafiltration; Nanofiltration; Micropollutants

1. Introduction

Rainwater contains various types of chemical and microbiological contaminants that can be hazardous to the environment and human health [1]. The rainwater from the streets may contain a lot of organic and inorganic pollutants, including heavy metals and polycyclic aromatic hydrocarbons (PAHs) [2,3]. The source of these pollutants is road traffic, such as wear and tear on tires, brake linings, engines and vehicle bodies [4,5]. For example, zinc is used in the manufacture of car tires as ZnO and various sulfur-containing organic compounds (e.g., dithiocarbonates and thiazoles) [6,7]. Estimated emissions from tire wear can range from about 2.4%–36% of the total amount of Zn in the atmosphere [8]. Particular attention is often paid to the presence of heavy metals in rainwater due to their toxicity [1]. However, the water flowing out of the streets accumulates much more pollution. Struk-Sokołowska et al. [9] showed in samples of runoff water from rainwater and meltwater in Poland the occurrence of benzotriazoles at a high level. They concluded that road activities are a common source of benzotriazole emissions in the urban environment, directly polluting human habitats with various roads and numerous urban vehicles. In turn, Sankoda et al. [10] showed a high

---

* Corresponding author.

Presented at the 3rd International Conference on Strategies toward Green Deal Implementation – Water, Raw Materials and Energy (ICGreenDeal2022), 5–7 December 2022, held online by the Mineral and Energy Economy Research Institute, Polish Academy of Sciences

proportion of toxic polycyclic aromatic hydrocarbons, that is, chrysene and benz[a]anthracene in rainwater samples. They also found that rainwater had a significant impact on the occurrence of PAHs in surface waters. Rainwater is contaminated with dangerous compounds that need to be removed before it can be used. Therefore, various chemical or physical methods are used to reduce pollution and improve the quality of the collected rainwater [11–15]. In order to purify the tested rainwater, membrane processes were proposed, including ultrafiltration and nanofiltration in a flow-through system, where the pollutant retention coefficient was determined. Membrane processes are widely known techniques in the field of water treatment, which are characterized by high purification efficiency and the equipment used occupies a small surface area [16]. Kim et al. [14] conducted a metal membrane filtration study. The test results showed a high reduction efficiency microbiological and dust contamination in rainwater. Baú et al. [15] conducted research on the use of ultrafiltration combined with chlorination for the production of drinking water. The water produced was shown to meet drinking water standards in terms of physical, chemical, and microbiological parameters (coliforms and *E. coli*). Until now, preliminary studies have been carried out on the use of the ultrafiltration process in combination with the UV process for the purification of water from the roof [17]. The applied membrane process showed high efficiency of removing organic and inorganic impurities from rainwater. Therefore, the next step in the research was to check the possibility of using these processes to remove micropollutants from water coming from the streets, also determining the toxicity of the tested water.

In the literature on the subject you can find many studies on the analysis of specific pollutants, for example, only organic or heavy metals or inorganic compounds found in rainwater [2,9,18–21]. However, many pollutants are still not analyzed in rainwater. Given the fact that rainwater is one of the main water resources, continuous improvement of knowledge about the pollutants present in it is required. The innovative point of this research was to conduct a broad analysis of rainwater flowing from the highway to the retention reservoir, and then an attempt to purify it in membrane processes. In summary, the objective of the study was to identify and quantify the concentration of organic and inorganic pollutants and micropollutants in rainwater from paved areas. In addition, the toxicity of rainwater was determined before and after the treatment process. This study can be used as a source of guidelines for rainwater quality.

Table 1
Physico-chemical characteristics of the tested rainwater

Parameter	Rainwater
COD, mg/dm^3	107
Phenol, mg/dm^3	0.72
Nickel, mg/dm^3	0,41
Zink, mg/dm^3	5
Lead, mg/dm^3	0.52
pH	7.815
Conductivity, μS/cm	5.26
TOC, mg/dm^3	7.84
Colour, mg·Pt/dm^3	23
N–NO$_3$, mg/dm^3	3.8
P–PO$_4$, mg/dm^3	1
N–NH$_4$, mg/dm^3	1.8

2. Methods and materials

2.1. Subject of research

Rainwater was collected in March 2022, as there has been moderate rain this month. At that time, higher concentrations of rainwater pollutants were found compared to months with heavy rainfall [22]. The amount of precipitation in March was 57 mm. The physicochemical analysis of rainwater is summarized in Table 1.

2.2. Analytical methods

The efficiency was evaluated by monitoring typical quality parameters (colour, COD, TOC, phenol, nickel, zinc, lead, nitrate nitrogen, ammoniacal nitrogen, phosphate phosphorus, conductivity, pH). All determinations except pH OWO and conductivity measurements were performed with a UV-Vis Spectroquant® Pharo 300 (Merck, Kenilworth, NJ, USA). Concentrations of this were determined spectrophotometrically with a Merck Test Kit. TOC was measured using a TOC-L series analyser (Shimadzu, Kioto, Prefektura Kioto, Japan). pH and conductivity were monitored with the multifunctional analyser CX-461 (Elmetron, Zabrze, Poland).

The chromatographic analysis of the extract was performed using a GC-MS(EI) 7890B gas chromatograph from Agilent Technologies (Santa Clara, USA). The analytical tool has been equipped with a 5 ms SLBTM capillary column (30 m × 0.25 mm with a film thickness of 0.25 μm) from Sigma-Aldrich (Poznań, Poland). Helium 5.0 with a flow rate of 1.1 cm^3/min acts as a carrier gas for chromatographic analysis. The injection volume was 1 μL and was injected automatically at a rate of 3,000 mm^3/min. The injector temperature was set to 250°C. The GC furnace temperature program was as follows: 80°C (6 min), 5°C/min to 260°C, 20°C/min to 300°C (2 min). The temperature of the ion trap and the ion source was 150°C and 230°C, respectively. The identification of compounds present in the collected water samples was made on the basis of their mass spectra obtained after chromatographic analysis was carried out in the total ionic current (TIC) mode. The range of monitored ion masses was determined to be 50–500 m/z [23].

Microbiological analysis including coliform bacteria, total number of microorganisms at 22°C ± 2°C after 72 h, *E. coli*, and *Enterococci* was performed by an external accredited laboratory according to ISO methods. Analyzes were performed according to standards PN-EN ISO 9308-1:2014-12/PN-EN; PN-EN ISO 6222:2004; ISO 9308-1/A1:2017; PN-EN ISO 7899-2:2004 (Water and Sewage Enterprise, Poland).

