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# Occurrence of specific pollutants in a mixture of sewage and rainwater from an urbanized area

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Urban runoff appears to be a pathway for transferring new emerging pollutants from land-based sources to the aquatic environment. This paper aimed to identify and describe the groups of pollutants present in rainwater surface runoff as well as their mixture with wastewater in the combined sewer system from urbanized catchments and to determine the correlations between these pollutants. Four leading groups of new emerging pollutants have been identified that may be present in rainwater and municipal wastewater mixtures. The samples were tested for microplastics, phthalic acid esters, pesticides, and polycyclic aromatic hydrocarbons as well as basic parameters. The pilot site was Słupsk (northwestern Poland). We conducted nine sampling campaigns at three points. The results of the present study revealed that (i) polycyclic aromatic hydrocarbons were not present in the tested samples; (ii) the selected organochlorine pesticides were detected during one campaign in the dry season and therefore were not of critical importance; (iii) out of the 11 analyzed phthalic acid esters, five selected substances released from commonly used plastic products were present; and (iv) the number of microplastics contained in the tested samples ranged from 1,400 to 14,036 pcs/L and even occurred during pure rainfall.

**Keywords** Urban runoff, Stormwater quality, Micropollutant concentration, Microplastics, Phthalates

A holistic approach to the efficient drainage of rainwater in cities is currently an important element of integrated water management in urban catchments<sup>1</sup>. The transformation of previously undeveloped areas into sealed surfaces disturbs the water balance of the catchment and adversely affects drain formation and quality. Due to the limited evaporation surface and storage capacity, the outflow is much faster. As surface sealing increases, infiltration decreases, and surface runoff increases, becoming the main component of runoff. Excessive sealing of the surface contributes to the rapid drainage (without infiltration) of large amounts of water, which results in the overflow of the sewage system transporting mixed sewage, especially when the nominal capacity of the sewage system is insufficient. Sewage systems that partly consist of combined sewers are a real problem in this respect<sup>2-4</sup>. Due to the difficulties in dimensioning the channels, they are not able to cope with periodic network overload, which is particularly dangerous in sanitary terms in the event of heavy rainfall. Therefore, devices that relieve the load of combined water network storm collectors and storm overflows are used. Excess rainwater is then discharged directly to the receiver (usually rivers and streams). Unfortunately, this accelerates and exacerbates flood waves, which results in local flooding. Moreover, the direct discharge of a mixture of diluted sewage and surface runoff into a watercourse results in deterioration not only of its water quality but also of the coastal waters into which the river flows<sup>5,6</sup>. This problem also applies to Baltic cities, where no rainwater drainage system is integrated with systems for effective pretreatment of surface runoff<sup>7</sup>. As a consequence, during torrential rains, rainwater is discharged directly into rivers, constituting an additional load of pollutants carried along with river waters to the Baltic Sea.

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The composition of rainwater discharged into the receiver is determined by the pollutants accumulated during the individual phases of pollutant migration (atmospheric passage, surface runoff phase, and secondary pollution when flowing through the sewer network). According to many authors, rainwater pollution is reflected in numerous quality parameters, which include the concentration of organic substances expressed as biochemical oxygen demand (BOD<sub>5</sub>) and chemical oxygen demand (COD); pH; conductivity; concentration of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions; nitrogen and phosphorus compounds (which determine the phenomenon of eutrophication of the receiver); and the concentration of the suspension, which is considered an excellent carrier of pollutants. The suspension can take part in the transport of specific pollutants, such as petroleum substances and heavy metals (i.e., Pb, Cd, Cu, Zn). However, it must be taken into account that these are only a few of the whole range of pollutants, as it was proven that stormwater might be contaminated with numerous mineral and organic substances<sup>8,9</sup>. Certain groups of pollutants, e.g., polycyclic aromatic hydrocarbons (PAHs), phthalates, pesticides, sodium percarbonates (SPCs), pharmaceuticals, polychlorinated biphenyls (PCBs) and microplastics, pose real threats<sup>10–14</sup>. Some of these substances are not regulated by applicable environmental protection law, and so are called emerging contaminants (ECs) or compounds of emerging concern (CECs). Especially in stormwater runoff, most of these groups occur in trace amounts and thus are classified as micropollutants. However, despite the low concentrations, they pose a serious threat to the aquatic environment, into which they enter from numerous sources. They are primary and secondary in nature, and exhibit synergistic effects and durability<sup>15,16</sup>. Research findings indicate that phthalates and PAHs have detrimental impacts on marine life, affecting organisms such as fish, crustaceans, mollusks, and phytoplankton. Prolonged exposure to these substances may result in hormonal imbalances, organ damage, decreased fertility, developmental impairments, and various adverse health outcomes among aquatic organisms<sup>17–20</sup>. In recent decades, phthalic acid esters have been found in substantial quantities in natural environments and, notably, even in drinking water sources<sup>21–23</sup>. In relation to European regulations, Directive 2013/39/EU identifies di(2-ethylhexyl) phthalate (DEHP) as a priority hazardous substance in the field of water policy. The Environmental Quality Standards (EQS) have established an annual average of 1.3 µg/L for DEHP in surface waters<sup>24</sup>. Additionally, the U.S. Environmental Protection Agency (EPA) has set the maximum allowable concentration (MAC) for this substance in water systems at 6 µg/L. In Regulation No. 1907/2006 of the European Parliament and the Council, di(2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), and dibutyl phthalate (DBP) are included in the list of substances subject to authorization as toxic for reproduction<sup>25</sup>.

Pesticides also exhibit harmful effects on aquatic organisms due to their toxicity and bioaccumulative properties. These chemical substances can disrupt physiological processes and lead to organ and system damage in aquatic organisms. Some pesticides may cause reduced fertility, developmental disorders, and increased susceptibility to diseases<sup>26–29</sup>. Additionally, pesticides can disturb the balance of aquatic ecosystems by reducing biological diversity and degrading habitats. Long-term exposure to pesticides can result in lasting health effects for aquatic organisms and impact entire aquatic ecosystems<sup>30–32</sup>.

