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CHANGES ANALYSIS OF MINERAL OIL INDEX IN NAREW AND BUG RIVER

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ABSTRACT

The aim of this study was to analyze changes in an index of mineral oil in the waters of Narew and Bug Rivers. Water analyses were carried out in two monitoring networks (1 for each River) based on 5 control points. To determine the index of mineral oil in water samples, the method of gas chromatography coupled with mass detection was used. Samples for organic compounds analysis were prepared and determined in accordance to the Polish Standard PN-EN ISO 9377-2. The resulting index of mineral oil value was ranging from 0.02 to 0.55 mg·dm^{-3}. In addition, nonparametric Spearman correlation coefficients between test components and the average daily, was calculated.

KEYWORDS: Index of Mineral Oil, Mineral Index, River, Surface Water

INTRODUCTION

Crude oil and its derivatives are commonly used, not only in every field of industry, but also in everyday life [Gierak 1995, Ankowski, Nowak 2010]. Such a broad application of this material may lead not only to direct migration of petroleum products to surface watercourses as a result of failure of the storage facilities and processing of oil, but also as a result of accidents that involve motor vehicles [Sudoł i in., 1996]. It is worth mentioning that with atmospheric precipitation, surface waters are receiving a significant amount of impurities, including suspensions, heavy metals and petroleum hydrocarbons [Gmitrzuk 2011, Bergier, Włodyka- Bergier 2009]. According to Rakowska (2012) and Steliga (2003), crude oil and its derivatives is are the main sources of River pollution in Poland. This situation is caused by the continuous development of industry and economy, which uses fossil fuels as almost unique and irreplaceable source of energy. It should be noted that the petroleum products, are not only difficult for removing from contaminated waters, but also pose a considerable threat to the health and life of organisms inhabiting degraded land [Izdebska- Mucha 2005, Guzik i in. 2010]. In addition, it is worth mentioning at this point that petroleum substances on the water surface form a thin layer so-called "film", which prevents the oxygen migration deep in the watercourse or water reservoir, which limits its ability to self-cleaning [Kaleta, Papciak, 2011].

The aim of this study was to analyze changes in an index of mineral oil in the waters of Narew and Bug Rivers. Water analyses were carried out in two monitoring networks (1 for each River) based on 5 control points.

RESEARCH METHODS

For the study purpose, five control points were chosen on each River. The study included section with a length of about 45 km for the Narew River and 40 km for the Bug River. Control points were designated to determine the possibility of oil derivatives discharge from linear sources of pollution. The analysis of mineral oil index changes was based on the results of two series of studies carried out since February to May 2013. Water samples were collected in 5 established points for each River; samples were collected in weekly intervals. Control points were located in a direct vicinity of the routes or bridges with varying traffic.

The first site of environmental sampling on the Narew River was Niwkowo village located in the municipality of Wizna. Control point was located in the center of Niwkowa, near the road leading to the Bronowo village. The second control point was in Krzewo, located in the municipality of Piatnica. The third and fourth control points were located before and behind the city of Lomza in the vicinity of bridges, which are important international transport routes. The fifth control point was located outside the town of Nowogrod in the vicinity of the bridge. Municipality of Nowogrod, in accordance with the classification of Polish land for agro-climatic districts, is located in the district of Podlasie.

The first environmental sampling point of monitoring network established for Bug River was located near the village of Nur. Nur Municipality is located in the district of Ostrów. The second control point was located near the village of Gąsiorowo, which is situated in the municipality of Serock. The municipality belongs to the Pas Wielkich Dolin, in which the weather is characterized by high variability. The third control point was located near the village of Gorna Malkinia in the municipality of Gorna Malkinia. The fourth control point was located directly in front of the village Brok, while the fifth environmental sampling point was located behind the city in the vicinity of the bridge on the road No 694.

The water samples were tested for concentration of petroleum hydrocarbons, expressed as an index of mineral oil, chemical oxygen demand by dichromate (COD_{Cr}), five-day biochemical oxygen demand (BOD_5), and total organic carbon (TOC). These components were studied in accordance with the following standards and procedures: CODCr - PN-EN ISO 8467, BOD5 - PN-EN1899-1, TOC - PN-C/04633-3, index of mineral oil - PN-EN ISO 9377-2. In each sample, analysis for petroleum hydrocarbons was performed by using gas chromatography coupled with mass spectrometer VARIAN 4000. The analyte separation was carried out on a 30m x 0.25 mm x 0.2 m VF-5MS column. Stationary phase of the column was polydimethylsiloxane with 5% of phenyl groups. Volume of 500 ml of test water was used to determine the index of mineral oil in collected samples.

