Short Communication

Petroleum in the Vistula River

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Received: 17 July 2013
Accepted: 28 April 2014

Abstract

This paper presents the petroleum concentration in the Vistula River measured in Tczew from the end of 2007 to October 2012. The most polluted water was after an oil spill, when the oil concentration exceeded 500 μg/kg. Most of the results ranged from 2 μg/kg to over 100 μg/kg and the mean concentration was 54 μg/kg. Petroleum content in the river appeared to be of seasonal variability. The oil concentrations were lowest in summer, while winter was the season when the water was most polluted with oil. The petroleum pollution of the Vistula corresponded to the general condition of its water quality expressed by the BOD_5. The annual input of petroleum to the Baltic Sea amounted to over 1,200 tons.

Keywords: Vistula River, petroleum, fluorescence, Baltic Sea

Introduction

Petroleum substances – many kinds of crude oil and different petrochemical products – have an adverse impact on the natural environment. This is already known and has been reported in many papers. A number of monographs [1-5] present lists of the relevant papers. This impact concerns especially marine environments, where all the pollutants inflow at the end. The annual input of petroleum to the world's oceans is estimated in a wide range, from 470 to 8,300 thousands of tons [3]. Chronic release from land-based sources (i.e., river discharges, municipal wastewaters, urban runoff, industrial discharges) are responsible for the majority of petroleum hydrocarbon input to the sea. The inputs from land-based sources are poorly understood and, therefore, estimates of these inputs have a high degree of uncertainty – the range of uncertainty in the estimated loadings is four orders of magnitude [3]. More often, conduced measurements of aromatic hydrocarbons (PAH) show that petroleum pollution is a great problem in regard to inland waters [6-11], but these studies do not allow us to determine petroleum content. The presence of these compounds even in drinking water testifies to the importance of the problem [12-14].

With a length of 1,047 km and a drainage area of 194,500 km^2, the Vistula is the second largest river flowing into the Baltic Sea. The river flows from south to north through the mountains and foothills of southern Poland and across the lowland areas of the North European Plain, ending in a delta estuary that enters Gdańsk Bay. The mean velocity in the river channel amounts to 0.8 m/s [15]. The water flow appears to be of seasonal variability [16]. The lowest flows occur in September and are related to precipitation deficit and the small storage capacity of the drainage basins. The river discharges increase steadily in the whole Vistula drainage area from October to the culmination of meltwater flow in April, and then discharges decrease. The mean annual flows increase with the course of the river due to its numerous tributaries (up to 1,080 m^3/s in Tczew) [16]. This value can be assumed as the mean inflow to the Baltic Sea. Furthermore, the Vistula River carries 0.6-1.5 million m^3 of sediment to the sea every year [17]. A number of large towns and industrial centers are situated along the Vistula and its tributaries, so the river carries a lot of different organic and inorganic pollutants [18-20]. Both water and bottom sediments are polluted. The sum of PAHs in sediments was in the range of 1.55 to 7.8 μg/g d.w. [21].

This paper presents concentrations of petroleum in the Vistula River in Tczew. The presented test was part of the

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study on petroleum presence in a water environment, including Gdańsk Bay and the small urban river Kacza flowing into the bay. The study started three days after an oil spill. The accident occurred near the town of Włocławek, 10 December 2007. Approximately 40 tons[1] of heating oil was released from an underwater pipeline crossing the river [22]. After a short period of disaster recovery monitoring, the water was sampled occasionally and 90 water samples were tested until October 2012. This paper also presents results of some complementary parameters characterizing tested water: water temperature, dissolved oxygen concentration, specific electric conductivity, and biochemical oxygen demand. These measurements were made for some of the samples.

Method and Materials

Water was sampled from the main stream of the river, from the pier near the left bank. The sampling point is situated circa 30 kilometers beyond the main mouth of the river. The coordinates of this mouth are: N54º21 and E18º57; and these of sampling point are N54º05” and E18º48”. A 0.5 dm^3 bottle was filled with water sampled at a depth of about 30 cm. Water was sampled into separate bottles for biochemical oxygen demand.