Rainwater before and after membrane processes was evaluated ecotoxicologically. Enzymatic tests with the bioluminescent bacteria *Vibrio fischeri* and growth tests with the aquatic plant *Lemna minor* were performed. Toxicity was assessed based on Microtox® test results. The degree of toxicity was assessed by the change in the intensity of light emitted by the bacteria. The experiment was carried out in the MicrotoxOmni WET (whole effluent toxicity) system [24]. The *Lemna* sp. the Growth Inhibition Test (GIT) was performed in freshwater vascular plants *L. minor* according to the OECD Guideline 221. For the study, a plant with two fronds from its own breeding was used. The test was carried out at 25°C ± 1°C with constant exposure to 6,000 lux light. The toxicological effect determined based on the morphological changes of the plants was assessed after 7 d as a percentage of inhibition of plant frond growth according to Eq. (1) [25].

$$E = \frac{\left(L_k - L_t\right)}{L_k} \times 100\% \tag{1}$$

where L_k is the number of living indicator organisms (number of fronds) for the control sample; L_t is the number of living indicator organisms (number of fronds) for the test sample.

2.3. Experimental procedure

The process of ultrafiltration and nanofiltration was carried out using polymer membranes. An ultrafiltration membrane with the symbol MT, manufactured by SUEZ (GE) TM, made of polyethersulfone, with a limiting molar mass of 5,000 Da was used. Then the nanofiltration membrane with the symbol NF-270, produced by FilmTec™, made of polyamide-TFC, with a limiting molar mass of 200 Da. Before the actual rainwater filtration process, the membranes were conditioned by passing deionized water through them. Transmembrane processes were carried out using a pressure for UF of 0.3 MPa and for NF 2 MPa, the flow velocity over the membrane surface was 18 cm/h and the temperature was maintained at 20°C. Each process was carried out for 4 h, rainwater was collected every 15 min, the volume of collected permeate was measured and the effectiveness of removing contaminants was measured every hour. Each process was carried out separately. The efficiency of the process was assessed by determining the volumetric stream of deionized water (J_w) and the volumetric stream of treated rainwater (J_v) and based on the degree of removal of the pollutant load. Physico-chemical processes and analyses were carried out three times.

Fig. 1. The catchment area of rainwater from the highway.

The volumetric permeate flux was calculated according to Eq. (2) [26]:

$$J = \frac{V}{\left(s \cdot t\right)} \tag{2}$$

The intensity of membrane blocking (IF) is described as follows [26]:

$$\text{IF} = \left(\frac{J_v}{J_w}\right) \times 100\% \tag{3}$$

where J – volumetric permeate flux, dm^3/m^2·h, V – permeate volume, dm^3, s – membrane area, m^2, t – time, h.

Separation properties were determined by calculating the pollutant retention coefficient (R%) [26]:

$$R\% = \left(1 - \frac{C_p}{C_r}\right) \times 100 \tag{4}$$

where R% –, C_p – concentrations in permeate, mg/dm^3, C_r – concentration of pollutants in rainwater, mg/dm^3.

Membrane processes were performed in a laboratory-scale cross-flow configuration equipped with a plate-frame membrane module SEPA CF-NP (GE Osmonics, Minnetonka, USA), as shown in Fig. 2.

3. Discussion of results

3.1. Transport properties of ultrafiltration and nanofiltration membranes

In the first stage of the research, the transport characteristics of the membranes used, that is, ultrafiltration and nanofiltration membranes for deionized water, were determined. The polyethersulfone membrane was characterized by a volume flux of deionized water at a level of 86.11 dm^3/m^2·h in the ultrafiltration process and 45.83 dm^3/m^2·h in the nanofiltration process. The change in the volumetric flow of rainwater depending on the time for the ultrafiltration and nanofiltration process is shown in Fig. 3.

Then the process of ultrafiltration of rainwater was carried out. After 15 min of process, the value of the volumetric permeate flux was 77.78 dm^3/m^2·h. Subsequently, this value decreased after 1 h of the process until the value of 66.67 dm^3/m^2·h was reached. There was a 22% reduction in the volumetric flow of permeate. It has been shown that during the process there was an intensification of the phenomenon of membrane fouling. Then the raw rainwater was processed nanofiltration. After 15 min the value of the volumetric permeate flux decreased by 12%. However, after 4 h of operation the flux decreased by 36% from the initial flux. The fouling followed slowly and stabilized. On the basis of the J_w and J_v fluxes, the value of the parameter that illustrates the intensity of membrane fouling was calculated. The