It is also necessary to look at the problem of rainwater quality from the point of view of the Urban Wastewater Treatment Directive, for which the proposal for the amended text was presented by the European Commission in October 2022 (it is still in the consulting phase). Particular attention was given to the appropriate management of rainwater. European Union member countries will be required to implement integrated stormwater management plans in all large agglomerations. The aim is to limit the transport of excessive loads of organic matter, nitrogen, and phosphorus to water reservoirs, as well as solid waste and microplastics, along with urban runoff. Moreover, the directive will organize the terminology regarding rainwater management and the sampling methodology (including samples collected for testing the presence of microplastics), which has thus far remained unregulated. Effective monitoring of microplastics is a crucial long-term goal that is essential for understanding the consequences and trends of microplastic pollution. The widespread distribution of microplastics in the natural environment is a source of many problems<sup>33–35</sup>. Plastic debris contains various additives, including phthalic acid esters, which serve as plasticizers and can be released into the aquatic environment during the aging of microplastics<sup>36,37</sup>. Urban runoff is an obvious pathway for transferring microplastics and phthalic acid esters from land-based sources to aquatic environments. However, this issue still lacks proper attention.

The identification of potential pollutants transported with rainwater and the sources from which they are introduced to the environment are extremely important and enable their effective removal at the source to protect the environment. Identification of pollutants characteristic of specific types of catchments, such as industrial areas dominated by the food industry or mixed urban-industrial catchments, as well as purely urban catchments like city centers (streets, shopping centers, residential buildings), and understanding the behavior of chemical substances (e.g., so-called precursors) that may enter surface runoff from these catchments, may make it possible to eliminate them or intervene at points as close as possible to their release into the environment. This approach can prevent their spread and the potential formation of much more persistent and difficult-to-remove complex chemical compounds in the environment. Therefore, this paper aims to identify and describe the groups of pollutants that are present in rainwater surface runoff from urbanized catchments and to determine the correlations between these pollutants and basic parameters and flow types (infiltration and surface runoff).

## Results and discussion

### Flow in a combined sewer system (CSS)

The total flow in the analyzed combined sewer system (CSS) included sanitary wastewater as well as groundwater and surface runoff (Table 1).

The total flow in the sewer system on the analyzed sample collection days was highly variable, ranging from 181.72 to 423.24 L/s at SP1, from 57.60 to 100.69 L/s at SP2, and from 37.17 to 58.72 L/s at SP3. These values correspond to the area of the catchment (points SP2 and SP3 are at the outflow of the catchment and are within the catchment closed with point SP1). However, it is worth mentioning that the total outflow measured at SP2

Data	Results of SWMM model calculations											
	Total flow			Wastewater			Infiltration			Surface runoff		
	L/s			%								
	SP1	SP2	SP3	SP1	SP2	SP3	SP1	SP2	SP3	SP1	SP2	SP3
02.12.2019	394.13	92.44	55.83	13.63	11.63	31.62	14.83	12.66	34.42	71.54	75.71	33.96
19.05.2020	320.82	73.15	52.31	16.74	14.70	33.75	15.11	13.27	30.46	68.15	72.04	35.79
23.06.2020	184.72	61.80	<b>37.17</b>	<b>29.08</b>	17.39	<b>47.50</b>	<b>14.40</b>	<b>8.62</b>	23.53	56.52	73.99	28.97
22.07.2020	<b>181.48</b>	<b>57.60</b>	37.73	29.59	<b>18.66</b>	46.79	14.44	9.11	<b>22.83</b>	55.96	72.23	30.38
14.10.2020	319.16	86.06	49.32	16.83	12.49	35.79	19.93	14.79	42.38	63.25	72.72	21.82
23.11.2020	260.78	<b>100.69</b>	43.84	20.60	<b>10.68</b>	40.26	23.40	12.13	45.75	56.00	<b>77.19</b>	<b>13.98</b>
22.12.2020	303.50	84.19	49.89	17.70	12.77	35.39	19.26	13.90	38.52	63.04	73.33	26.09
12.03.2021	259.60	83.38	51.14	20.69	12.89	34.52	<b>30.79</b>	<b>19.18</b>	<b>51.38</b>	<b>48.52</b>	<b>67.92</b>	14.10
25.05.2021	228.64	69.01	41.34	23.49	15.58	42.70	21.21	14.06	38.55	55.30	70.36	18.75
05.11.2021	<b>423.24</b>	98.72	<b>58.72</b>	<b>12.69</b>	10.89	<b>30.06</b>	14.42	12.37	34.16	<b>72.89</b>	76.74	<b>35.77</b>

**Table 1.** Total flow and the shares of wastewater, infiltration and surface runoff; bold indicate minimum and maximum values.

is 40% greater (on average) than the outflow measured at SP3, while the area of the catchment closed by SP2 is 27% greater. This result was due to the greater inflow of surface runoff in the SP2 area, 5.3% of which was the combined sewer system catchment.

The share of wastewater at the analyzed points varied from 12.69 to 29.59% at SP1 and from 10.68 to 18.66% at SP2. The SP3 point differed greatly in this regard (with a wastewater contribution ranging from 30.06 to 47.50%) because it was the only point without a contribution from the combined sewer system. In the case of infiltration, its share ranged from 14.40 to 30.79% at SP1, from 8.62 to 19.18% at SP2 and from 22.83 to 51.38% at SP3. The largest infiltration in the area closest to point SP3 resulted from the high density of pipes and relatively low level of wastewater in these pipes. This low level of wastewater is related to the limited contribution of surface runoff entering the system. Moreover, the SP3 catchment has the lowest share of impervious area, at 22%, while in the remaining two catchments, this value is 33%. This allows more precipitation to percolate and increase the saturation of soils.

Finally, the surface runoff was estimated to be 48.52% to 72.89% at SP1, 67.92% to 77.19% at SP2, and 13.98% to 35.79% at SP3. Thus, for SP1 and SP2 on all the analyzed days, the surface runoff had the highest share of the total flow. The catchments at these points are similar in terms of the average slope (6.3% for SP1 and 5.1% for SP2, while 8.2% for SP3), imperviousness (values mentioned above), and density of the main pipes (121.9 m/ha for SP1 and 121.1 for SP2).

These results revealed and confirmed high variability in the spatial distribution of wastewater, infiltration, and surface runoff within the same city—sampling points not very far from each other. This leads to the conclusion that each microcatchment could have its own characteristics and should be treated individually with different measures in the holistic approach of integrated water management in urban catchments<sup>1,6,38–41</sup>.

