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FORMS OF ORGANIC AND INORGANIC CARBON IN RIVERS WATER OF THE VISTULA BASIN

There is a growing interest in the measurement of organic carbon content in waters. Very often total organic carbon and dissolved organic carbon contents are measured. According to regulations adopted in various countries the values of TOC and DOC should be limited. After reviewing these regulations we propose to introduce the TOC parameter into Polish law. In this paper, the information about the content of organic carbon in many surface waters of the world is given. The results of one-year measurements of IC, TOC, DOC and POC in such main Polish rivers as the Vistula, the Bug and the Narew are presented. The TOC is in the range of 6.1–23.2 mg C/dm^3, DOC in the range of 4.6–20.6 mg C/dm^3, POC in the range of 0.1–9.9 mg C/dm^3 and IC in the range of 19.1–53.6 mg C/dm^3. The correlations between BOD_5 and TOC, COD-Cr and TOC, POC and SS are discussed. The highest values of organic carbon were measured in warm periods of the year.

1. INTRODUCTION

The overall concentrations of organic compounds in water are usually determined by BOD_5 and COD. Both those indicators of organic pollution are responsible for a part of organic compounds only. BOD_5 refers to the organic compounds that are biochemically oxidized by naturally occurring bacteria, while COD refers to a higher percent of organic compounds that are oxidized at high temperature and in the presence of strong oxidizing agent such as potassium dichromate. But in these circumstances some compounds are not oxidized. Only determination of organic carbon gives full information on an organic pollution of water. In organic carbon measurement, all organic compounds are converted into CO_2. That is why the determination of organic carbon in water and wastewater is used more often every year.

2. FORMS OF ORGANIC CARBON IN WATER

Many forms of organic carbon in water are determined [1], [2]. They may be itemized as follows:

• Total organic carbon (TOC) determined in water samples without their filtration. TOC describes total concentration of all organic compounds given as carbon in mg/dm^3.

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• Dissolved organic carbon (DOC) determined in water samples after their filtration through a filter with a pore diameter of 0.45 μm.

• Particulate organic carbon (POC), organic carbon in the suspended solids retained by a filter with a pore diameter of 0.45 μm.

• Volatile organic carbon (VOC), carbon in volatile organic compounds. This form is determined very seldom, and usually the concentration of VOC in natural water is below 0.05 mg C/dm^3.

• Inorganic carbon (IC) is common in water. It is the sum of various forms of inorganic carbon, CO_2, bicarbonates and carbonates. The content of inorganic carbon in water is unstable.

• Total carbon (TC) can be defined as the sum of organic and inorganic carbon.

3. ORGANIC CARBON IN SURFACE WATERS

The instrumental method for the determination of organic carbon in water was published by Van HALL [3] in 1963. Since then, there have been more publications dealing with organic carbon content in waters and wastewaters.

MAIER and McCONNELL [4] presented the results of organic carbon determination in 1968–1969. They found that the content of TOC in the Lake Superior ranged from 1 mg C/dm^3 to 7 mg C/dm^3, in the St. Louis River from 21 mg C/dm^3 to 41 mg C/dm^3 and in the Mississipi River from 15 mg C/dm^3 to 23.5 mg C/dm^3. The highest TOC was measured in August, and the lowest during the spring.

CRAWFORD [5] described the results of the study done in 1975–1980 for small rivers in North Caroline. The TOC was in the range from 5 mg C/dm^3 to 21 mg C/dm^3 with a mean value of 10.5 mg C/dm^3.

SMOOT [6] stated that mean concentrations of TOC for the rivers in Kentucky State in 1976–1986 ranged from 1.7 mg C/dm^3 to 6.3 mg C/dm^3.

JORDAN and STAMER [7] presented the results of the study carried out in 1978–1986 for the rivers in the southest part of Nebraska State and the northest part of Kansas State. The mean values of TOC were in the range from 5 mg C/dm^3 to 21 mg C/dm^3. For the Big Blue River in Kansas State mean TOC was 6.5 mg C/dm^3 and mean value of DOC was 6.2 mg C/dm^3. In the Kansas River they measured mean TOC and mean DOC which were equal to 11 mg C/dm^3 and 5.7 mg C/dm^3, respectively. They found the values of TOC higher in spring and summer compared to those in autumn and winter.