For the isolation of the compounds forming part of mineral oil, the extraction in the liquid-liquid system was used. Separation process was carried out at room temperature, equilibrated to ± 20 °C, on a magnetic stirrer at a rotational speed of about 800 RPM, using 50 ml of hexane. The extract was then separated from the sample water and concentrated to a volume of 1.5 ml. The concentrated extract was subjected to separation and detection on the GC/MS with following operating parameters: dispensed sample volume 1 ml – splittless mode, injector temperature of 250 °C, carrier gas flow - $1 ml \cdot min^{-1}$, the initial oven temperature 40˚C – isotherm - five minutes, the final temperature 300˚C oven - 20 minutes isotherm, temperature buildup $10˚C \cdot min^{-1}$, the temperature of the transfer line - 230 °C, the ion source temperature of 180 °C - mass scan range - 40-400 $m \cdot z^{-1}$. Helium of a purity grade 6.0 was used as a carrier gas.

Study of the compounds in water was carried out in the Department of Technology and Environmental Protection Engineering, Technical University of Bialystok.

Based on the results of measurements, statistical analysis was carried out, including the arithmetic mean, median, standard deviations, minimums, maximums, the first and third quartile and nonparametric Spearman correlation coefficients. Significant correlations were considered with a modulus equal or greater than 0.70. Statistical calculations were performed using STATISTICA 10 software.

RESULTS AND DISCUSSIONS

The average daily road traffic Table 1 near the three control points on Narew River ranged from 4867 to 13996 vehicles per day, in the other two ones, the traffic was small and GDDKiA did not conduct any research for these routes. In the case of Bug River, control points were located near roads, where traffic was ranging from 687 to 6273 vehicles per day.

Table 1: Average Daily Road Traffic at Various Points [GDDKIA 2010]

Control Point		Narew	Bug
1	Amount of vehicles per day	-	2333
2		-	2554
3		5651	687
4		13996	2566
5		4867	6273

Index of mineral oil Figure 1 in Narew River did not significantly change during the study period. In both series, similar concentrations of petroleum hydrocarbons, expressed as an index of mineral oil, were obtained. Low values of index of mineral oil were observed at points where traffic was the lowest – points No 1, 2, 3 and 5, while the highest index was observed in point No 4, which was 0.0616 $\mu g \cdot dm^{-3}$ in the first series of tests and 0.0642 $\mu g \cdot dm^{-3}$ in the second. At 4th point, the amount of vehicles per day was also the largest and amounted to 13996.

For Bug River Figure 2, there was a significant difference in index of mineral oil values between research series. In the first series of test, results are similar to values obtained in Narew River, while in the second series, they are significantly higher. In the second series, a gradual increase in index of mineral oil was observed. The lowest index was obtained at the point No 4 - 0.0170 $mg \cdot dm^{-3}$ and the highest in point No 5 - 0.5548 $mg \cdot dm^{-3}$. In second series, the sampling at 2nd, 3rd and 5th points was each time made while raining for a few days.

It is also noted that the mineral index increases along with increased run-off of pollutants from meltwater. Meltwater, that flows from the road surface after winter, is significantly polluted. Significant amount of pollutants is accumulated in snow and ice, including large amounts of suspensions, lead, zinc [Gierak 1995], oils, and other petroleum substances. Hydrocarbons are not subject to decomposition processes in winter conditions as intensively as in warm periods. The highest runoff of pollutants from meltwater occurs in the spring and decreases every month until complete melting of ice and snow [Liszkowska E., Kaczyńska E. 2004].