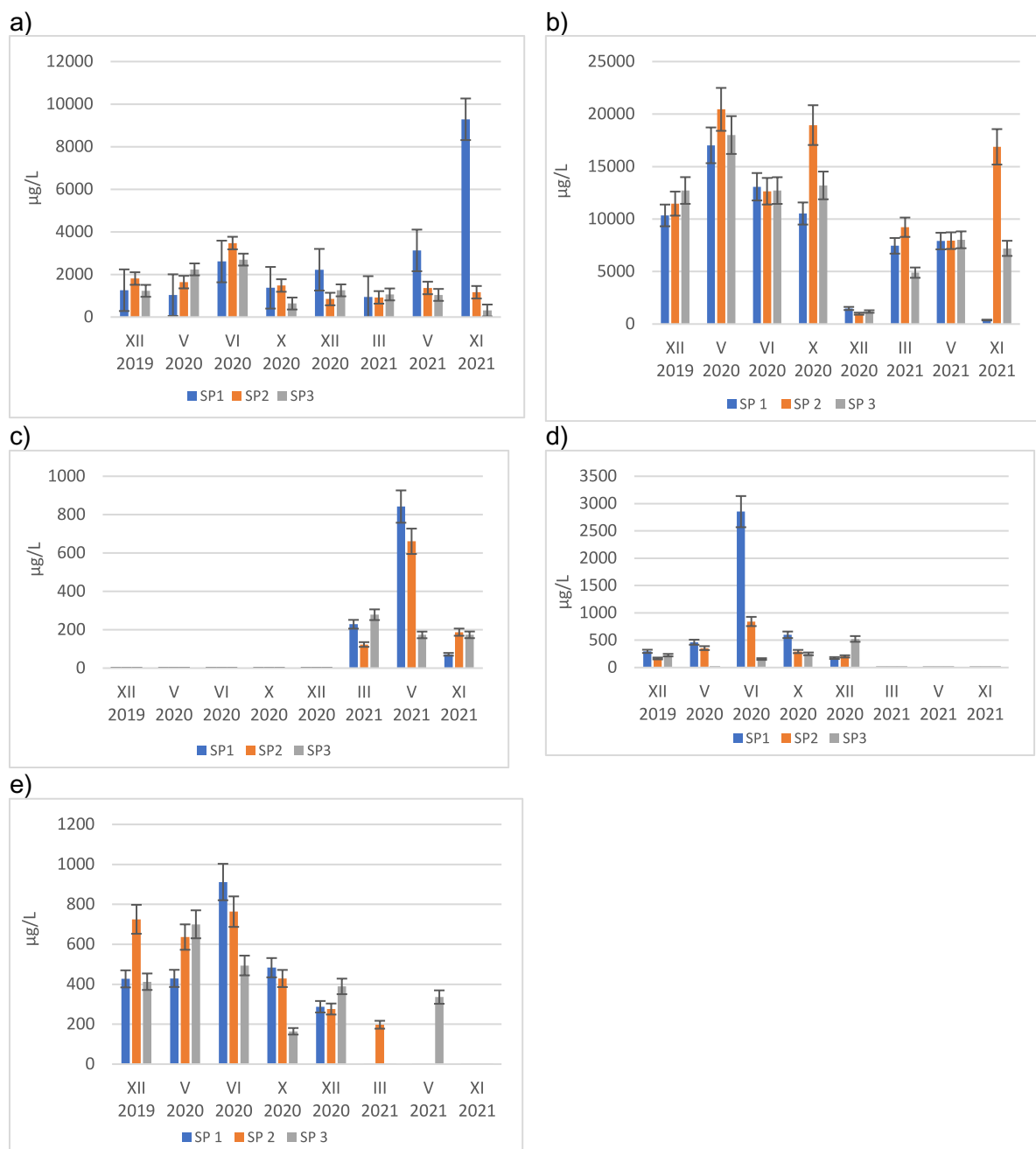
### Monitoring of micropollutants

The micropollutants were monitored for four groups of chemical substances: phthalic acid esters, polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, and microplastics. Rainwater often contains a blend of organic pollutants, some of which have not been thoroughly studied. In addition, rainwater contains other known substances whose levels are influenced by various factors<sup>42–44</sup>. PAHs are generated in the environment as a result of natural and anthropogenic combustion processes. According to Guzel<sup>45</sup>, the main anthropogenic sources of PAHs in the environment are heating, energy, transport, and industry, including petroleum processing<sup>45</sup>. Although PAHs are said to be common atmospheric pollutants that can be washed out during precipitation<sup>46–48</sup>, the concentration of compounds from this group of contaminants were below the limit of detection (LOD) in all tested samples. Additionally, the presence of PAHs in surface runoff was confirmed in research conducted by Jakubowicz et al.<sup>11</sup>. Selected pesticides were only present in one sampling campaign during a dry period (23/06/2020). It should be mentioned that in this case, the collected samples consisted mainly of wastewater (without drainage and rainwater). In the investigated samples, heptachlor epoxide and endrin were detected. Other researchers have proven that pesticides are pollutants that are not found in clean rainwater<sup>49–51</sup>. It can therefore be assumed that the accidental detection of pesticides in the tested samples may be the result of secondary contamination of runoff. Most likely, the presence of pesticides in samples composed of wastewater is related to agricultural activities, which was also confirmed by Moawed et al.<sup>52</sup>. In the case of the cities, it could be connected with some accidental treatment of greenery.

For all these reasons, PAHs and pesticides were not included for further consideration. Due to the importance and their quantities (in our case, the highest detected concentration), this article focuses on the presence and concentrations of a group of phthalic acid esters and microplastics.

### Phthalic acid esters

Out of the 11 analyzed phthalates concentrations in the samples, six were classified below the LOD. Among the tested compounds, five were detected at concentrations that allowed for their identification (over LOD), either periodically or throughout the study. Tests of samples of a mixture of surface runoff from rainwater and domestic sewage carried out for the NOAH project showed the presence of five selected esters of phthalic acid: di-*n*-butyl phthalate, di-2-ethylhexyl phthalate, diethyl phthalate, dimethyl phthalate, and di-*n*-octyl phthalate. The concentrations of the tested compounds ranged from 306.81 to 9288.76  $\mu\text{g/L}$  for di-2-ethylhexyl phthalate (Fig. 1a), from 379.38 to 20,445.9  $\mu\text{g/L}$  for di-*n*-butyl phthalate (Fig. 1b), from 71.83 to 841.98  $\mu\text{g/L}$  for dimethyl phthalate (Fig. 1c), from 155.2 to 53,837.2  $\mu\text{g/L}$  for diethyl phthalate (Fig. 1d) and from 164.37 up to 911.7  $\mu\text{g/L}$  for di-*n*-octyl phthalate (Fig. 1e). In the pure rainwater samples, the concentrations of all the tested compounds were very low and below the LOD. It should be mentioned that plastic processing and packaging production is most likely one of the main industrial sources of phthalic acid esters in the Słupsk catchment area.