The oil concentration in water was determined by an improved fluorescent method [23, 24]. This method consists of measuring the fluorescence of 295 nm wavelength emitted by hexane extract of tested water. The fluorescence is excited by a radiation of a 210 nm wavelength. The result of this test is compared with the fluorescence of the pattern that is the solution of the North Sea crude oil. This method allows us to determine the oil concentration to accuracy of 50%. Extraction was performed by adding hexane to a bottle with the capacity of 0.5 dm^3 containing approximately 350 cm^3 of water. Next the bottle was shaken so as to obtain uniform emulsion and then it was kept in a fridge for at least two days. The masses of the examined sample as well as the added hexane were measured by weighing the bottle with water on an electronic scale at accuracy of 1 g and 0.01 g for hexane. The petroleum concentration C was calculated from the following formula:

$$C = \frac{m}{M} \frac{w}{w_{ref}} C_{ref} \qquad (1)$$

...where M is the mass of the examined sample, m is the mass of hexane used for extraction, w is the result of fluorescence measurement of tested sample, w_{ref} is the result of fluorescence of the pattern, and C_{ref} is the pattern solution concentration.

While obtaining the samples, the water temperature and dissolved oxygen concentration were measured for some samples. The electric conductivity and biochemical oxygen demand (BOD_5) tests were conducted in laboratory conditions at a temperature 20ºC. Biochemical oxygen demand was defined as the difference between oxygen concentration measured after sample intake and after 120 hours [25]. The electric conductivity and dissolved oxygen were measured by a Eutech PSD-650 multimeter provided with proper sensors. The readings of an oxygen probe were periodically compared with the measurement results conducted by the Winkler method. Data of the water flow were noted from the website of the Polish Institute of Meteorology and Water Management (*www.imgw.pl*).

Results

The first sample was taken on December 13 at 11:00. The second, collected at 14:00 same day, was the most polluted sample. Since the next day’s concentration of oil descended with the time, after five days it was on its average level. Fig. 1 presents these data graphically as a result of monitoring of remote effects of the oil spill. A few days later some media reported another oil spill (probably diesel fuel), but it was impossible to confirm this fact officially. However, December 29, 2007, and January 7, 2008, petroleum concentrations were – respectively – 243 μg/kg and 346 μg/kg. These results confirmed that an oil spill really occurred. Such a high petroleum concentration was not recorded later.

Table 1 presents the results of oil concentration measurements together with complementary parameters characterizing tested water: temperature, electric conductivity, dissolved oxygen concentration, biochemical oxygen demand (BOD_5), and water flow in the sampling point. The relative concentration of petroleum pollutants in the water ranged from 2 μg/kg to 554 μg/kg, but most of the results (over 90 %) did not exceed 100 μg/kg. The highest oil concentrations were noticed at the beginning of the study as results of the oil spills. Distribution of these data is presented in Table 2.

The oil pollution of the river shows seasonal changeability. In general, winter was the season when the water was most polluted. Petroleum concentration was highest in

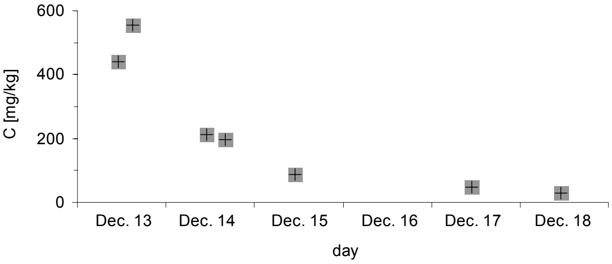

Fig. 1. Petroleum concentration C in the Vistula River in Tczew after an oil spill.

[1] It should be mentioned that some media reported higher values of amount of spilled fuel, up to 120 tons. Most spilled oil had been removed from the river. These days a pier stands on the river in the town of Tczew (water was sampled from this pier). The men who worked there continuously said that they did not notice any oil slick on the water surface at the time.

Table 1. The measurement results of petroleum concentration, temperature, conductivity, dissolved oxygen concentration, biochemical oxygen demand (BOD_5), and flow of tested water.