HELGESEN [8] described the results of his study done in 1987–1990 for the rivers in Nebraska and Kansas States. The DOC values were varying from 1.5 mg C/dm^3 to 5.2 mg C/dm^3 and POC values from 0.2 mg C/dm^3 to 3.0 mg C/dm^3.

MARTINELLI [9] measured the organic carbon contents in the rivers in Brazil. He found the DOC for the Jaguari and the Atibaia Rivers in the range from 2.4 mg C/dm^3 to 2.7 mg C/dm^3 and for the Piracicaba River from 3.4 mg C/dm^3 to 4.3 mg C/dm^3.

Table 1

DOC and POC in Polish rivers in 1995 [11]

River and its locality	DOC range [mg C/dm^3]	POC range [mg C/dm^3]
The Vistula, Płock	12.7–14.7	1.0–7.3
The Odra, Słubice	12.4–14.2	0.9–7.2
The Warta, Poznań	10.2–11.9	0.6–12.6

BARAŁKIEWICZ [10] presented the results obtained for 11 lakes in the Wielkopolski National Park. The values of DOC were in the range from 10.5 mg C/dm^3 to 17.1 mg C/dm^3. A greater variation was found in the case of POC; the lowest value (0.8 mg C/dm^3) was measured in February, and the highest one (5.6 mg C/dm^3) in June.

Table 2

TOC in Polish rivers in August 1994 [11]

River and its locality	TOC [mg C/dm^3]
The Vistula, Cracow	11.2
The Vistula, Warsaw	18.2
The Narew, Pułtusk	23.0
The Bug, Wyszków	28.9
The Odra, Chałupki	13.0
The Odra, Wrocław	13.0
The Odra, Krajnik	23.8
The Warta, Poznań	20.7

SIEPAK [11] described organic carbon contents in main Polish rivers in 1995 (table 1). He also presented the results of TOC determination in August 1994 for several Polish rivers (table 2) and in 1991 for 13 Polish rivers (table 3).

Table 3

TOC in Polish rivers in 1991 [11]

River and its locality	Range [mg C/dm^3]	River and its locality	Range [mg C/dm^3]
The Vistula, Cracow	4.9–9.3	The Rega, Trzebiatów	7.1–10.5
The Odra, Chałupki	7.0–15.8	The Ina, Goleniów	7.8–12.0
The Odra, Wrocław	6.8–14.6	The Pasłęka, Nowa Pasłęka	8.0–14.0
The Odra, Krajnik	7.0–12.6	The Reda, Wejcherowo	5.7–11.1
The Warta, Poznań	10.1–14.0	The Łeba, Cecenowo	8.4–16.0
The Wieprza, Stary Kraków	5.7–9.5	The Łupawa, Smołdzina	6.5–10.5
The Grabowa, Grabowo	3.0–5.6	The Słupia, Charnowo	7.5–16.1
The Parsęta, Bardy	5.5–10.3		

4. REGULATIONS IMPOSED ON ORGANIC CARBON CONTENT IN WATERS

In Poland we have not introduced any regulations limiting the content of organic carbon in surface waters. In the case of the wastewater discharge into receivers (water and soil) [16], the maximum permissible value of TOC reaches 40.0 mg C/dm^3.

In some countries, the content of organic carbon is limited by an official regulation.

In Hungary [17], we deal with different concentrations of total organic carbon for different quality classes of surface water:

class	I	II	III	IV	V
TOC, mg C/dm^3	3	5	10	15	>15

In Germany [18], the concentrations of organic carbon dissolved in surface water are included in the following quality classes:

class	I	II	III	IV
DOC, mg C/dm^3	1.5	3.5	6.0	8.0
maximum DOC, mg C/dm^3	3.0	5.5	8.5	11.0

Additionally, in Northern Rhineland Westphalia [19], the maximum value for TOC is established as <7 mg C/dm^3.