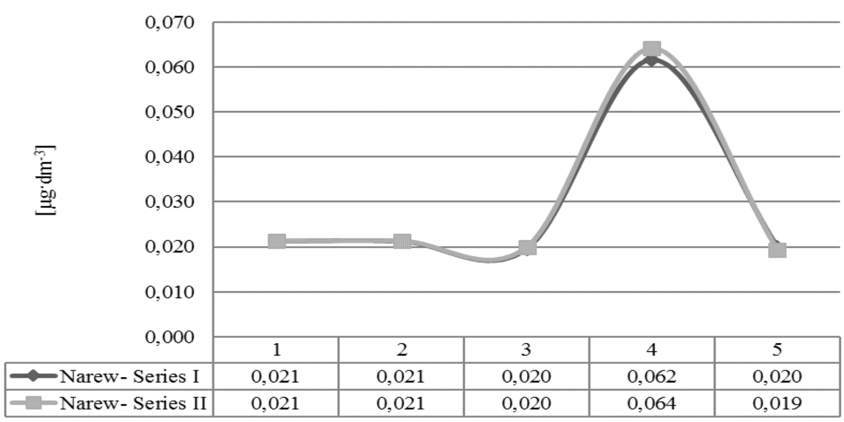


Figure 1: Changes in Concentrations of Petroleum Hydrocarbons - Narew River

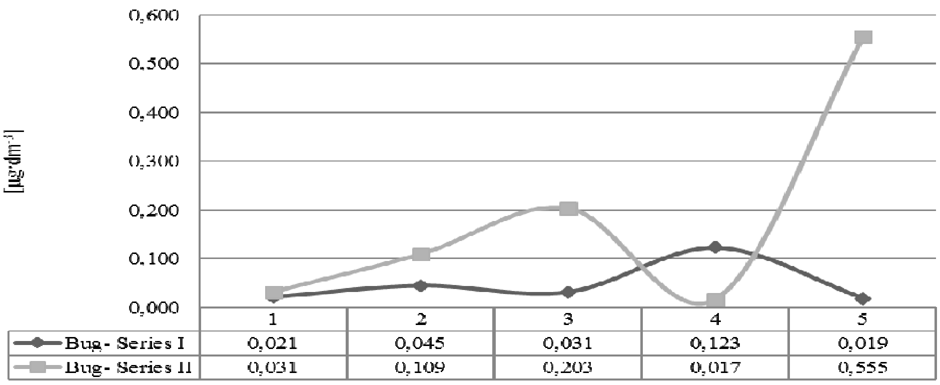


Figure 2: Changes in Concentrations of Petroleum Hydrocarbons - Bug River

Nonparametric correlation analysis table 2 confirms the relationship between index of mineral oil values, and average daily traffic intensity. The resulting value of the correlation coefficient (0.71) between the variables for Narew River shows a strong correlation between the analyzed variables. This relationship was not observed in the Bug River. The correlation coefficient for a pair of variables was -0.02, indicating a negligible impact of motor vehicle traffic on the index of mineral oil in studied points. The correlation coefficient obtained for Narew River at an average daily traffic for tested River section was equal to 8,171 vehicles, while in Bug River- 2,883 vehicles. Based on this, it can be concluded that a strong correlation between the index of mineral oil and the number of motor vehicles occurs for more than 8000 vehicles per day.

Table 2: Spearman Nonparametric Correlation Coefficients

The correlation Coefficients in Narew					
	COD_{Cr}	BOD_5	TOC	IOM	ADRT
COD_{Cr}	1,00	0,32	-0,05	-0,20	-0,84
BOD_5	0,32	1,00	0,25	-0,59	-0,91
TOC	-0,05	0,25	1,00	-0,18	-0,23
IOM	-0,20	-0,59	-0,17	1,00	0,71
ADRT	-0,84	-0,91	-0,23	0,71	1,00
The correlation Coefficients in Bug					
	COD_{Cr}	BOD_5	TOC	IOM	ADRT
COD_{Cr}	1,00	0,88	0,72	-0,51	-0,34
BOD_5	0,88	1,00	0,73	-0,50	-0,35
TOC	0,72	0,73	1,00	-0,48	-0,05
IOM	-0,51	-0,50	-0,48	1,00	-0,02
ADRT	-0,34	-0,34	-0,05	-0,02	1,00

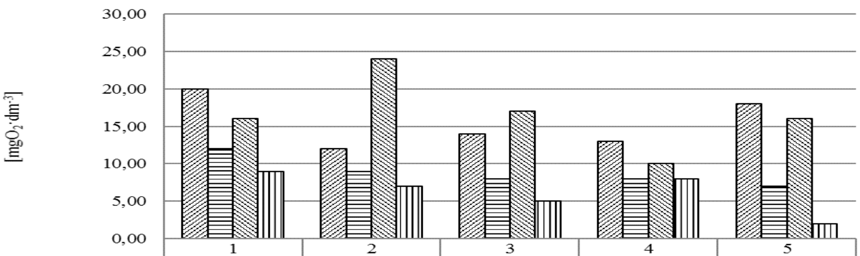
where: ADRT - average daily road traffic, IOM - index of mineral oil

Based on statistical analysis, it was found that there is a correlation between other studied parameters. Strong correlations between road traffic were obtained compared to the COD_{Cr} (-0.84) and BOD_5 (-0.91) in Narew River. However, in Bug River, like for mineral oil index, bindings for COD_{Cr} and BOD_5 are significantly lower. The resulting correlation coefficients were equal to 0.34, which suggests a weak relationship between variables. Ascertained relationship was found by Piekutin in Suprasl River [Piekutin 2009]. Therefore, it must be assumed that their number will increase along with road traffic, even despite many renovations and construction of new roads at present time.

