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Examples for elimination of selected groups of petroleum-derived compounds from rainwater and meltwater

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ABSTRACT

This study shows examination results pertaining to the assessment of operation of coalescence separations installed on the way of flow of rainwater and meltwater to Słupia river. The study was performed within Słupia river water protection programme. Content of total suspension as well as concentrations of organic compounds from the BTEX and paraffin group were determined in samples taken from the inlet to and outlet from the separators. It appears from the study performed that in no case admissible content (> 15 mg/dm^3) of determined petroleum-derived substances had occurred in the samples of rainwater and meltwater and a high degree of elimination of those compounds, due to separators operation, was achieved. In 13 samples taken from the separator outlet, the admissible total suspension content was exceeded (above 100 mg/dm^3). Efficiency of all separators operation reflected in the elimination of total suspension amounted, on average, to 67.5%. The lowest total suspension elimination efficiency has been noted for separator No. 14 (40%).

Keywords: BTEX; Paraffins; Total suspension; Coalescence separators; Meltwater; Rainwater

1. Introduction

Rainwater and meltwater from urban areas contain a number of organic pollutants, also those counted as petroleum-derived substances. The source of such pollutants can be products of crude oil processing containing, among other, aliphatic, carbocyclic and heterocyclic hydrocarbons. Crude oil products, such as fuels, get into rainwater and meltwater and can be associated with intense traffic, mainly in urban areas [1]. Pollutants contained in rainwater and meltwater quite frequently migrate to surface waters and even ground waters [2,3]. Usually, during assessment of aquatic environment pollution with petroleum-derived compounds, the so-called "ether extract" or "substances extracted by petroleum benzin", which comprise the majority of crude oil products, as well as vegetable oils and animal fats, are used [1]. Unfortunately, the result of this determination is also interfered with by other compounds that do not belong to the petroleum-derived products, as the earlier mentioned vegetable oils and animal fats. For this reason, beside of other specific rainwater and meltwater pollution indicators, in the assessment of separator operation efficiency, petroleum-derived substances can be used as indicators; among those monoaromatic

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hydrocarbons such as benzene, toluene, ethylbenzene and xylene (BTEX) as well as paraffins are counted [4]. Another group can comprise polycyclic aromatic hydrocarbons and olefins. This paper comprises the study on content of the above-mentioned first group of petroleum-derived pollutants in mixed rainwater and meltwater as a result of their elimination following pretreatment in coalescence separators [5–7]. In effect, such waters can be discharged, without any hesitation, to surface water without causing its eutrophication.

2. The objective and scope of this study

The research work was performed within the Słupia river water protection against pollutants contained in rainwater and meltwater programme framework. Contents of organic compounds of the BTEX group and paraffins were tested. This was based on the analysis of the physical and chemical composition of rainwater and meltwater pretreated in experimentally installed four coalescence separators. Such water, treated as wastewater, was tested on the inlets and outlets of said separators associated with sedimentation tanks performing the role of the pretreatment plant [8,9]. Considering specific climate conditions featuring diversified frequency of rainfall and snowfall in particular months, rainwater and meltwater sample taking procedure was adjusted to those conditions.

The purpose of fitting pretreatment facilities (separators) was to get such wastewater parameters, which would comply, following treatment, with relevant Ordinance by the Minister of Environment (of 28 January 2009) concerning the conditions that have to be complied with when discharging wastewater to water or ground and concerning substances that are particularly harmful for the aquatic environment [10]. Therefore, the separator-treated rainwater and meltwater flowing through connection chambers could be, in the majority of cases, discharged to the existing sewerage systems and further on to river Słupia.

Two-stage treatment of rainwater sewerage system effluents discharged to surface water was set up. The first pretreatment stage was performed in a sedimentation tank where solids and suspended matter were separated due to flow settling. The second treatment stage was performed, as needed, in a selected type of coalescence separators: NG100 (nominal flow rate 100 L s^{-1}) and NG125 (nominal flow rate 125 L s^{-1}), in which petroleum-derived pollutants were removed. Specific features of separators operation and design are described in a source paper (Engineering Office Gazda) [8]. It has been assumed that operation of those facilities could be assessed based on the results of determination of selected chemical compounds group content counted among petroleum-derived substances, including monoaromatic hydrocarbons (BTEX), paraffins (C7–C11) and total suspension in rainwater and meltwater.