In Norway [20], the content of organic carbon in water is limited:

class	I	II	III	IV
$C_{organic}$, mg C/dm^3	2.5	4.2	6.7	>6.7

In Slovakia [21], the content of TOC is as follows:

class	I	II	III	IV	V
TOC, mg C/dm^3	5	8	11	17	>17

In Sweden [22], the following concentrations of organic carbon are proposed:

class	I	II	III	IV	V
$C_{organic}$, mg C/dm^3	5	10	15	20	>20

The directives of the European Union involve organic carbon. In the Council Directive [23] concerning the quality of surface water used for the drinking purposes, the following parameters can be found:

- total organic carbon, but this value is not given,
- residual organic carbon after flocculation and membrane filtration (no value).

In the Council Directive [24] dealing with the drinking water quality, total organic carbon (TOC) is taken into account, but its values are not given.

Considering the maximum permissible concentrations of organic carbon in surface waters found in the regulations of various countries, it seems reasonable to propose the following values for water quality classes described in the Polish Disposition from 1991 [16].

class	I	II	III
TOC, mg C/dm^3	6	12	15

5. METHODS

5.1. METHODS OF MEASUREMENT

Carbon analyzer Shimadzu TOC-5000A was used. The analyzer can measure: total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) [12].

Measurement of TC. Not stabilized water samples were introduced into the combustion tube with oxidation catalyst and heated to 680 °C. TC was decomposed into CO_2 and then measured using non-dispersive infrared gas analyzer (NDIR).

Measurement of TOC. The water samples were stabilized with hydrochloric acid to a pH<3, purged by flushing with air for 20 minutes to remove CO_2, and then the TOC component in the sample was measured as a TC.

Measurement of IC. The water samples were introduced using a sample injector into an IC reaction vessel. Only IC component in the sample was decomposed into CO_2 which was detected by the NDIR.

Measurement of DOC. The water samples were filtrated through a filter with a pore diameter of 0.45 μm, then stabilized with hydrochloric acid to pH<3, purged by flushing them with air for 20 minutes to remove CO_2, and the DOC component in the samples was measured as a TC.

Calculation of POC. POC was calculated from the equation: POC = TOC – DOC.

Measurements of BOD_5, COD-Cr and suspended solids (SS). BOD_5, COD-Cr and suspended solids were measured in accordance with Polish Standards [13]–[15].

5.2. SAMPLING

Water samples were taken to the glass bottles in such a way as to omit air bubbles formation. They were transported to laboratory (which lasted 2–3 hrs) and kept at the temperature of 4 °C. Samples from the following rivers were taken:

- the Vistula in Cracow (63.7 km from its source),
- the Vistula in Warsaw (510.0 km from its source),
- the Narew in Pułtusk (63.0 km from its source),
- the Bug in Wyszków (33.0 km from its source).

The samples were taken every month, from January 1999 to December 1999.

The following parameters were measured: TC, TOC, IC, DOC, POC and BOD_5, COD-Cr and total suspended solids (SS).

6. RESULTS AND DISCUSSION

The results of determinations are presented in tables 4–9.

Table 4

The Vistula River in Warsaw

Month	TC	IC	TOC	DOC	POC	BOD_5	COD-Cr	SS
	[mg C/dm^3]					[mg O_2/dm^3]		[mg/dm^3]
January	44.9	38.4	6.7	5.8	0.9	2.8	18.3	13.8
February	43.1	37.3	7.0	6.9	0.1	3.0	20.3	2.8
March	35.6	25.5	9.3	7.1	2.2	4.5	34.2	50.4
April	43.4	34.6	8.3	5.1	3.2	5.0	30.2	24.2
May	46.4	34.7	12.4	7.0	5.4	5.9	34.6	43.2
June	48.1	35.1	11.4	5.5	5.9	8.1	33.7	26.8
July	46.1	32.1	12.4	6.0	6.4	10.4	62.2	40.0
August	44.4	30.3	14.8	5.6	9.2	11.4	43.2	44.2
September	44.2	26.9	13.2	4.6	8.6	9.9	40.7	73.8
October	47.4	38.5	7.2	5.6	1.6	3.3	34.3	33.4
November	48.5	40.8	6.1	4.6	1.5	2.3	29.5	31.6
December	46.4	38.8	6.9	5.6	1.3	2.6	16.0	12.8
Average	44.9	34.4	9.6	5.8	3.8	5.8	33.1	33.1