**Figure 1.** Concentrations of the analyzed pollutants in CSS: (a) di-2-ethylhexyl phthalate, (b) di-*n*-butyl phthalate, (c) dimethyl phthalate, (d) diethyl phthalate, and (e) di-*n*-octyl phthalate (roman numerals denote the month).

The wide range of concentrations of phthalic acid esters in the tested samples resulted not only from the type of identified substance. Variations also depended on the composition of the samples (mixture of rainwater and sewage, pure rainwater or rainwater from a rainwater channel (only surface stormwater runoff)), the location of the sampling point, and the period (seasons) in which the samples were taken.

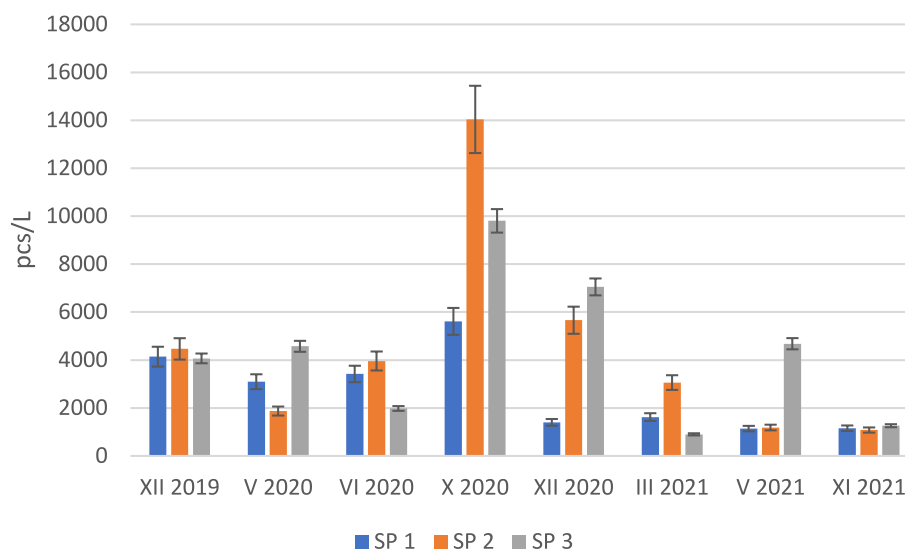
The presence of phthalic acid esters (PAEs) in rainwater samples was also confirmed by other researchers. Fernández-Amado et al.<sup>44</sup> were looking for optimal methods of their detection. This research showed that diethyl phthalate and di-*n*-octyl phthalate were present in six of the analyzed samples. Their concentrations were from 1.82 to 189 µg/L. Whereas the presence of di-*n*-butyl phthalate and diethylhexyl phthalate was confirmed in all eight analyzed pure rainwater samples<sup>44</sup>. On the other hand, in new research from an urban catchment, Hajjoui et al.<sup>53</sup> reported average concentrations of phthalates in runoff from eight selected sampling points along the Bushehr coast at a level of 53.57 µg/L. Cao et al.<sup>36</sup> investigated 15 PAEs in rainwater from six major stormwater drains in heavily urbanized Hong Kong. Phthalic acid esters were ubiquitous in rainwater in Hong Kong, with total concentrations ( $\Sigma$ 15PAEs) ranging from 0.195 to 80.5 µg/L. This study demonstrated that urban stormwater can be an important pathway for the transmission of PAEs to receiving environments.

There are numerous potential reasons for the presence of PAEs in the tested samples, mainly resulting from migration to the environment from various sources related to the way people live today and industrial activities. The multitude and availability of products that contain phthalates, the developing industry, and globalization have resulted in a significant increase in environmental pollution from these compounds<sup>54,55</sup>. Currently, phthalic acid esters are among the emerging environmental pollutants and are particularly harmful to the environment, making their management crucial for environmental protection and public health. The most dangerous of those listed, di-2-ethylhexyl phthalate and di-*n*-butyl phthalate, were considered. They can cause many diseases and dysfunctions and strongly affect reproduction<sup>56</sup>. However, the health effects associated with potential exposure to phthalates in the broader environment are more extensive than those previously discussed.

### Microplastics

The conducted physicochemical analysis showed that surface runoff from rainwater contains significant amounts of microplastics. The amount of microplastics contained in the surface runoff of rainwater ranged from 1400 to 14,036 pcs/L, as shown in Fig. 2.

The highest amounts of microplastics were observed in samples taken in October (14/10/2020): for SP1, the content of plastic microparticles in the runoff of rainwater was 5612 pcs/L, for SP3 up to 9805 pcs/L, and for SP2, it was as high as 14,036 pcs/L. For samples taken at SP1, the number of microplastics was the lowest in the sample from 14/10/2020, whereas higher values were observed for samples taken at SP2 and SP3. In addition, the research showed that for samples taken at SP2, the content of microplastic particles was the highest with samples collected on 14/10/2020. This value was the highest recorded value not only among all the sampling points but also among all the series of tests carried out. The average microplastic content in the surface runoff of rainwater was also calculated for each sampling site, and the following values were obtained: SP1—3187 pcs/L, SP2—5535 pcs/L, and SP3—5047 pcs/L. These values confirm that, at SP2, the contamination with microplastic particles was the highest, while it was the lowest at SP1. It can be assumed that the discrepancies in the number of microplastics contained in the surface runoff at each sampling point depend on many factors, such as location and land use (residential, industrial, service or green area) of the catchment area, road traffic intensity, length of rainless days preceding the occurrence of precipitation, and daily maintenance of city cleanliness, including waste collection systems. The importance of the latter factor can be observed in the results of the samplings presented in this study, as the peak concentration of microplastics occurred on the day when there was relatively intensive



**Figure 2.** Amount of microplastic particles in CSS (expressed in pcs/L) (roman numerals denote the month).

rainfall detected by rain gauges in all three analyzed catchments, and this day was preceded by three dry days. In addition to the determination of microplastics in surface runoff, samples of clean rainwater were also collected, which were the background for the research. The samples were taken twice (02/12/2019 and 14/10/2020). The results of the analysis showed that microplastics were present in pure precipitate, and their concentrations reached 2952 pcs/L and 1120 pcs/L, respectively. These results confirm that microplastics are present not only in aquatic ecosystems but also in the air and in precipitation, which was also reported by Zhang et al.<sup>57</sup>. Other sources report that plastic fragments originating, for example, from clothes or city dust, can float in the atmosphere and then be caught by water drops during rainfall<sup>58</sup>. This shows that even in a seemingly clean environment, there is a transfer of microplastic pollutants in the atmosphere, which in turn combines with atmospheric precipitation. Thus, at the wet deposition stage, microplastics become a component of precipitation (and rain), which has been proven by studies of pure precipitation as a background carried out as part of the NOAH project.