Zanardi et al. [1999] also achieved similar mineral oil index values. The concentrations obtained by the authors ranged from 0.35 to 2.50 µg·dm-3. Zanardi also emphasizes that water samples were collected from an area slightly exposed to the pollution of petroleum products.

Higher mineral oil index values were obtained by Zhang et al. in their studies [Zhang J. et al., 2014]. The average index of mineral oil in surface water samples studied by the authors was 59.05 $\mu g \cdot dm^{-3}$. The authors point out that the samples were collected from the arable land area located in monsoon climate with an average annual precipitation ranging from 595.9 to 732.9 mm.

COD_{Cr} Figure 3 was characterized by a downward changes trend occurring between research series. This trend is clearly visible in Bug River, where the value of CODCr in second series was lower or equal to the concentration obtained in the first one. However, in the case of Narew River Figure 3, this relationship was disrupted at points 2 and 3 probably due to uncontrolled discharge the pollutants of anthropogenic origin into the River above the first control point. The lowest concentration of COD_{Cr} was observed in Bug River in point 5, in second series and was equal to 2.00 mg $O_2 \cdot dm^{-3}$, and the largest concentration of COD_{Cr} was observed in Narew River in 2nd control point, in the second series, which was equal to 24.00 $mgO_2 \cdot dm^{-3}$. Similar results were obtained by Łobos-Moysa [Łobos-Moysa 2013] in studies on selected watercourses that form tributary to the Gliwice channel. Similar correlation results were obtained by Cieszyńska et al. in their work [Cieszyńska et al., 2009]. The correlation coefficient determined by the authors ranged from 0.51 to 0.77.



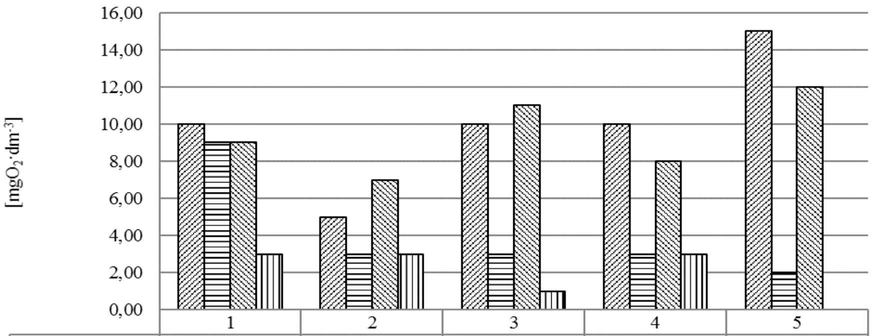
	1	2	3	4	5
Narew- Series 1	20,00	12,00	14,00	13,00	18,00
Bug- Series 1	12,00	9,00	8,00	8,00	7,00
Narew- Series 2	16,00	24,00	17,00	10,00	16,00
Bug- Series 2	9,00	7,00	5,00	8,00	2,00

Figure 3: The Concentration of COD_{Cr} in Analyzed Samples

Obtained BOD_5 values Figure 4 were subject to analogical to CODCr trend of changes during the period of the research. In the second series, BOD_5 was lower or equal to the concentrations obtained in the first series of research. As in the case of COD_{Cr}, this relation is more visible in Bug River. In a second series at the 5th point, BOD_5 values were below the measuring range of devices used for analysis; therefore, to facilitate further statistical calculations, the value at this point was taken as equal to 0.00. Krzemińska and Andrykiewicz-Piragas [Krzemińska, Andrykiewicz-Piragas 2006] achieved similar BOD_5 results. Similar to the achieved BOD_5 results were obtained by Krzemińska and Andrykiewicz-Piragas [Krzemińska, Andrykiewicz-Piragas 2006]. In studies carried out on water samples taken from the lower section of Smortawa, authors obtained BOD_5 remaining at the level from 1.50 to 8.10 $mgO_2 \cdot dm^{-3}$.