The content of total carbon in the rivers investigated varied from 27.0 mg C/dm^3 (the Vistula River in Cracow, in June) to 69.2 mg C/dm^3 (the Bug River, in September).

Table 5

The Bug River in Wyszków

Month	TC	IC	TOC	DOC	POC	BOD_5	COD-Cr	SS
	[mg C/dm^3]					[mg O_2/dm^3]		[mg/dm^3]
January	62.8	51.4	12.3	11.6	0.7	2.6	27.4	6.4
February	63.9	53.6	12.3	11.7	0.6	2.6	31.6	6.8
March	48.5	34.8	13.8	12.6	1.2	3.1	30.5	7.6
April	58.1	42.9	15.2	13.5	1.7	2.7	50.5	3.4
May	63.5	39.9	23.2	20.6	2.6	6.5	42.6	10.8
June	63.2	40.5	20.1	10.4	9.7	11.6	50.0	62.0
July	58.1	33.9	19.0	9.3	9.7	15.4	76.5	70.2
August	64.5	39.3	19.0	9.1	9.9	12.6	45.3	73.6
September	69.2	50.2	14.9	7.8	7.1	8.3	46.2	49.6
October	60.6	50.8	9.2	8.2	1.0	2.5	49.6	24.0
November	61.7	47.6	11.2	7.4	3.8	4.6	31.0	8.0
December	64.4	51.8	11.8	10.9	0.9	2.8	24.5	9.6
Average	61.5	44.7	15.2	11.1	4.1	6.3	42.2	27.7

The highest content of inorganic carbon (53.6 mg C/dm^3) was found in the Bug River in February, and the lowest (19.1 mg C/dm^3) in the Vistula River in Cracow in

June. On average, the content of inorganic carbon approached 75% of a total carbon concentration.

Table 6

The Narew River in Pułtusk

Month	TC	IC	TOC	DOC	POC	BOD_5	COD-Cr	SS
	[mg C/dm^3]					[mg O_2/dm^3]		[mg/dm^3]
January	55.5	43.9	12.7	11.7	1.0	2.0	31.4	2.0
February	55.6	45.4	12.1	11.4	0.7	2.4	22.6	3.2
March	46.0	32.9	13.6	12.2	1.4	2.4	39.4	3.4
April	58.1	41.3	16.2	14.3	1.9	2.4	36.5	7.4
May	62.5	42.8	19.6	17.3	2.3	3.6	28.0	4.4
June	62.0	43.8	16.7	13.8	2.9	3.4	43.5	6.8
July	55.9	39.4	15.7	11.7	4.0	5.8	55.8	11.6
August	52.2	38.6	12.7	9.6	3.1	4.8	31.6	9.2
September	53.9	41.6	11.2	9.2	2.0	3.5	30.2	9.2
October	54.7	42.3	10.0	9.2	0.8	2.2	45.8	7.4
November	51.7	40.8	9.5	8.8	0.7	1.5	35.0	3.2
December	56.0	43.1	12.0	11.5	0.5	1.6	27.2	3.6
Average	55.3	41.3	13.5	11.7	1.8	3.0	35.6	6.0

The total organic carbon was in the range from 6.1 mg C/dm^3 (the Vistula River in Warsaw, in November) to 23.2 mg C/dm^3 (the Bug River, in May) (tables 4–7).