### Correlation analysis

Tables 2, 3, and 4 present the results of the correlation analysis of the selected parameters of quality as well as flow in the CSS for the sample points. Only the subset of parameter pairs for which correlations were determined to be significant (p-value less than 0.05) is presented. The basic quality parameters used in the statistical analysis are presented in the article<sup>3</sup> and in the Supplementary Materials (Table S3). In the specified tables, red denotes a strong positive correlation, whereas blue indicates a strong negative correlation. The displayed number is Kendall's tau correlation coefficient value for the considered pair of variables, along with its significance (p value).

Strong negative correlations were observed between the di-*n*-octyl phthalate concentration and pH (tau = 0.762). This may indicate that at this measurement point, di-*n*-octyl phthalate could be formed as a result of chemical reactions, such as the decomposition of other phthalate compounds<sup>59</sup>. Additionally, a strong negative correlation was found between diethyl phthalate and NOx. The negative correlation between diethyl phthalate and NOx may suggest that diethyl phthalate originates mainly from sources unrelated to NOx emissions. For example, it could be associated with everyday products such as PCPs, packaging, or food items, which are not directly linked to processes causing NOx emissions. The highest negative correlation was found between microplastic content and pH (tau = -0.810). As a result of microplastic degradation processes (such as photodegradation, biodegradation), byproducts can be formed that affect pH<sup>60,61</sup>. For heptachlorepoxyd, a weak negative correlation with infiltration flow and surface runoff was found, as was a weak positive correlation with di-*n*-octyl phthalate and diethyl phthalate.

A strong negative correlation between infiltration flow and diethyl phthalate concentration was observed (tau = -0.714). This may indicate that, at this sample point, wastewater is the primary source of diethyl phthalate. Strong positive correlations were observed for bis(2-ethylhexyl) phthalate and di-*n*-octyl phthalate (tau = 0.714).

X1	X2	Kendall's tau	p value
di- <i>n</i> -octyl phthalate	Heptachlorepoxyd	0.286	0.0486
di- <i>n</i> -octyl phthalate	pH	-0.762	0.0227
diethyl phthalate	Heptachlorepoxyd	0.286	0.0412
diethyl phthalate	NOx	-0.714	0.0355
flow infiltration	Heptachlorepoxyd	-0.286	0.0412
flow runoff	Heptachlorepoxyd	-0.286	0.0412
Microplastic	pH	-0.810	0.0163

**Table 2.** Significant correlation coefficients at SP1.

X1	X2	Kendall's tau	p value
bis(2-ethylhexyl) phthalate	di- <i>n</i> -octyl phthalate	0.714	0.0355
bis(2-ethylhexyl) phthalate	Endrin	0.286	0.0412
bis(2-ethylhexyl) phthalate	Heptachlorepoxyd	0.286	0.0412
di- <i>n</i> -octyl phthalate	Endrin	0.286	0.0412
di- <i>n</i> -octyl phthalate	Heptachlorepoxyd	0.286	0.0412
diethyl phthalate	Endrin	0.286	0.0412
diethyl phthalate	flow infiltration	-0.714	0.0355
diethyl phthalate	Heptachlorepoxyd	0.286	0.0412
Endrin	flow infiltration	-0.286	0.0410
Endrin	pH	-0.286	0.0412
flow infiltration	Heptachlorepoxyd	-0.286	0.0412
Heptachlorepoxyd	pH	-0.286	0.0412

**Table 3.** Significant correlation coefficients at SP2.

X1	X2	Kendall's tau	p value
bis(2-ethylhexyl) phthalate	Endrin	0.286	0.0412
bis(2-ethylhexyl) phthalate	Heptachlorepoxid	0.286	0.0412
bis(2-ethylhexyl) phthalate	pH	-0.667	0.0483
Conductivity	diethyl phthalate	0.762	0.0227
Endrin	flow infiltration	-0.286	0.0412
Endrin	flow runoff	-0.286	0.0412
Endrin	pH	-0.286	0.0253
flow infiltration	Heptachlorepoxid	-0.286	0.0412
flow runoff	Heptachlorepoxid	-0.286	0.0412
Heptachlorepoxid	pH	-0.286	0.0253

**Table 4.** Significant correlation coefficients at SP3.

The results suggest that these two compounds at SP2 may have a common origin or undergo similar degradation or transport processes, leading to their strong correlation<sup>62</sup>. Other pairs of new emerging pollutants with basic parameters and flow indications were weakly correlated (either positive or negative) or uncorrelated.

It was found that bis phthalate concentrations are strongly negatively correlated with pH ( $\tau = -0.667$ ). A lower environmental pH may facilitate the release of these compounds from municipal and industrial pollution sources<sup>63</sup>. Diethyl phthalate was strongly correlated with conductivity ( $\tau = 0.762$ ). This correlation may indicate the industrial origin of this compound<sup>64</sup>. In other cases, there were weak or no correlations.

While correlations were examined for all the analyzed pollutants and flows, significant correlations were identified in very few cases. Moreover, these significant correlations were not consistent across individual sampling points. Therefore, with regard to pollutants delivered to the CSS by rainfall waters, making any general statements is challenging. In this regard, quality is highly variable and depends on numerous factors. Additionally, the lack of similar correlations in sample points may indicate different origins of the analyzed micropollutants in the mixture of rainwater, surface runoff, and sewage.