Samples of rainwater and meltwater (following rainfall and/or snowfall occurrence) were taken for examination from separator inlets and outlets. A total of 10 test series for BTEX and total suspension for each of four separators were performed. Commencing from the fifth series, paraffin with various number of carbon atoms in the chain from C7 to C11 content determination was started.

The aim of the study was assessment of separator operation efficiency used for the removal of petroleum-derived substances from wastewater.

3. Materials and methods

3.1. Determination of easily settling suspension

Determination of easily settling suspension in wastewater was done in Imhoff funnel featuring the capacity of 1 dm^3. Samples of polluted waters were analysed in the certified Laboratory of Spectral Analysis, Department of Waste Management, Technical University of Koszalin. Samples were being transferred to Imhoff funnel, which was rotated around its axis in 30 min cycles to prevent deposition of suspension on funnel walls. Volume of settled suspension was read from the funnel scale after two hours. The measurement results were indicated in cm^3/dm^3. Total suspension tests were performed for comparison purposes. This was carried out by application of the gravimetric method on the day of sampling. The procedure was performed in line with the generally recommended examination methods in accordance with the Polish standard PN-72/C-04559/01, PN-72/C-04559/02, PN-72/C-04559/03.

3.2. Determination of petroleum-derived substances

3.2.1. Wastewater sampling methodology

Samples of polluted water from separators were taken with a sample scoop directly into glass containers. Such method of sampling prevented secondary contamination with organic compounds and change of pressure in the vessel during sampling, and therefore, it prevented water degassing, so that no petroleum-derived volatile compounds were lost.

3.2.2. Methodology of determination of monoaromatic hydrocarbons in wastewater

To determine monoaromatic hydrocarbons in water samples, the “purge and trap” technique comprising final determination in gas chromatograph HP 5890, with flame ionisation detector, was used. The carrier gas was helium. To separate the analyte mixture, HP1 nonpolar column was used. The method sensitivity level was, under such conditions, 0.01 μg L^{-1}.

The “purge and trap” technique is based on the utilization of a dynamic equilibrium occurring between the flowing gaseous phase and liquid phase. Any nonpolar or slightly polar substances with boiling point not exceeding 300˚C diffuse from water into gas bubbles and leave the liquid phase with them. They are bound by Tenax sorbent at a later stage. Following thermal desorption, the analytes are directly proportioned to the chromatographic column. Due to long desorption, time an intermediate stage (often called “focusing”) was applied; this was based on resorption and desorption of the determined substances in the so-called “sorption trap” having considerably smaller volume then the first sorbent [11].

The feeder for “purge and trap” operated with the gas chromatograph in the “online” system thanks to which very high sensitivity of determinations could be achieved. Efficiency of the “purge and trap” technique depends greatly on analytes polarity. The greater the polarity of the determined chemical compound, the lesser its recovery from the solution. For this reason, this technique is used, first and foremost, for the analysis of non-polar or slightly polar substances comprising volatile hydrocarbons such as benzene, toluene, ethylbenzene and xylene as well as its derivatives [12,13].

The so-called external standard method was used in quantitative analysis of those substances. Determination based on a standard mixture of volatile hydrocarbons with known concentrations was performed in the conditions in which the environmental samples analysis was performed. The mixture comprised the following chemical compounds: benzene, toluene, xylene and ethylbenzene. Using the fact of directly proportional relation between the peak area and given analyte concentration, concentrations of the above-mentioned organic compounds in the samples were determined [14,15].

4. Test results

The example results of physical and chemical analyses for the 10th test series comprising definitely most polluted rainwater and meltwater pretreated in two separators No. 14 and 17 have been listed in Tables 1 and 2.