	N	Unit	Average	Min.	Max.	Median	Standard deviation
Oil concentration	90	[μg/kg]	57.4	2	554	37	83
Temperature	68	[ºC]	12.9	0	22.0	–	–
Conductivity	81	[mS/m]	712	494	980	722	126
Dissolved oxygen	21	[mg/dm³] [%]	10.09 100.2	8.36 84.7	11.56 123.8	10.11 97.4	0.97 10.5
BOD_5	42	[mg/dm³]	3.27	0.24	8.76	3.05	1.74
Water flow	66	[m³/s]	1173	439	3484	892	784

The columns present the measured quantity, the number *N* of tested samples, and the unit in which the average values, the minimum (min.) and maximum (max) values, and the median and standard deviation are presented

Table 2. Distribution of petroleum concentration *C* in Vistula River.

Range of concentration *C* [μg/kg]	Number of results	Range of concentration *C* [μg/kg]	Number of results
C < 10	12	40 ≤ C < 60	17
10 ≤ C < 20	9	60 ≤ C < 80	12
20 ≤ C < 30	18	80 ≤ C < 100	4
30 ≤ C < 40	10	C ≥ 100	8

Table 3. Average values of petroleum concentration *C* corresponding to particular BOD_5 ranges of water, where N is the number of results.

BOD_5 [mg/dm3]	*N*	*C* [μg/kg]
$BOD_5 < 1$	2	8.5
$1 \leq BOD_5 < 2$	9	33.8
$2 \leq BOD_5 < 3$	9	29.6
$3 \leq BOD_5 < 4$	12	45.2
$4 \leq BOD_5 < 6$	7	54.2
$BOD_5 \geq 6$	3	68.8

January and in March, slightly lower concentrations occurred in December and February. Relatively low concentrations (below 10 μg/kg) occurred from April to October. June and August were months when the petroleum content was the lowest. Fig. 2 presents the average values of oil concentrations in particular months. The highest data resulting from the incidental oil spills were omitted here.

The BOD_5 of the Vistula River water was changing in a wide range from 0.24 mg/dm³ to 8.76 mg/dm³ with the average value of 3.05 mg/dm³ for 42 tested samples. The oil concentration in this water (in separate samples, but taken from the same place and at the same time) was within the range of 4 to 114 μg/kg, with the average value of 40.8 μg/kg. Direct correlation between BOD_5 characterizing water and petroleum concentration was not distinct. Table 3 presents mean oil concentrations in water in relation to the range of BOD_5.

The petroleum concentration also was compared with the water flow characterizing the Vistula River on the day a particular sample was taken. No correlation was between the water flow and petroleum content. The Pearson function value is 0.10 for the linear regression. It is a function of water flow *Q*:

$$C = aQ + b \tag{2}$$

The petroleum concentration *C* (expressed in μg/kg) is presented in dependence on the water flow (in m³/s), where particular coeficients are following: $a = 3.46.10^{-3}$ μg·s/m³kg and $b = 34.3$ μg/kg. Fig. 3 presents this comparison. The line at the figure is the plot of linear regression.

Discussion

A small number of literature data makes it difficult to compare obtained results for the petroleum concentration in other rivers. Available data showed that the Vistula River was moderately polluted with petroleum. Its pollution was at the same level that the one characteristic for the Danube River (oil concentration ranged from 1 to 300 μg/dm³ [26]) and the Daliao River (aliphatic hydrocarbons ranged there from 13 to 283 μg/dm³ [27]). The Vistula was a little more

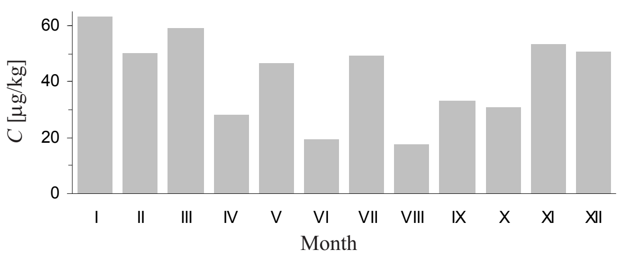

Fig. 2. Petroleum concentration *C* in the Vistula River in particular months of the year.