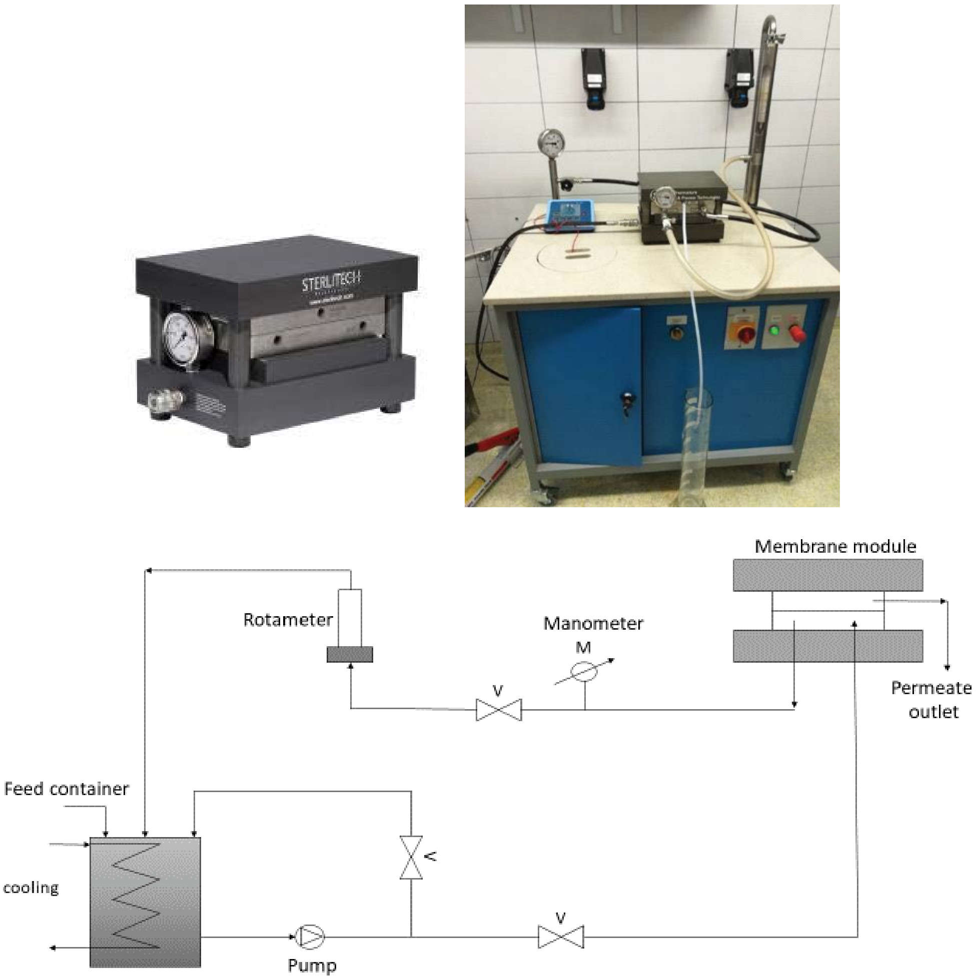

Fig. 2. Cross-flow filtration set-up (photo and scheme) [26].

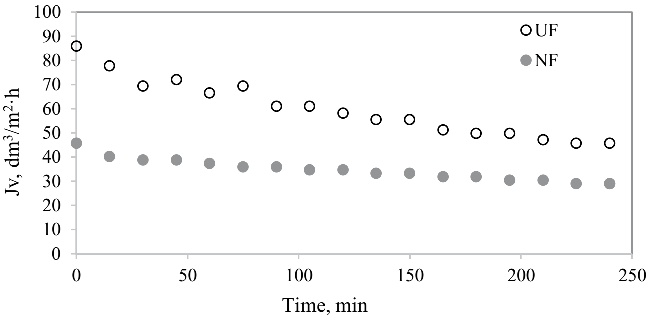

Fig. 3. Change in the volumetric flow of rainwater according to the time for the ultrafiltration and nanofiltration process.

lower their values, the more intensively the surface of the membranes is covered with a layer of substances contained in the purified solution. Fig. 4 shows the intensity of membrane blockage in the UF and NF processes.

Organic and inorganic impurities, colloids, and microorganisms are considered the main cause of membrane pollution. Fouling membranes have a strong effect on the filtration stream, and which limits the purification process, increases operating costs and shortens the life of the membrane. Therefore, periodic chemical cleaning should be considered, which can effectively reduce irreversible fouling, achieving greater membrane filtration efficiency.

The efficiency of rainwater pretreatment was evaluated on the retention coefficient of total organic carbon, phenol, colour, and heavy metals. Fig. 5 shows the dependence of the concentration of individual impurities on the time of ultrafiltration and nanofiltration.

The effectiveness of rainwater pretreatment was evaluated, among others, on the basis of the assessment of the concentration of organic compounds. The total organic carbon in rainwater in the studies conducted studies was at a level of 7.84 mg/dm^3 before pretreatment. In the UF process, the average retention rate was 9%. On the contrary, in the NF process, a complete reduction in TOC was observed. Ba et al. also confirms in his research that the UF membrane is not an ideal barrier to smaller pollutants, such as dissolved organic matter, which can be suspected to constitute the whole TOC [15].

In the further course of research, the analyzed rainwater parameter was phenol. According to the Polish regulation, the limit value of phenol is 0.1 mg/dm^3 [27]. Its concentration

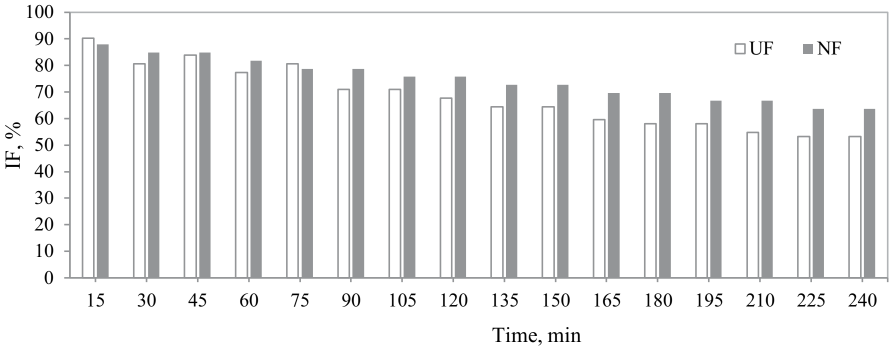

Fig. 4. The intensity of the membrane fouling phenomenon depending on the time.