Graphs illustrating the level of pollution of those waters and pollutant elimination effects were also made and they were used, consequently, for the assessment of particular separators operation. To assess operation of the selected separator No. 14, graphs showing the degree of elimination (%) of total suspension (Fig. 1), BTEX (Fig. 2) and paraffins (C7–C11) (Fig. 3) depending on the number of observations of the pollution-level featuring similar concentration, using STATISTICA computer programme, have been given. Furthermore, collective histograms for all four separators operating at that time in the same order were made (Figs. 4–6).

Also, graphs of correlation between concentration of given pollutant (BTEX and paraffins) with the elliptic area for single observations and confidence interval for the mean value (Figs. 7 and 8) have been included. Those relations were described by multiple regression equations based on the correlation coefficient of 0.95.

Table 1
Results of total suspension, BTEX and paraffin content in wastewater samples from the separator No. 14

Series	Determination (mg L^{-1})	1	2	3
I	Total suspension	266.4	60.0	77.5
	BTEX	0.0025	0.0047	−88.0
II	Total suspension	295.2	294.8	0.1
		0.0025	0.0047	−88.0
III	Total suspension	242.0	28.0	88.4
	BTEX	0.0048	0.0044	8.3
IV	Total suspension	412.0	241.0	41.5
	BTEX	0.0048	0.0043	10.4
V	Total suspension	40.0	21.0	47.5
	BTEX	0.0035	0.0013	62.9
	Paraffin (C7–C11) content	0.0055	0.0045	18.2
VI	Total suspension	918.8	904.4	1.6
	BTEX	0.0162	0.0112	30.9
	Paraffin (C7–C11) content	0.0077	0.0020	74.0
VII	Total suspension	64.0	0.60	99.1
	BTEX	0.0116	0.0017	85.3
	Paraffin (C7–C11) content	0.0122	0.0015	87.7
VIII	Total suspension	350.0	333.6	4.7
	BTEX	0.0049	0.0007	85.7
	Paraffin (C7–C11) content	0.0077	0.0035	54.5
IX	Total suspension	348.0	347.2	0.2
	BTEX	0.0054	< 0.0001	100.0
	Paraffin (C7–C11) content	0.0039	0.0036	7.7
X	Total suspension	354.0	310.0	12.4
	BTEX	0.0117	< 0.0001	100.0
	Paraffin (C7–C11) content	0.0042	< 0.0001	100.0

Notes: 1—value before the separator; 2—value behind the separator; 3—degree of elimination (+) or pollution increase (−) [%].

Table 2
Results of total suspension, BTEX and paraffin content in wastewater samples from the separator No. 17

Series	Determination (mg L^{-1})	1	2	3
I	Total suspension	8.0	4.8	40.0
	BTEX	0.0018	0.0008	55.6
II	Total suspension	64.0	10.4	83.7
	BTEX	0.0018	0.0008	55.6
III	Total suspension	56.0	18.0	67.8
	BTEX	0.0033	0.0020	39.4
IV	Total suspension	118.4	60.4	49.0
	BTEX	0.0013	0.0006	53.8
V	Total suspension	8.8	4.8	45.4
	BTEX	0.0015	0.0028	−86.7
	Paraffin (C7–C11) content	0.0076	0.0103	−35.5
VI	Total suspension	58.4	23.2	60.3
	BTEX	0.0098	0.0068	30.6
	Paraffin (C7–C11) content	0.0168	0.0032	80.9
VII	Total suspension	0.6	0.4	33.3
	BTEX	0.0032	0.0010	68.7
	Paraffin (C7–C11) content	0.0066	0.0052	21.2
VIII	Total suspension	242.4	156.8	35.3
	BTEX	0.0007	0.0069	−885.7
	Paraffin (C7–C11) content	0.0072	0.0014	80.6
IX	Total suspension	184.0	146.4	20.4
	BTEX	< 0.0001	< 0.0001	–
	Paraffin (C7–C11) content	0.0034	0.0027	20.6
X	Total suspension	37.3	41.0	−9.9
	BTEX	0.0007	< 0.0001	100.0
	Paraffin (C7–C11) content	0.0031	< 0.0001	100.0

Notes: 1—value before the separator; 2—value behind the separator; 3—degree of elimination (+) or pollution increase (−) [%].