Table 7

The Vistula River in Cracow

Month	TC [mg C/dm^3]	IC [mg C/dm^3]	TOC [mg C/dm^3]	DOC [mg C/dm^3]	POC [mg C/dm^3]
April	37.4	30.0	7.0	5.6	1.4
May	52.7	38.8	11.4	6.4	5.0
June	27.0	19.1	7.4	7.1	0.3
July	38.5	28.2	8.0	5.5	2.5
August	43.1	34.0	7.6	6.1	1.5
September	48.0	38.4	7.1	5.0	2.1
October	40.5	26.1	9.8	8.2	1.6
November	43.6	33.4	6.5	5.5	1.0
December	42.6	34.8	6.6	6.5	0.1
Average	41.5	31.4	7.9	6.2	1.7

In general, the content of TOC in Polish rivers was higher than in other rivers in the world (table 9). The highest TOC was found in the Bug and the Narew Rivers.

Table 8

The values of ratios: BOD_5/TOC, COD-Cr/TOC and POC/SS for various rivers

Month	The Vistula in Warsaw			The Bug in Wyszków			The Narew in Pułtusk		
	BOD_5 /TOC	COD-Cr /TOC	POC /SS	BOD_5 /TOC	COD-Cr /TOC	POC /SS	BOD_5 /TOC	COD-Cr /TOC	POC /SS
January	0.4	2.7	0.07	0.2	2.2	0.11	0.2	2.5	0.50
February	0.4	2.9	0.04	0.2	2.6	0.09	0.2	1.9	0.22
March	0.5	3.7	0.04	0.2	2.2	0.16	0.2	2.9	0.41
April	0.6	3.6	0.13	0.2	3.3	0.50	0.2	2.3	0.26
May	0.5	2.8	0.13	0.3	1.8	0.24	0.2	1.4	0.52
June	0.7	3.0	0.22	0.6	2.5	0.16	0.2	2.6	0.43
July	0.8	5.0	0.16	0.8	4.0	0.14	0.4	3.6	0.34
August	0.8	2.9	0.21	0.7	2.4	0.13	0.4	2.5	0.34
September	0.8	3.1	0.12	0.6	3.1	0.14	0.3	2.7	0.22
October	0.5	4.7	0.05	0.3	5.4	0.04	0.2	4.6	0.11
November	0.4	4.9	0.05	0.4	2.8	0.48	0.2	3.7	0.22
December	0.4	2.3	0.10	0.2	2.1	0.09	0.1	2.3	0.14
Average	0.6	3.5	0.11	0.4	2.9	0.15	0.2	2.7	0.30

Table 9

Mean values of TOC, DOC and POC in the rivers studied and other rivers in the world [2]

River	TOC	DOC		POC	
	[mg C/dm^3]	[mg C/dm^3]	[% of TOC]	[mg C/dm^3]	[% of TOC]
The Vistula in Warsaw*	9.6	5.8	60	3.8	40
The Vistula in Cracow*	7.9	6.2	78	1.7	22
The Bug in Wyszków*	15.2	11.1	73	4.1	27
The Narew in Pułtusk*	13.5	11.7	87	1.8	13
The Rhine	8.5	5.5	65	3.0	35
The Loire	5.5	3.5	64	2.0	36
The Garonne	5.7	3.2	56	2.0	44
The Danube	–	5.8	–	–	–
The Yukon	10.0	8.8	88	1.2	12
The Columbia	3.3	2.7	82	0.6	18
The Alabama	5.3	4.7	89	0.6	11
The Missouri	24.5	20.0	82	4.5	18
The Amazon	10.0	5.0	50	5.0	50
The Orinoco	6.0	5.0	83	1.0	17
The Rio Negro	11.0	8.0	73	3.0	27
The Congo	10.0	9.0	90	1.0	10
The Ganges	–	5.0	–	0.2	–
The Yangtse-Kiang	–	7.0	–	–	–

*Determined in this paper.