### Impact of flow on concentrations of micropollutants

Table 5 presents the significance of the linear regression model (Eq. 1) coefficients and their adjusted coefficient of determination ( $\text{adj. } R^2$ ) between new emerging pollutants and infiltration flow as well as surface runoff. If

Site	Infiltration flow model			Runoff flow model		
	adj. $R^2$	Intercept p value	flow coefficient p value	Adj. $R^2$	Intercept p value	Flow coefficient p value
Diethyl phthalate						
SP1	0.667	$8.71 \cdot 10^{-35}$	$1.79 \cdot 10^{-4}$	0.257	$1.26 \cdot 10^{-16}$	0.120
SP2	0.774	$8.63 \cdot 10^{-75}$	$1.68 \cdot 10^{-7}$	0.547	$7.40 \cdot 10^{-20}$	0.00189
SP3	0.109	$1.350 \cdot 10^{-2}$	$3.23 \cdot 10^{-1}$	0.156	$1.78 \cdot 10^{-9}$	0.228
Di-n-butyl phthalate						
SP1	0.025	0.057	0.332	-0.180	0.271	0.785
SP2	-0.155	0.185	0.814	0.047	0.431	0.291
SP3	0.056	0.049	0.280	-0.114	0.240	0.615
Bis(2-ethylhexyl) phthalate						
SP1	0.259	0.019	0.139	0.149	0.023	0.211
SP2	0.643	0.0011	0.010	0.095	0.068	0.236
SP3	0.458	0.0062	0.039	-0.162	0.149	0.879
Di-n-octyl phthalate						
SP1	0.222	$4.20 \cdot 10^{-3}$	0.173	$2.27 \cdot 10^{-1}$	0.669	0.173
SP2	0.014	$5.92 \cdot 10^{-2}$	0.737	$3.91 \cdot 10^{-2}$	0.124	0.572
SP3	0.433	$1.17 \cdot 10^{-5}$	0.021	$3.14 \cdot 10^{-5}$	0.034	0.987
Microplastic						
SP1	-0.191	0.239	0.853	0.079	0.737	0.273
SP2	-0.126	0.812	0.660	-0.145	0.911	0.748
SP3	-0.164	0.444	0.916	-0.150	0.167	0.779

**Table 5.** Linear regression lines for micropollutants and flows: infiltration/runoff.

a relationship between exists the variables,  $\text{adj. } R^2$  is large (meaning values above 0.5 and up to 1.0). If  $\text{adj. } R^2$  equals zero or is negative, this denotes a situation in which the obtained model does not provide any predictive capability.

Table 5 displays the  $\text{adj. } R^2$  and the significance of the linear regression model coefficient and intercept (Eq. 1). If the  $\text{adj. } R^2$  of the model is high and the flow coefficient  $p$  value is significant (assuming that a  $p$  value of less than 0.05 is significant), the obtained model has the capability to predict the micropollutant concentration based on the flow. This situation may indicate that the considered flow type and micropollutant concentration are connected. These occurrences are highlighted in bold.

In the case of diethyl phthalate, it was found that, at SP1 and SP2, there was a relationship between these pollutants and the infiltration flow, and for SP2, there was also a relationship with runoff flow. No relationship was found for SP3 in the infiltration model and for all the sample points for runoff. Thus, it can be suspected that the source of the diethyl phthalate at SP1 was infiltration flow and that at SP2, it was both infiltration and surface runoff. For di-*n*-butyl phthalate, no relationships were found for either infiltration or runoff. In the case of bis(2-ethylhexyl)phthalate, several significant flow coefficients were found. In the case of infiltration flow, it was found that at SP2 and SP3, the obtained model could predict the bis(2-ethylhexyl) phthalate concentration based on the infiltration flow discharge. For di-*n*-octyl phthalate, a relationship was found only at SP3 for the infiltration flow model. For microplastics, no relationship with infiltration or runoff was found.

There are several significant regressions between flow (infiltration/runoff) and micropollutants. However, in general, no clear relationships or patterns can be extracted. This is probably due to the high variability of both flows and concentrations of specific pollutants. This may also indicate that commonly used mathematical models are insufficient for predicting potential pollutant concentrations and their correlation with flow. Therefore, similar to correlation patterns, determining relationship patterns between flows and pollutant concentrations is highly difficult.

## Methods

### Sampling campaigns

Based on the research conducted within the NOAH Project<sup>7</sup>, four leading groups of new emerging pollutants have been identified that may be present in the mixture of rainwater and municipal wastewater. The samples were tested for microplastics, phthalic acid esters, pesticides, and polycyclic aromatic hydrocarbons as well as basic parameters (Table S2).

Ślupsk (northwestern Poland), located approximately 20 km from the Baltic Sea, was chosen as a pilot site. The area of the city is 43.15 km<sup>2</sup>, and urban areas account for approx. 17.40% of this space. Ślupsk has 86,027 inhabitants, which gives a population density equal to 1,631.77 people/km<sup>2</sup>. The study area (pilot site) included part of the sewer system operated by the Ślupsk Water Supply, covering the most densely built-up area of 22.03 km<sup>2</sup>, with separate and combined sewer systems. The overflow (which serves as an outfall in the pilot area) is placed before the main pumping station. The overflow separates excess wastewater and directs it to the receiver, the Ślupia River, which has a catchment area of 1,620 km<sup>2</sup>. The river is 159.57 km long, and the width of the riverbed ranges from 7 m in the upper part of the river to 40 m at the mouth. The average flow at the mouth is approximately 15.5 m<sup>3</sup>/s, whereas the average slope is approximately 1.3‰.

Samples were collected from a combined sewer system (CSS) as a mixture of wastewater and rainfall (including infiltration and surface runoff) from December 2019 to May 2021 during rain events (at least one hour after the start of rain) or immediately after heavy rainfall by an autosampler. In each series, samples were collected from the same three points (presented in Fig. 3).



**Figure 3.** Catchment area with the locations of the sampling and monitoring points (source: Google Maps<sup>3</sup>).

The first sampling point, SP1—Orzeszkowej Street (54°28'35.4" N, 17°01'48.6" E), is located in the northeastern part of the city of Słupsk, where residential and service buildings dominate, as well as facilities of technical infrastructure. Moreover, the SP1 sampling point is located at the end of the sewage network, so it can be assumed that domestic wastewater is transported to these points throughout the city. Sampling point SP2—Mickiewicza Street (54°27'54.5" N, 17°01'19.8" E), is located in the city center with areas of residential and service buildings. Sampling point SP3—Nad Słuzami/Wiejska Street (54°27'45.4" N, 17°02'30.9" E), is located in the eastern part of the city. Even though the sampling points are mainly situated in residential and green areas, there are also industrial areas within the catchment. Słupsk is a city with a medium level of industrial development with a special economic zone, which also covers the surrounding towns. There are several factories located in the city of Słupsk, e.g. car glass factory, means of heavy transport (trucks and buses) factory, food industry factories (brewery, confectionery plant, seafood processing) as well as plastic processing and packaging production. Until 2021 (i.e. during the implementation of the NOAH project), the leather and footwear industry also operated in the city.