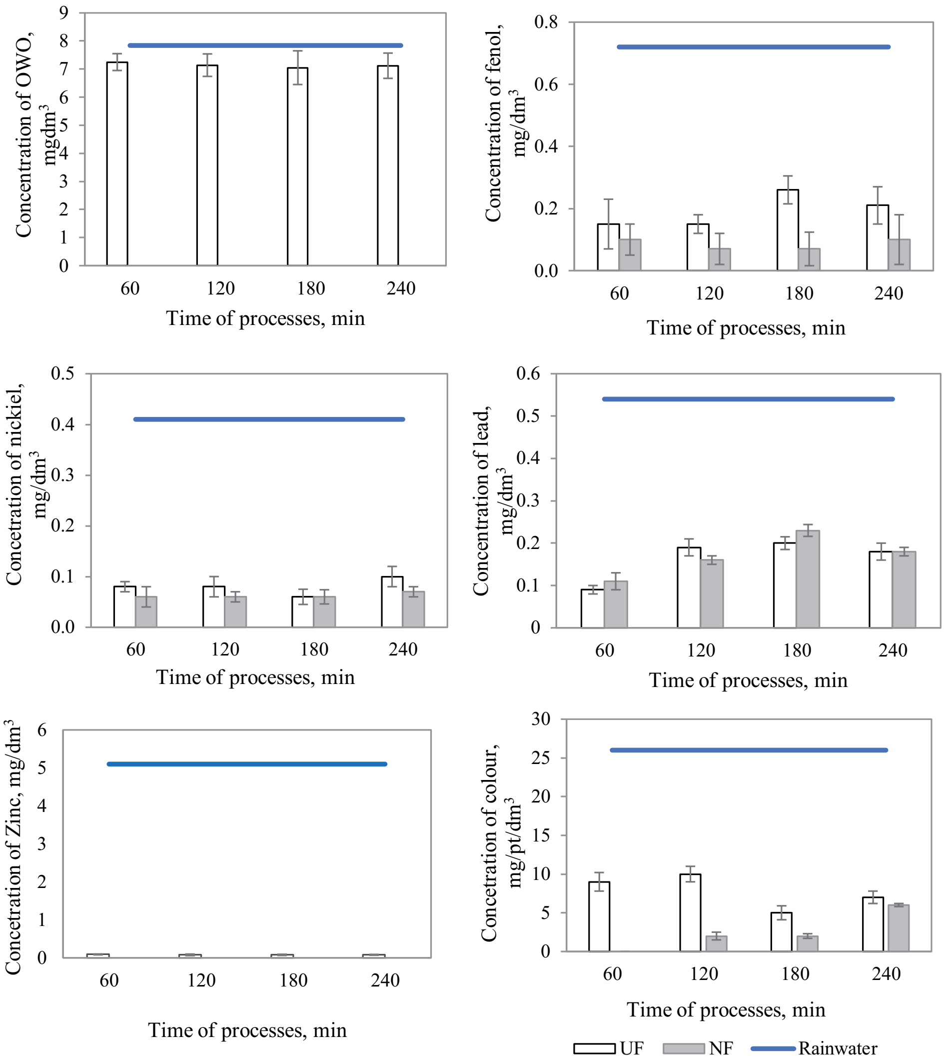

Fig. 5. Dependence of individual pollutants on the duration of the UF and NF process.

in rainwater was 0.7 mg/dm^3. On the graph, a decrease in phenol concentration is noticeable during the process. In the ultrafiltration process, the concentration of phenol was recorded at the level of 0.15 mg/dm^3 (79% reduction). However, the value of this compound still exceeds the limit value. Only in the nanofiltration process was the phenol concentration 0.07 mg/dm^3 (R = 90%). Another important element of the research of the ultrafiltration process was the concentrations of heavy metals, the content of which was recorded in rainwater taken from the highway. According to the said regulation, the limit value for zinc is 2 mg/dm^3, while for nickel and lead 0.5 mg/dm^3. Compared to other heavy metals, the zinc concentration from the rainwater intake was high and was 5 mg/dm^3. Fuerhacker et al. [28] also observed a high concentration of zinc in the water flowing from the parking lot. This is probably due to the fact that zinc is used in the production of car tires and accounts for 1.5% of the material. As a result of tire wear, tire wear are released into the atmosphere which, together with rainwater, penetrate the soil. The collected rainwater comes from the highway, which is an highway and heavy vehicle traffic, and as a result a possibly high concentration of zinc in the tested rainwater [29,30]. The heavy metal retention coefficient in the ultrafiltration process was Ni(II) = 75%, Pb(II) = 67%, Zn(II) = 98%, while in the nanofiltration process Ni = 82%, Pb(II) = 67%, Zn(II) = 98%. Heavy metals are known to exist as free ions in highly acidic environments. Under these conditions, their molecular sizes are smaller than those of the pore sizes of ultrafiltration membranes and freely pass through the membranes. The reason for such a high removal of these ions in the ultrafiltration process may be electrostatic interactions between the membrane and the contaminating components. The studied rainwaters were complex mixtures containing a wide range of pollutants. Interactions between these substances and the surface of the membrane can significantly change the surface charge resulting from interactions between charges on the membrane surface and charged solutes. Therefore, it is the surface charge that has a significant impact on the separation properties of the membrane, the nature and extent of contamination [30]. The tested rainwater was characterized by a pH of 7.8. At neutral pH, membranes made of derivatives of sulfonic acid have a negative charge. Mechanisms of fouling of UF membranes, that is, pore blockage, gel formation, cake formation and adsorption, may also be affected. However, more than one contamination mechanism may be involved at the same time [31]. This negative membrane charge can attract and bond with positive feed components, such as divalent ions (e.g., zinc), causing a drop in permeate flux. In the case of metal removal with NF, it is achieved by size exclusion and electrical interactions between the ions in the feeding aqueous solution and the charged NF membranes [32,33].

There was also a very high degree of colour removal from treated rainwater, namely this value decreased to 5 mg·Pt/dm^3 (81%). Reliable identification of sources of particulate pollutants accumulated on road surfaces and characterization of particle composition are important for the development of best management practices to mitigate stormwater quality. According to many studies, the chemical composition of road dust and soils indicates that the material associated with vehicle movement is the main source of amorphous content, consisting of a significant amount of heavy metals. Furthermore, the surrounding soil is the source of Fe, Al, and Mn in road dust, while the sources of Zn, Cu, Pb, Ni, Cr, and Cd are associated with vehicle traffic [34,35].

Chromatographic analysis allowed for the identification of organic micropollutants contained in the tested solutions. Fig. 6 shows the chromatogram of the sample before the implementation of the membrane filtration processes. Each of the peaks corresponds to the presence of a different organic compound. The number of peaks and the intensity of the detector signal (which may indirectly indicate the concentration of individual compounds in the sample), indicate a very complex composition of the tested sample, which may explain its toxic nature towards the test organisms used in the Microtox Test (Table 5). Figs. 7 and 8 show the chromatogram for the sample after the implementation of the membrane filtration processes.