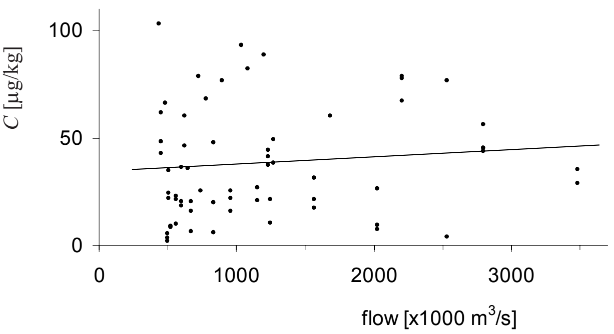

Fig. 3. Petroleum concentration C in the Vistula River in dependence on the water flow. The line is the plot of linear regression (2).

polluted with oil than the Sakarya River [28], and much less than the La Plata; concentration of aliphatic hydrocarbon alone ranged from 0.4 mg/dm^3 to 262 mg/dm^3 in its estuary [29].

Results of simultaneous studies of Gdańsk Bay and the Kacza River are most important for the assessment of results presented in this work. While the Vistula River was tested occasionally, these studies consisted of constant monitoring of oil pollution carried out almost seven years. The mean oil concentration was 11.7 μg/kg in coastal seawater and 146 μg/kg in the Kacza River.

It is impossible to compare directly two different rivers, especially small municipal watercourses with a great river crossing the whole country. Moreover, the Vistula depends on its major tributaries. Anyone of the major tributaries carries water from different draining area, which is more or less wide. A draining area gives meaning when any river will be considered like a sum of its smaller tributaries, and then small watercourses derived from this area. Although the Kacza river does not flow into the Vistula, it is an example of such a small tributary.

Study of the Kacza River confirmed the results obtained for the Vistula River. The same dependence was observed between petroleum concentration and the BOD_5 of water. Petroleum concentration is almost proportional to the BOD_5 characterizing water. Also, seasonal variability of petroleum content was closely similar in both rivers. Most polluted water was in winter, while both rivers were most pure in summer except July, when the oil concentrations were relatively high. Comparison of the seasonal variability of oil concentration allows us to notice a shift. The highest concentrations occurred in December and in February in the Kacza River, while most polluted water of the Vistula River was in January and in March. Also, relatively clean water of the Kacza River in May preceded the low concentrations of oil in the Vistula River in June. The petroleum concentration in the small urban river was highly dependent on rainwater and melted snow inflow. These phenomena caused increasing of the oil content in water immediately. Taking into account that the Vistula River carries water derived from its tributaries, the shift shows a late effect of environmental pollution observed in the great river.

Loading petroleum into a marine environment is one of the main questions of this study. Assuming that petroleum concentration is independent of water flow, the magnitude of petroleum reaching the sea in a time unit can be estimated by multiplying the mean concentration and mean water flow. A separate question is value of the mean concentration. Because of the limited amount of data, the highest concentrations resulted from the incidental oil spills had significant impact on the mean concentration that was calculated as algebraic average value. For finding more adequate value, all results were divided into quintiles. The extreme quintiles (1 and 5) were omitted and average value was calculated for the remaining data. This value is 37.3 μg/kg and it can be taken as the mean concentration (it is similar to the median 37 μg/kg). Assuming the mean flow of the water as 1,080 m^3/s (stated at the beginning of the paper), the mean inflow of petroleum is 40.3 g/s. Taking into consideration the possible relationship between water flow and petroleum content, the oil concentration should be calculated from the formula (2). Oil concentration $C = 38.1$ μg/kg corresponds to the water flow Q = 1,080 m^3/s. This means that mean inflow of petroleum to the sea is 41.1 g/s. Both calculations lead to the conclusion that almost 1,300 tons of petroleum reach the Baltic Sea every year.

Conclusions

Obtained results make it possible to draw some conclusions referring to the occurrence of petroleum in the Vistula River. The conclusions can be formed as follows:

- The Vistula River is a significant source of petroleum in the Baltic Sea with its mean annual input reaching almost 1,300 tons.
- Oil pollution shows seasonal changeability. It is highest in winter and lowest in summer.
- The petroleum concentration in water corresponds to its general pollution expressed by the BOD_5.

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