### Reagents and materials

A standard solution of phthalic acid esters (PAEs) with a concentration of 2000 µg/mL for each substance was obtained from Sigma-Aldrich (Darmstadt, Germany). The solution comprised 11 substances, including, 4-chlorophenyl phenyl ether, 4-bromophenyl phenyl ether, bis(2-chloroethoxy)methane, bis(2-chloroethyl)ether, bis(2-chloroisopropyl)ether, bis(2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), diethyl phthalate (DEP), dimethyl phthalate (DMP), di-*n*-butyl phthalate (DBP), and di-*n*-octyl phthalate (DOP). Similarly, a standard solution of polycyclic aromatic hydrocarbons (PAHs) was purchased from Reagecon (Shannon, Ireland). This solution contained 16 substances, each at a concentration of 2000 µg/mL, dissolved in toluene (acenaphthene, anthracene, benz(a)anthracene, chrysene, fluoroanthene, fluorene, naphthalene, phenanthrene, pyrene, benzo(a)pyrene, benzo(b)fluoroanthene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, benzo(k)fluoroanthene, indeno(1,2,3-cd)pyrene, and acenaphthylene). Additionally, a standard solution of organochlorine pesticides, comprising 20 substances at a concentration of 2000 µg/mL each, was obtained from Sigma-Aldrich ( $\alpha$ -BHC,  $\beta$ -BHC, Lindane,  $\delta$ -BHC, Heptachlor, Aldrin, Heptachlor epoxide Isomer B,  $\gamma$ -Chlordane,  $\alpha$ -Chlordane, Endosulfan I (alpha), 4,4'-DDE, Dieldrin, Endrin, Endosulfan II (Beta Isomer), 4,4'-DDD, Endrin aldehyde, Endosulfan sulfate, 4,4'-DDT, Endrin Ketone, and Methoxychlor). Internal standards including benzyl benzoate (1 g/mL), naphthalene-d8 (2000 µg/mL in dichloromethane), phenanthrene-d10 (2000 µg/mL in dichloromethane), perylene-d12 (2000 µg/mL in dichloromethane), and decachlorobiphenyl (ampule of 100 mg) were acquired from Sigma-Aldrich. Methanol, *n*-hexane, acetone, Na<sub>2</sub>SO<sub>4</sub>, NaCl, and NaOH solutions were purchased from POCH (Gliwice, Poland). Ultra-pure water was obtained from a Purix CNX-100 system (Polwater, Cracow, Poland). All glassware underwent a 24-h soaking in NaOH solution, followed by rinsing with ultra-pure water and drying for 5 h. An additional rinse with acetone was performed before heating at 280 °C for 5 h.

### Sample preparation

Phthalates were isolated from the tested samples by solid-phase extraction (SPE). For the extraction, CHROMABOND® C18 SPE columns from Macherey–Nagel (Germany) were used. The SPE column was conditioned by first adding 5 mL of methanol to the SPE column, ensuring it was not dry after adding the methanol, and allowing it to soak for 10 min to ensure proper conditioning of the stationary phase. Following this, 5 mL of distilled water was added to the column. 100 mL of aqueous samples containing the internal standard (50 µL/mL) were passed through SPE cartridges. They were then dried under a vacuum for 20 min to remove the retained water. The analytes were eluted with 6 mL of methanol and dichloromethane solutions (1:1, v/v) and the collected fraction was concentrated to 1 mL under a nitrogen atmosphere before being subjected to chromatographic analysis. Extracts were passed through a 0.45 µm filter (PTFE), with the aid of a glass syringe. The samples were concentrated to 1 mL under a nitrogen atmosphere. Three replicates were performed for each solution analyzed.

To isolate PAHs and pesticides, solvent extraction by shaking was utilized. The aqueous layer necessary for conducting the extraction processes was separated using 10 mL of hexane through shaking (5 min) with the addition of an internal standard (25 µL/mL) and 1 g of NaCl, which enhances the extraction efficiency. Subsequently, the organic layer was separated from the aqueous layer. The drying step was carried out by adding a drying agent (anhydrous Na<sub>2</sub>SO<sub>4</sub>), which was activated by roasting in a muffle furnace at 550°C for 4 h. The obtained extract was concentrated to a volume of 1 mL using a nitrogen stream and subjected to chromatographic analysis. Detailed information about the GC–MS System operating conditions is presented in the supplementary materials (Table S1).

### Instrumental analysis

For the quantitative determination of all the analyzed substances, the obtained extracts were subjected to a chromatographic separation process using gas chromatography coupled with mass spectrometry (GC/MS) (Thermo Scientific, Waltham, USA). The analysis utilized the electron ionization (EI) technique to ionize organic compounds, enabling precise determination of their molecular structure and quantities in the research samples. Chromatographic separation was accomplished using a DB-5MS chromatographic column coated with 5% phenyl-95% dimethylpolysiloxane (30 m × 0.25 mm, 0.25 µm film thickness). Internal standard quantification was employed, and the method demonstrated linearity, with a coefficient of determination ( $R^2$ ) exceeding 0.99. The calibration curve was established based on six replicates for each concentration, with determinations made referring to the relationship between the concentration of the analyte and the peak area ratio of the analyte to the internal standard peak area used. The validation was based on results obtained from six replicates of calibration solutions at various concentrations. Parameters such as linearity, repeatability, and recovery were determined. The linearity of the method was assessed based on the calibration curve and it was 0–30 mg/L for pesticides,

0–50 mg/L for PAHs, and 0–100 mg/L for phthalates. Method repeatability was estimated using the coefficient of variation (CV), expressed as a percentage. Method accuracy was evaluated through recovery determination. The LOD was estimated based on recorded chromatograms, using a criterion of three times the signal-to-noise ratio (S/N) value of the analytical signal to the average noise level. For LOQ, it was assumed that its value is three times the determined limit of detection (LOD). The quality control parameters are presented in Table 6.

### Microplastic quantitative analysis

The collected stormwater samples with a volume equal to 0.5 L were subjected to chemical oxidation using Fenton's reagent to remove organic matter. The process was carried out at room temperature for 24 h, after which the pH was maintained at < 5.0. Then, the samples were subjected to vacuum filtration (decantation) using a membrane filter with a pore size of 0.45 µm. The filter was placed in a petri dish and stored in a closed vessel to prevent possible contamination. Quantitative analysis of the microplastics was performed using an Olympus BX51 fluorescence microscope.

### Model

The Storm Water Management Model (SWMM) was applied to construct the model of the sewer system in Slupsk<sup>65</sup>.