The mass spectra analysis of the compounds noted on the chromatogram allowed for their identification. In this case, it was decided that a compound is considered identified if its mass spectrum coincides with the mass spectrum of the NISTv17 database in not less than 70%. Table 2 lists the determined compounds as well as their retention time and peak area. Particular attention should be paid to the chromatogram obtained after the UF process. The four peaks with the highest signal intensity correspond to compounds that were not determined in raw rainwater. It can therefore be assumed that they come from the membrane itself, or rather from the agent used by its manufacturer for maintenance. Despite the procedure to remove the preservative indicated by the manufacturer, it remained in the pores of the membrane and migrated into the permeate. However, it should be emphasised that the peaks corresponding to specific preservative compounds do not interfere with the

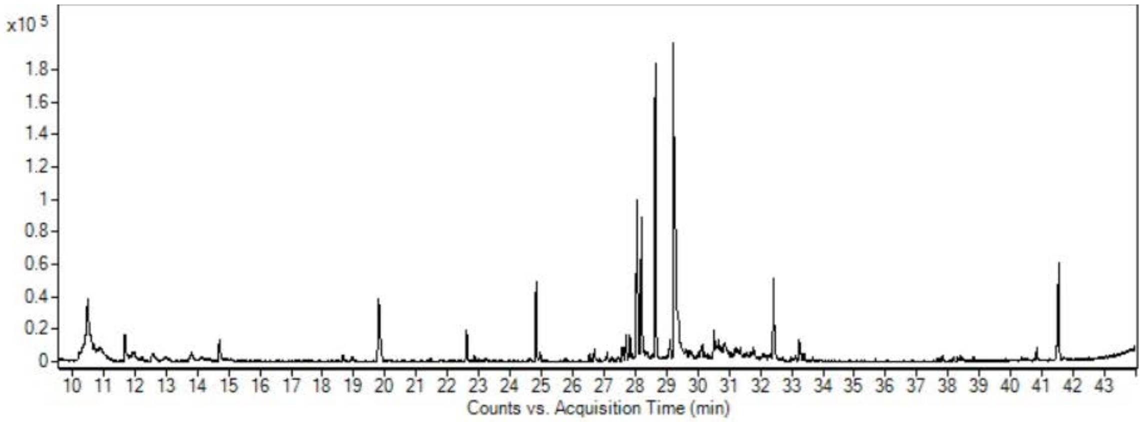

Fig. 6. Chromatogram obtained for rainwater before the treatment process.

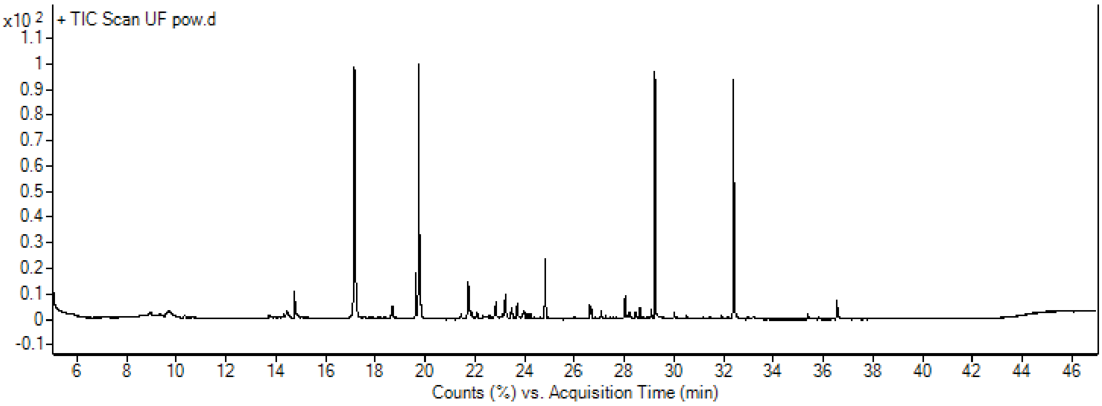

Fig. 7. Chromatogram obtained for rainwater after the UF process.

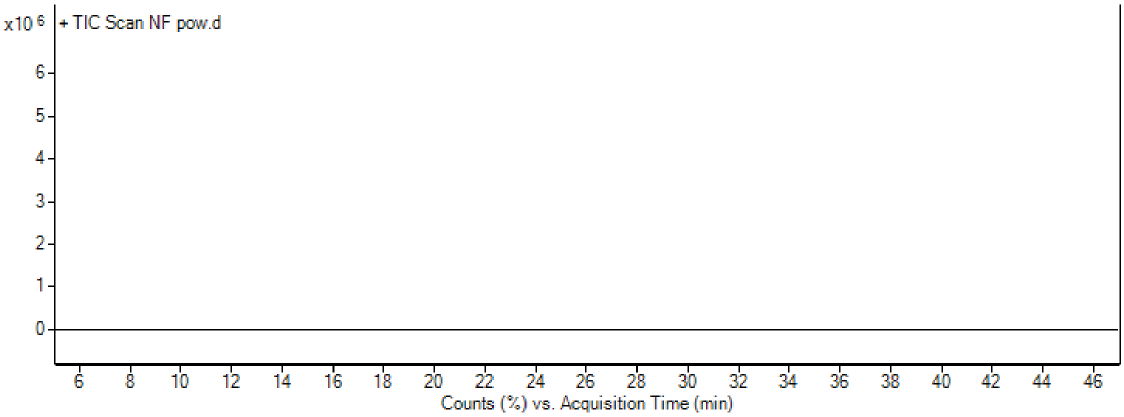

Fig. 8. Chromatogram obtained for rainwater after the NF process.

Table 2
Organic compounds identified in rainwater before and after the membrane filtration process

Compound	R_t (min)	Pow. (u.j.p)		
		RW	After UF	After NF
2,4-Di-tert-butylphenol	22,608	54,818.2	n.d.	n.d.
Butyl octyl phthalate	24,829	118,109.64	76,611.89	69,732.04
2,6-Diisopropylnaphthalene	27,581	23,755.36	n.d.	n.d.
Bisfenol A	27,694	41,063.23	n.d.	n.d.
1,3-Diisopropylnaphthalene	27,825	52,730.05	n.d.	n.d.
7-Methylheptadecane	28,05	332,810.11	122,709.80	14,531.82
4-Ethyltetradecane	28,201	249,969.85	142,744.25	5,102.78
3-Methylheptadecane	28,645	454,304.87	84,894.25	14,993.50
Octadecane	29,264	17,249,130.6	2,510,496.00	147,169.19
1-Iodo-2-methylundecane	33,242	44,293.56	n.d.	n.d.
1-Nitroheptane	33,668	5,707.93	4,269.18	2,894.06
Trans-2-hexenal	34,831	2,129.12	n.d.	n.d.
Butyl citrate	37,671	2,914.38	542.00	n.d.
1-(4-Nitrophenyl)piperazine	38,172	5,649.83	5,410.23	n.d.
Silane, diethyloctadecyloxy(3-phenylpropoxy)	41,531	178,576.43	3,426.73	n.d.
Oktylofenol	41,693	4,745.94	n.d.	n.d.

correct analysis of the composition of rainwater after the filtration process. Retention times of the preservative compounds do not coincide with the retention times of the compounds identified in the rainwater prior to the process.