The concentration of TOC Figure 5 was not changed significantly between the different points in studied Rivers. However, a significant decrease in the concentration of this component was observed between control series in each control point. The highest concentration of TOC was observed in Bug River in the first control series, the 1st control point, which was 103.97 $mgC \cdot dm^{-3}$. In contrast, the smallest concentration of TOC was observed in Narew River in the 3rd control point, in second series, the value of which was equal to 16.31 mgC·dm^{-3}. Similar concentrations of TOC were obtained by Kiryluk in his studies [Kiryluk, 2006].

Correlation analysis Table 2 showed statistically significant relationship between TOC and BOD_5 (-0.73) and COD_{Cr} (-0.72) only for the Bug River. In contrast, in Narew River, TOC concentration was not related to any of the tested water components.

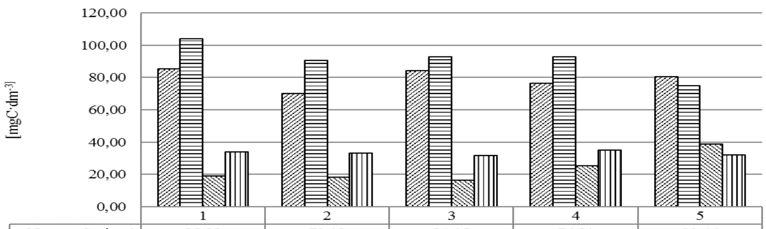


	1	2	3	4	5
Narew- Series 1	10,00	5,00	10,00	10,00	15,00
Bug- Series 1	9,00	3,00	3,00	3,00	2,00
Narew- Series 2	9,00	7,00	11,00	8,00	12,00
Bug- Series 2	3,00	3,00	1,00	3,00	0,00

Figure 4: BOD_5 Concentration in Analyzed Samples

Standard deviations in the Narew River Table 3 take the highest values for the concentration of TOC and index mineral oil. These components were characterized by the greatest degree of change during the study period. For other ingredients, standard deviations are not significant, which suggests that changes in the concentrations are the result of natural processes occurring in surface water during snow layer melt period.

Similar relationships were noted in Bug River Table 4. The standard deviations with the highest values were observed for the same analyzed components.



	1	2	3	4	5
Narew- Series 1	85,22	70,12	84,15	76,21	80,46
Bug- Series 1	103,97	90,43	92,90	92,93	74,94
Narew- Series 2	18,89	18,35	16,31	25,34	38,80
Bug- Series 2	33,95	33,22	31,79	35,10	32,03

Figure 5: The Concentration of TOC in Analyzed Samples

Table 3: Basic Statistics for the Results from Narew River

	COD_{Cr}	BOD_5	TOC	IOM	ADRT
Arithmetic mean	16,00	9,70	51,39	0,03	8171
Median	16,00	10,00	54,46	0,02	5651
Standard deviation	4,08	2,75	30,27	0,02	4525
Minimum	10,00	5,00	16,31	0,02	4867
Maximum	24,00	15,00	85,22	0,06	13996
<25%	13,00	8,00	18,89	0,02	4867
>75%	18,00	11,00	80,46	0,02	13996

where: ADRT - average daily road traffic, IOM - index of mineral oil

Table 4: Basic Statistics for the Results from Bug River

	COD_{Cr}	BOD_5	TOC	IOM	ADRT
Arithmetic mean	7,50	3,00	62,13	0,12	2883
Median	8,00	3,00	55,02	0,04	2554
Standard deviation	2,64	2,36	31,27	0,17	1934
Minimum	2,00	0,00	31,79	0,02	687
Maximum	12,00	9,00	103,97	0,55	6273
<25%	7,00	2,00	33,22	0,02	2333
>75%	9,00	3,00	92,90	0,12	2566

where: ADRT - average daily road traffic, IOM - index of mineral oil

CONCLUSIONS

Based on the research carried out in Narew and Bug Rivers, the following conclusions were drawn:

- The largest non-parametric correlation coefficients were obtained between the index of mineral oil and average daily traffic in the Narew River; this regularity has not been noted in Bug River. It is believed that a clearer relationship can only occur at a relatively high traffic.
- The correlation coefficients suggesting a strong relation between variable pair: index of mineral oil and average daily road traffic, are possible to observe at daily average amount of vehicles greater than 8000.
- Index of mineral oil in Narew River was similar in each control series in each of the control points.

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