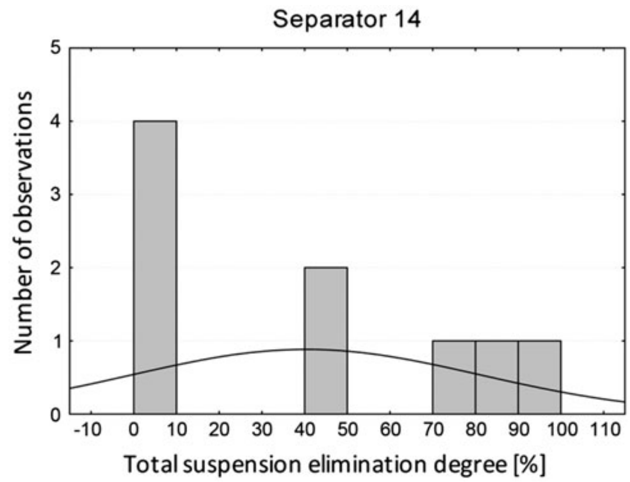

Fig. 1. Total suspension elimination degree in the separator No. 14 [%].

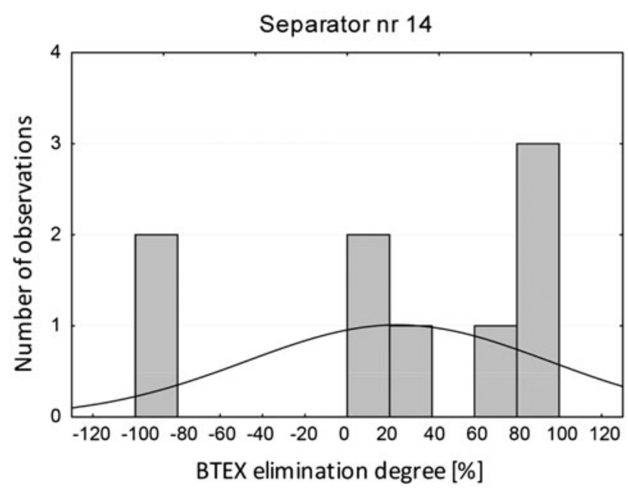

Fig. 2. BTEX elimination degree in the separator No. 14 [%].

5. Test results description

Fitting of the wastewater pretreatment plant (wastewater sedimentation tank + separator) in rainwater sewers has shown that pollutants counted as petroleum-derived substances are eliminated from rainwater and meltwater. In the majority of cases, the pollutant elimination effect was highly positive (Tables 1 and 2). An attempt was made to interpret the phenomena assessing this process efficiency. This is illustrated in particular graphs showing change of pollutant concentration at separator inlet and outlet expressed by the degree of elimination of particular groups (in %) for BTEX group compounds, paraffins C7–C11 and total suspension (Figs. 1–3).

Considering the fact that more than 90% of the easily settling suspension was eliminated in the separator, statistical assessment was abandoned. Similar phenomena had very often occurred in the case of petroleum-derived substances elimination. In few cases, particularly, at the preliminary stage of this research work, insignificant or negative result of operation of some separators exposed to flooding was observed. In some cases, erroneous wastewater sampling could happen (this pertains to wastewater that stagnated in sewers for a long time) also due to difficult access to proper sampling point.

All those phenomena illustrate the course of changes of given pollutant in the function of its elimination. The collective histograms made (Figs. 4–6) in which correlations between the given constituent elimination degree and number of observations (occurrence) were given, show highly positive result of separators operation. Analysing the graphs showing the correlation of concentration of given pollutant and elliptic area for single observations as well as

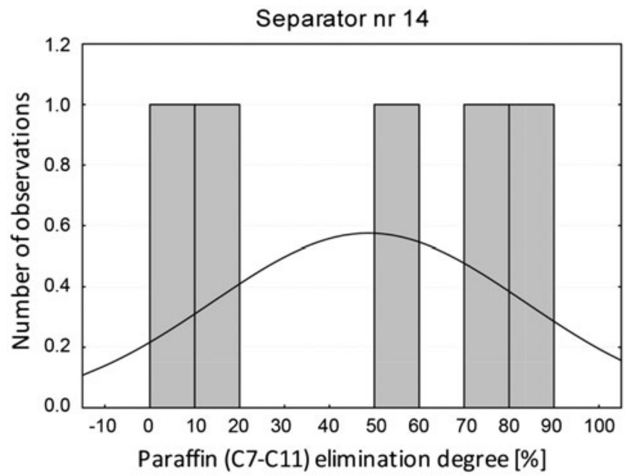

Fig. 3. Paraffin (C7–C11) elimination degree in the separator No. 14 [%].