The main source of the inputs used for the preparation of projected rainfall events for Slupsk was the Klimada 2.0 project (<https://klimada2.ios.gov.pl/en>). The source data had a spatial resolution of 12.5 km and were based on 12 climate models used for EURO-CORDEX simulations; these models were statistically downscaled based, among others, on precipitation observations provided by the National Hydrological and Meteorological Service in Poland.

Direct surface runoff was applied to the catchments with a combined sewer system only. Runoff was calculated based on the rainfall intensity and catchment features, such as area, slope, imperviousness and roughness, according to the nonlinear reservoir model described by Chen & Shubinski<sup>66</sup> and extended by additional components of the water cycle<sup>67</sup>.

It was assumed that the variation in the seasonal dry period outflow was caused by infiltration, which is usually greater in winter due to more intense percolation and, consequently, a greater soil water content and higher elevation of the groundwater table. To reflect these variations in the model, a monthly infiltration pattern was used, and the volume of monthly infiltration was calculated for each month based on the difference between the total observed outflow in dry periods and the calculated production of wastewater<sup>3</sup>.

### Statistical analysis

A common characteristic of environmental data is the absence of detection due to concentrations not reaching the LOD. In such cases, appropriate estimators for the left-censored data need to be used. The analysis, including suitable estimators, was performed using the NADA and NADA2 packages<sup>68–70</sup>.

The main goal of the statistical analysis was to determine the possible relationships between micropollutants and flows as well as other chemical parameters. Knowledge of correlations can, among other things, indicate the source of pollutants and suggest directions of further research. For this purpose, a correlation analysis was performed using Kendall's tau. In the case of environmental data, this is the best method for determining correlations, especially for data where some of the pollutant concentrations are below the LOD. For the variables with left-censored data, the adjusted Kendall's tau was used, assuming the log-normal distribution of the parameter. This kind of distribution is commonly used with the environmental parameters.<sup>71</sup> Kendall's tau makes it possible to seamlessly include the censored data. Additionally, Kendall's tau has the ability to reflect weak nonlinear relationships. This approach is beneficial since, due to the limited number of observations, it was impossible to analyze nonlinear correlations using appropriate nonlinear analysis. A Kendall's tau value close to 1 indicates a strong positive association between the two variables. A Kendall's t value close to -1 suggests a strong negative

	Retention time RT (min)	Linearity R <sup>2</sup>	CV (%)	Recovery (%) n = 3	LOQ, n = 5 (µg/L)
Bis(2-chloroethyl)ether	6.92	0.9482	2.55	92	25
Bis(2-chloroisopropyl)ether	8.13	0.995	1.67	86	27
Bis(2-chloroethoxy)methane	9.94	0.9919	3.25	103	20
Dimethyl phthalate	14.41	0.9939	1.58	98	12
Diethyl phthalate	16.31	0.995	0.94	105	15
4-Chlorodiphenyl ether	16.50	0.9775	2.33	89	18
4-Bromodiphenyl ether	17.79	0.9872	1.57	69	22
Di- <i>n</i> -butyl phthalate	20.71	0.9885	0.87	119	10
Butylbenzyl phthalate	24.68	0.9776	0.92	111	13
Bis(2-ethylhexyl) phthalate	26.31	0.9747	1.11	90	10
Di- <i>n</i> -octyl phthalate	27.96	0.9446	1.23	95	10
Heptachlorepoxyde Isomer B	10.06	0.9994	1.48	90	15
Endrin	12.07	0.9945	2.19	93	20

**Table 6.** Quality control parameters for the extraction and analysis of PAEs, PAH and pesticides.

association between the two variables. A Kendall's tau value close to 0 indicates little to no association between the two variables<sup>72</sup>.

The relationship between micropollutants and flows was also analyzed using a linear regression model. In the case of regression, due to the number of data points, only parametric models are valid for consideration of the relationships. For the same reason, the reasonable choice of model is linear regression. In the case of left-censored observations, appropriate regression techniques are used assuming a log-normal distribution of the chemical parameters. The linear model was built for the pairs of variables and took the following form:

$$y = a \cdot x + b, \quad (1)$$

where  $a$  is the variable coefficient and  $b$  is the intercept, whereas  $x$  and  $y$  are the analyzed variables (for example,  $x$  may be the flow and  $y$  can be the concentration of micropollutants).

The statistical analysis was performed using the R Project for Statistical Computing<sup>73</sup>.

## Conclusions

The scope of the performed research was very wide in terms of tested parameters, and even so, it has been difficult to demonstrate a clear trend in the obtained research results. The conducted research confirmed that rainwater and its surface runoff and their mixture with wastewater are a qualitatively variable medium. The analysis of rainwater the test results requires taking into account many factors, including hydraulic, meteorological, and environmental, as well as microcatchment characteristics.

The example of Slupsk, (c.a. 100,000 PE city) shows that even within one catchment, there are very large discrepancies for the same collection points over the years. The results of the conducted analyses show that any attempts to generalize knowledge about the quality of rainwater (or interpolation to other, seemingly analogous, catchments) are burdened with a very large error.

The concentrations of PAHs and organochlorine pesticides (heptachlor epoxide and endrin) below the LOD indicate that they are not of critical importance from the perspective of rainwater. Among the 11 tested compounds, five were detected at concentrations that allowed for their identification (over the LOD), either periodically or throughout the study. Most likely, they have industrial origin and the main source may be plastic processing and packaging production. The differences in the number of microplastics in surface runoff at each sampling point can be attributed to various factors, such as the location and land use of the catchment area, road traffic intensity, duration of dry periods before rainfall, and daily city cleanliness maintenance. Moreover its, presence in pure rainwater confirms the migration of microplastic pollutants with atmospheric air.

There are numerous strong correlations spotted occurring between micropollutants, however, these correlations vary depending on the sampling points. Overall, there are no clear relationships or patterns between flow (infiltration/runoff) and micropollutant concentrations, which may indicate that the commonly used mathematical models are insufficient for predicting potential pollutant concentrations and their correlation with flow.

## Data availability

All data generated or analysed during this study are included in this published article and its supplementary information files.

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## Author contributions

M.G. and K.K. conceived the article, wrote the article, and supervised its execution, K.F. conducted the experiments, analysed the results and wrote the paper, W.A. and R.U. analysed the results and wrote the paper, M.K. conducted the experiments and wrote the paper. All authors corrected the manuscript according to Reviewer’s suggestions.

## Competing interests

The authors declare no competing interests.

## Additional information

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