Compounds that have been determined in rainwater due to their origin are both typically industrial compounds (biphenyls, polycyclic saturated hydrocarbons, aromatic hydrocarbons phenols, and bisphenol A), naturally occurring compounds, and components of plant protection products (pesticides), the so-called xenoestrogens. Octylphenol, a xenoestrogen that has been labelled in rainwater, is still a common substance used in industry, although its use to dissolve pesticides has been banned since 2005. In addition to the estrogenic effect, octylphenol also has toxic effects on aquatic organisms as well as humans. On the contrary, bisphenol A, which also belongs to the group of xenoestrogens, is one of the most important chemicals used mainly in the production of epoxy resins, polyesters (mainly polycarbonates), polyether's (polysulfons) and some high-quality transparent plastics, fungicides and antioxidants used worldwide in very large quantities [8].

Based on the peak area of compounds present in rainwater before and after the membrane filtration process, it can be concluded that the UF process allowed for complete removal of 2,4-di-tert-butylphenol, 2,6-diisopropylnaphthalene, bisfenol A, 1,3-diisopropylnaphthalene, 1-iodo-2-methylundecane, trans-2-hexenal and oktylofenol. Furthermore, the concentration of 3-methylheptadecane, octadecane, butyl citrate, and silane, diethyloctadecyloxy(3-phenylpropoxy) was reduced by more than 81%. The permeate after the NF process did not contain 2,4-di-tert-butylphenol, 2,6-diisopropylnaphthalene, bisfenol A, 1,3-diisopropylnaphthalene, 1-iodo-2-methylundecane, trans-2-hexenal, butyl citrate, 1-(4-nitrophenyl)piperazine, silane, diethyloctadecyloxy(3-phenylpropoxy) and oktylofenol. In addition, the concentration of 7-methylheptadecane, 4-ethyltetradecane, 3-methylheptadecane and octadecane was reduced by more than 85%. Table 3 summarize the reduction of the compound concentration after the UF and NF processes, respectively.

3.2. Microbiological analysis

Immediately after collecting raw rainwater samples, microbiological analyses were performed, and the results are presented in Table 4.

There were no *Escherichia coli* and *Enterococci* in both rainwaters. The total number of microorganisms 22°C ± 2°C after 72 h was above the laboratory's upper measuring range. There are no norms that define the number of the microorganisms in the rainwater.

3.3. Toxicity test

In the studies, toxicity tests were also performed with the use of *V. fischeri* bacteria. The results are presented in Table 5.

The toxic effect of rainwater was expressed as the percentage inhibition of luminescence after 5 and 15 min of incubation. Rainwater before pretreatment showed a toxicity level of 27.52% for a contact time of 5 min, and after 10 min the toxicity decreased to 16.26%. The results showed that the rainwater was toxic, but it was of low toxicity. The ultrafiltration process ensured a reduction of toxicity to 16% and nanofiltration to 5% after 5 min of contact. Depending on the environmental conditions, urban runoff may be toxic to both marine and freshwater species, where the main cause of toxicity may be cationic metals, mainly Cu and Zn [36]. According to the procedure described in Section 2.5, the toxicity of raw and treated rainwater was tested for *L. minor*, the toxicity level was 33%. After the

Table 3
Reduction of the compound concentration after the UF and NF process

Compound	Removal of compounds after membrane filtration, % (average values)	
	UF	NF
2,4-Di-tert-butylphenol	–	–
Butyl octyl phthalate	35.13 ± 0.88	40.96 ± 0.23
2,6-Diisopropylnaphthalene	–	–
Bisfenol A	–	–
1,3-Diisopropylnaphthalene	–	–
7-Methylheptadecane	63.13 ± 0.58	95.63 ± 0.39
4-Ethyltetradecane	42.90 ± 0.07	97.96 ± 0.45
3-Methylheptadecane	81.31 ± 0.03	96.70 ± 0.42
Octadecane	85.45 ± 0.14	99.15 ± 0.48
1-Iodo-2-methylundecane	–	–
1-Nitroheptane	25.21 ± 0.63	49.30 ± 0.23
Trans-2-hexenal	–	–
Butyl citrate	81.40 ± 0.94	–
1-(4-Nitrophenyl)piperazine	4.24 ± 0.11	–
Silane, diethyloctadecyloxy(3-phenylpropoxy)	98.08 ± 0.45	–
Oktylofenol	–	–

Table 4
Microbiological analysis of rainwater

Parameter	Results	UF	NF
Coliform bacteria, CFU/100 mL	19 ± [11; 32]	0	0
Escherichia coli, CFU/100 mL	0	0	0
Enterococci, CFU/100 mL	0	0	0
Total number of microorganisms at 22°C ± 2°C after 72 h, CFU/1 mL	>300	>300	101 ± [72; 139]

Notes: The number after the given result after the symbol ± represents the expanded uncertainty calculated for the coverage factor $k = 2$, which corresponds to a confidence interval of approximately 95%. For microbiology, the confidence interval of the obtained was given according to PKN-ISO/TS 19036:2011. The sign ">" indicates that the test result is above the laboratory's upper measuring range.

Table 5
Toxic effect of rainwater is expressed as a percentage of inhibition of luminescence

Type of rainwater	Toxicity effect	
	Contact time 5 min	Contact time 15 min
Rainwater	27.52%	16.26%
Rainwater after UF	16.45%	10.34%
Rainwater after NF	5.12%	1.23%

use of membrane processes, that is, UF, the toxic effect was reduced to 25%. Similarly, in the nanofiltration process. Carrying out extensive pollution studies can help pinpoint the factor that falls short of being toxic to flora and fauna [37]. The analysis of micropollutants showed the presence of pesticides in the tested water, which, in addition to heavy metals, could also affect the toxic effect. This has been extensively described by Rouvalis et al. [38] in studies on the determination and toxicity of pesticides from rainwater samples in western Greece. Among the pollutants detected in the tested rainwater, fatty and carboxylic acids, which are present in higher concentrations in urban areas, may be toxic [39]. The toxicity of rainwater toward the tested organisms was influenced by phenol, the overestimated concentration of which was already detected at the level of spectrophotometric analyses [40]. Based on the peak areas of compounds present in water, both straight (octadecane) and branched (7-methylheptadecane) alkanes were etched. Octodecane is one of the components of petroleum. Gasoline-powered cars emit harmful hydrocarbons, nitrogen oxides, carbon monoxide, and lead compounds into the atmosphere [41]. It can be assumed that these pollutants also contributed to the toxicity of the studied rainwater.