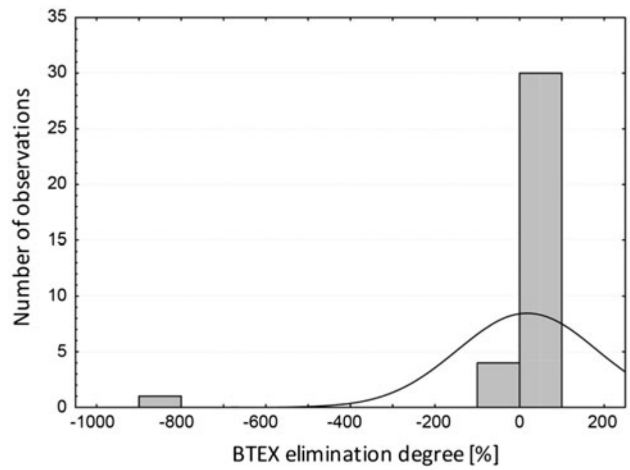

Fig. 5. BTEX elimination degree—collective histogram for 4 separators [%].

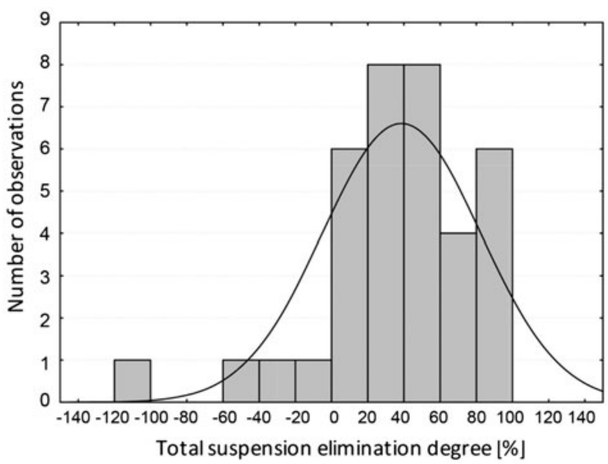

Fig. 4. Total suspension elimination degree—collective histogram for 4 separators [%].

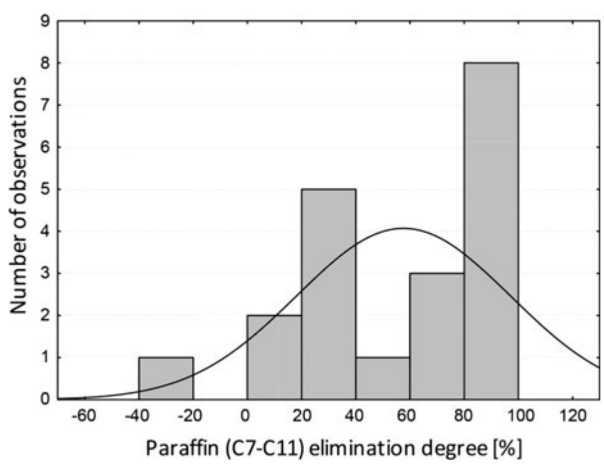

Fig. 6. Paraffin (C7–C11) elimination degree—collective histogram for 4 separators [%].

confidence interval for the mean value, we can see that the pollutant elimination process performed in the separator is very efficient in the case of BTEX and paraffins (C11–C17). There is also a strong correlation between the analysed compound groups both in samples taken before and behind a separator (Figs. 7 and 8). In practice, those graphs allow for the assessment of wastewater parameters and separator operation efficiency. As the reader can see, positive results of pollutants elimination, due to coalescence separators operation during the course of the entire test period, were achieved. The expected results of those facilities operation occur in the majority of cases, and they can be assessed, on the average, as from 40 to 80% omitting test results from the period of occurrence of some anomalies (e.g. sewer flooding).