4. Conclusion

The following conclusions were drawn on the basis of the conducted research:

- Rainwater contained heavy metals in the amount as follows: nickel 0.41 mg/dm^3, zinc 5 mg/dm^3, lead 0.52 mg/dm^3. In rainwater, both typically industrial compounds (biphenyls, polycyclic saturated hydrocarbons, aromatic hydrocarbons, phenols, and bisphenol A), naturally occurring compounds, and components of plant protection products were determined.
- The intensity of fouling ultrafiltration membranes within 4 h of the process was 53.2%, while in the case of nanofiltration it was 63.6%. A lower value indicates a more intensive phenomenon of membrane fouling.
- In the ultrafiltration process, the retention coefficient of organic compounds, that is, TOC and phenol, was respectively 9% and 79%, while in the case of heavy metals, the following values were obtained: Ni(II) = 75%, Pb(II) = 67%, Zn(II) = 98%.
- In the nanofiltration process, the retention coefficient was higher and was at the level of TOC = 100%, Phenol = 90%, Ni(II) = 82%, Pb(II) = 67%, Zn(II) = 98%.
- UF process allowed for complete removal of Bisphenol A and octylphenol, the concentration of octadecane was reduced by over 81%.
- The permeate after the NF process did not have many micropollutants compared to the raw rainwater, and the concentration of octadecane was reduced by more than 85%.
- Highway rainwater showed a low toxicity to *V. fischeri* bacteria at a level of 27.5%. The ultrafiltration process reduced toxicity to 16%, and the nanofiltration process to 5% after 5 min of contact. In the case of *L. minor*, the level of toxicity of rainwater was 33%. After using membrane processes, both the toxic effect of UF and NF was reduced to 25%.

Acknowledgements

This research was funded by the Polish Ministry of Science and Higher Education.

References

[1] R. Shaheed, W.H.M.W. Mohtar, A. El-Shafie, Ensuring water security by utilizing roof-harvested rainwater and lake water treated with a low-cost integrated adsorption-filtration system, Water Sci. Eng., 10 (2017) 115–124.

[2] N. Esfandiar, R. Suri, E.R. McKenzie, Competitive sorption of Cd, Cr, Cu, Ni, Pb and Zn from stormwater runoff by five low-cost sorbents; effects of co-contaminants, humic acid, salinity and pH, J. Hazard. Mater., 423 (2022) 126938, doi: 10.1016/j.jhazmat.2021.126938.

[3] M. Mattonai, T. Nacci, F. Modugno, Analytical strategies for the quali-quantitation of tire and road wear particles – a critical review, TrAC, Trends Anal. Chem., 154 (2022) 116650, doi: 10.1016/j.trac.2022.116650.

[4] V.N. Nagara, D. Sarkar, E.J. Elzinga, R. Datta, Removal of heavy metals from stormwater runoff using granulated drinking water treatment residuals, Environ. Technol. Innovation, 28 (2022) 102636, doi: 10.1016/j.eti.2022.102636.

[5] J. Szmagliński, N. Nawrot, K. Pazdro, J. Walkusz-Miotk, E. Wojciechowska, The fate and contamination of trace metals in soils exposed to a railroad used by diesel multiple units: assessment of the railroad contribution with multi-tool source tracking, Sci. Total Environ., 798 (2021) 149300, doi: 10.1016/j.scitotenv.2021.149300.

[6] A. Moezzi, A.M. McDonagh, M.B. Cortie, Zinc oxide particles: synthesis, properties and applications, Chem. Eng. J., 185 (2012) 1–22.

[7] W. Geiger, H. Dreiseitl, New Ways to Drain Rainwater, Poradnik, Wyd. Oficyna Wydawnicza Projprzem-EKO, Bydgoszcz, 1999.

[8] I. Sadiktsis, C. Bergvall, C. Johansson, R. Westerholm, Automobile tires a potential source of highly carcinogenic dibenzopyrenes to the environment, Environ. Sci. Technol., 46 (2012) 3326–3334.

[9] J. Struk-Sokołowska, J. Gwoździej-Mazur, Ł. Jurczyk, P. Jadwiszczak, U. Kotowska, J. Piekutin, F.A. Canales, B. Kaźmierczak, Environmental risk assessment of low molecule benzotriazoles in urban road rainwaters in Poland, Sci. Total Environ., 839 (2022) 156246, doi: 10.1016/j.scitotenv.2022.156246.

[10] K. Sankoda, S. Ishikawa, K. Sekiguchi, Levels and compositions of polycyclic aromatic hydrocarbons in rainwater and their implication for aquatic environments in urban area in Saitama, Japan, Polycyclic Aromat. Compd., 42 (2022) 5661–5670.

[11] W. He, X. Lin, Z. Shi, J. Yu, S. Ke, X. Lu, Z. Den, Nutrient removal performance and microbial community analysis of amended bioretention column for rainwater runoff treatment, J. Cleaner Prod., 374 (2022) 133974, doi: 10.1016/j.jclepro.2022.133974.

[12] S. Singh, R. Yadav, S. Kathi, A.N. Singh, Chapter 14 – Treatment of Harvested Rainwater and Reuse: Practices, Prospects, and Challenges, S. Kathi, S. Devipriya, K. Thamaraiselvi, Eds., Cost Effective Technologies for Solid Waste and Wastewater Treatment: Advances in Environmental Pollution Research, Elsevier, 2022, pp. 161–178.

[13] P.C.L. da Costa, A.R.G. de Azevedo, F.C. da Silva, Rainwater treatment using an acrylic blanket as a filtering media, J. Cleaner Prod., 303 (2021) 126964, doi: 10.1016/j.jclepro.2021.126964.

[14] R.H. Kim, S. Lee, J.O. Kim, Application of a metal membrane for rainwater utilization: filtration characteristics and membrane fouling, Desalination, 177 (2005) 121–132.

[15] S.R.C. Baú, M. Bevegnu, G. Giubel, V. Gamba, Development and economic viability analysis of photovoltaic (PV) energy powered decentralized ultrafiltration of rainwater for potable use, J. Water Process Eng., 50 (2022) 103228, doi: 10.1016/j.jwpe.2022.103228.

[16] X. Liu, Z. Ren, H.H. Ngo, X. He, P. Desmond, A. Ding, Membrane technology for rainwater treatment and reuse: a mini review, Water Cycle, 2 (2021) 51–63.

[17] A. Marszałek, M. Dudziak, Application of the ultrafiltration and photooxidation process for the treatment of rainwater, Water Air Soil Pollut., 232 (2021) 1–9.

[18] R.N. Mead, J.D. Felix, G.B. Avery, R.J. Kieber, Characterization of CHOS compounds in rainwater from continental and coastal storms by ultrahigh resolution mass spectrometry, Atmos. Environ., 105 (2015) 162–168.

[19] M.P.S. Ferreira, P.S.M. Santos, A.C. Duarte, Oxidation of small aromatic compounds in rainwater by UV/H_2O_2: optimization by response surface methodology, Sci. Total Environ., 815 (2022) 152857, doi: 10.1016/j.scitotenv.2021.152857.

[20] K.M. Mullaugh, J.M. Hamilton, G.B. Avery, J.D. Felix, Temporal and spatial variability of trace volatile organic compounds in rainwater, Chemosphere, 134 (2015) 203–209.

[21] K. Palawat, R.A. Root, L.I. Cortez, T. Foley, Patterns of contamination and burden of lead and arsenic in rooftop harvested rainwater collected in Arizona environmental justice communities, J. Environ. Manage., 337 (2023) 117747, doi: 10.1016/j.jenvman.2023.117747.

[22] F.J. Charters, T.A. Cochrane, A.D. O'Sullivan, Untreated runoff quality from roof and road surfaces in a low intensity rainfall climate, Sci. Total Environ., 550 (2016) 265–272.

[23] E. Kudlek, Decomposition of contaminants of emerging concern in advanced oxidation processes, Water, 10 (2018) 955, doi: 10.3390/w10070955.

[24] A. Marszałek, J. Bohdziewicz, E. Puszczało, Co-treatment of municipal landfill leachate with dairy wastewater in membrane bioreactor, Ecol. Chem. Eng. S, 27 (2020) 139–149.

[25] M. Dudziak, D. Kopanska, Indirect effect of made grounds on the aquatic flora and fauna, Environ. Prot. Eng., 43 (2017) 15–24.

[26] G. Kamińska, A. Marszałek, Advanced treatment of real grey water by SBR followed by ultrafiltration – performance and fouling behavior, Water, 12 (2020) 154 (1–16).

[27] Regulation of the Minister of Maritime Economy and Inland Navigation of 12 July 2019 on Substances Particularly Harmful to the Aquatic Environment and the Conditions to be Met When Introducing Sewage into Waters or Into the Ground, as well as When Discharging Rainwater or Meltwater Into Waters or to Devices Water, Journal of Law 2019, Item 1311.

[28] M. Fuerhacker, T.M. Haile, B. Monai, A. Mentler, Performance of a filtration system equipped with filter media for parking lot runoff treatment, Desalination, 275 (2011) 118–125.

[29] F.S. Degaffe, A. Turner, Leaching of zinc from tire wear particles under simulated estuarine conditions, Chemosphere, 85.5 (2011) 738–743.

[30] M.A. Barakat, E. Schmidt, Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater, Desalination, 256 (2010) 90–93.

[31] R. Shoshaa, M.Y. Ashfaq, M.A. Al-Ghouti, Recent developments in ultrafiltration membrane technology for the removal of potentially toxic elements, and enhanced antifouling performance: a review, Environ. Technol. Innovation, (2023) 103162, doi: 10.1016/j.eti.2023.103162.

[32] J. Kumar, H. Joshi, S.K. Malyan, Removal of copper, nickel, and zinc ions from an aqueous solution through electrochemical and nanofiltration membrane processes, Appl. Sci., 12 (2021) 280, doi: 10.3390/app12010280.

[33] V. Kočanová, J. Cuhorka, L. Dušek, P. Mikulášek, Application of nanofiltration for removal of zinc from industrial wastewater, Desal. Water Treat., 75 (2017) 342–347.

[34] T.B. Councell, K.U. Duckenfield, E.R. Landa, Tire-wear particles as a source of zinc to the environment, Environ. Sci. Technol., 38 (2004) 4206–4214.

[35] C. Gunawardana, A. Goonetilleke, P. Egodawatta, Source characterisation of road dust based on chemical and mineralogical composition, Chemosphere, 87 (2012) 163–170.

[36] S. Lindfors, H. Österlund, L. Lundy, M. Viklander, Metal size distribution in rainfall and snowmelt-induced runoff from three urban catchments, Sci. Total Environ., 743 (2020) 140813, doi: 10.1016/j.scitotenv.2020.140813.

[37] D. Vlastos, M. Antonopoulou, A. Lavrano, Assessment of the toxic potential of rainwater precipitation: first evidence from a case study in three Greek cities, Sci. Total Environ., 648 (2019) 1323–1332.

[38] A. Rouvalis, C. Karadima, I.V. Zioris, V.A. Sakkas, Determination of pesticides and toxic potency of rainwater samples in western Greece, Ecotoxicol. Environ. Saf., 72 (2009) 828–833.

[39] R.S.L. Martins, D.M.S. Abessa, A. Fornar, Rainwater toxicity and contamination study from São Paulo metropolitan region, Brazil, Environ. Monit. Assess., 186 (2014) 1183–1194.

[40] M. Dudziak, S. Werle, A. Marszałek, S. Sobek, Solar pyrolysis tars treatment using oxidation processes–efficiency and toxicity analysis, Fuel, 318 (2022) 123678, doi: 10.1016/j.fuel.2022.123678.

[41] H.M. Hwang, M.J. Fiala, D. Park, Review of pollutants in urban road dust and stormwater runoff: part 1. Heavy metals released from vehicles, Int. J. Urban Sci., 20 (2016) 334–360.