The differences in the degree of removal of petroleum-derived pollutants and suspension in samples collected at the outlet separators are mainly due to physicochemical composition of wastewater.

The water supply and wastewater disposal permit provided for discharge of purified rainwater and meltwater into river Słupia conditioned on the occurrence of total suspension up to 100 mg L^{-1} and petroleum-derived substances up to 15 mg L^{-1} has been complied with. It appears from this research work that content of the petroleum-derived substances in tested samples of rainwater and meltwater (Tables

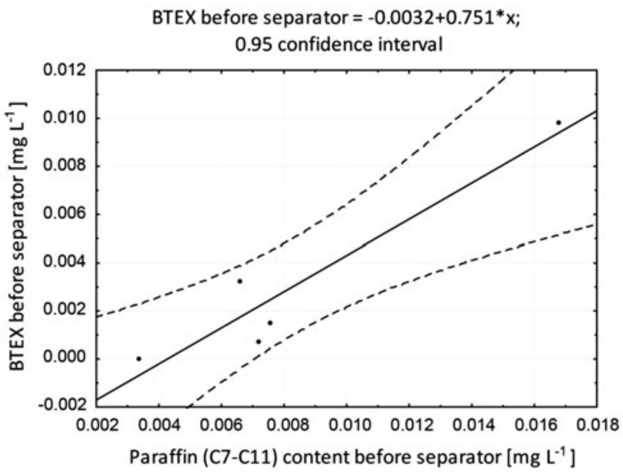

Fig. 7. The relationship between paraffins content and BTEX content before separator No. 14.

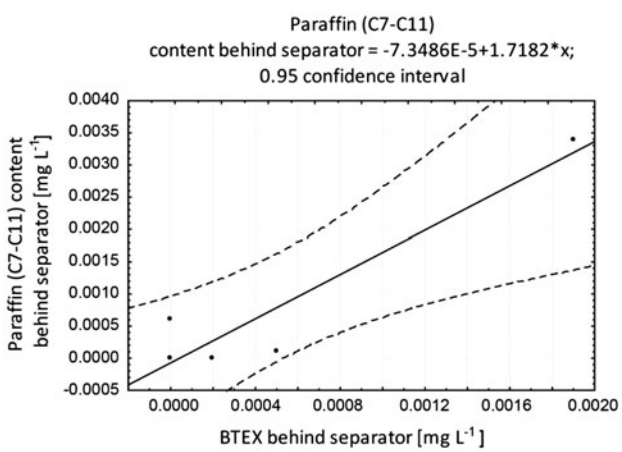

Fig. 8. The relationship between paraffins content and BTEX content behind separator No. 14.

1 and 2) was not exceeded in any case; on the contrary, those substances were being eliminated almost totally, down to trace concentrations. In the case of total suspension, any concentration exceeding 100 mg L^{-1} in 10 series performed for each separator appears to be as follows:

- Separator No. 13—exceeded threefold,
- Separator No. 14—exceeded sixfold,
- Separator No. 5—exceeded twofold, and
- Separator No. 17—exceeded twofold.

Therefore, for 40 series of tests (4 separators × 10 series), such total suspension exceedance had occurred 13 times. This means that the average operation efficiency for all separators is 67.5%, and for separators No. 5 and 17, it is 80%, for separator No. 13—70% and for separator No. 14—only 40%.

6. Conclusions

Determination of petroleum-derived substances in rainwater and meltwater has shown that:

- Fitting of coalescence separators on the rainwater and meltwater flow path eliminated significantly BTEX group compounds, paraffins (C11–C17) and suspension,
- The fitted separators assure correct operation of the wastewater pretreatment system,
- Effects of petroleum-derived pollutants elimination from rainwater to meltwater discharged into surface waters can be forecast,
- The anticipated installation of further separators should significantly limit influx of petroleum-derived pollutants contained in rainwater and meltwater having thus considerably improved quality of river Słupia water.

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