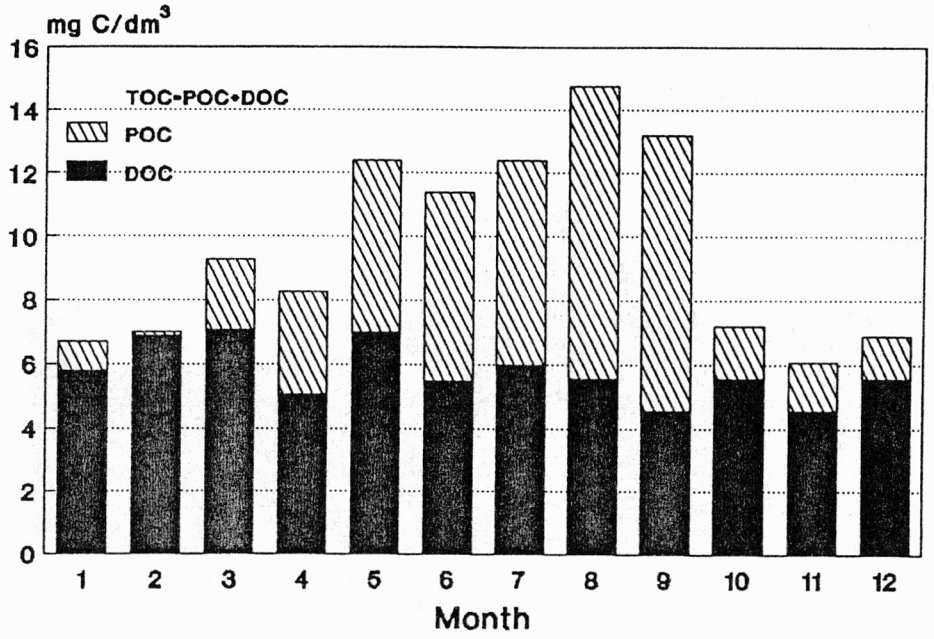

Fig. 1. Changes of DOC and POC in the Vistula River (Warsaw)

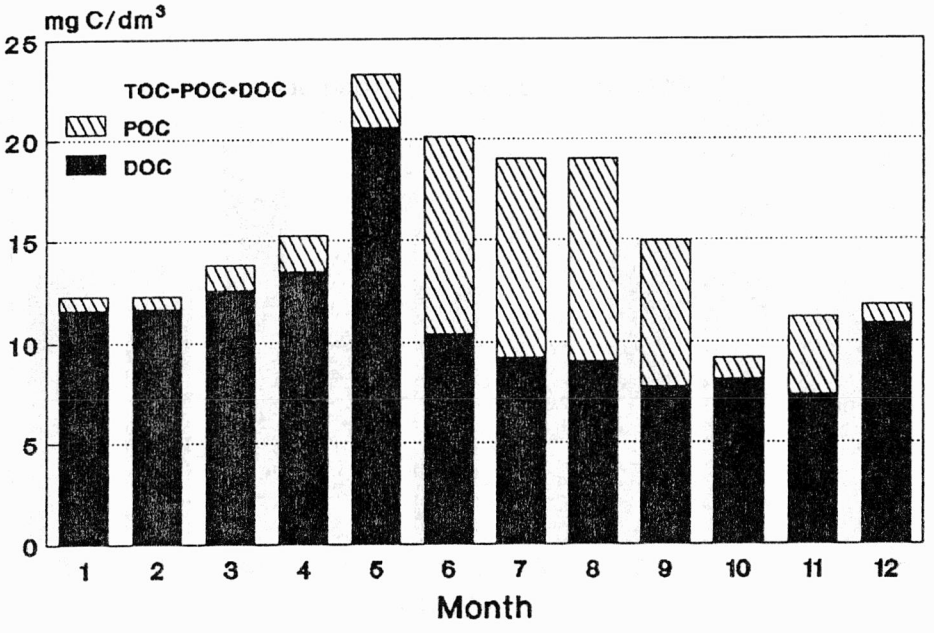

Fig. 2. Changes of DOC and POC in the Bug River (Wyszków)

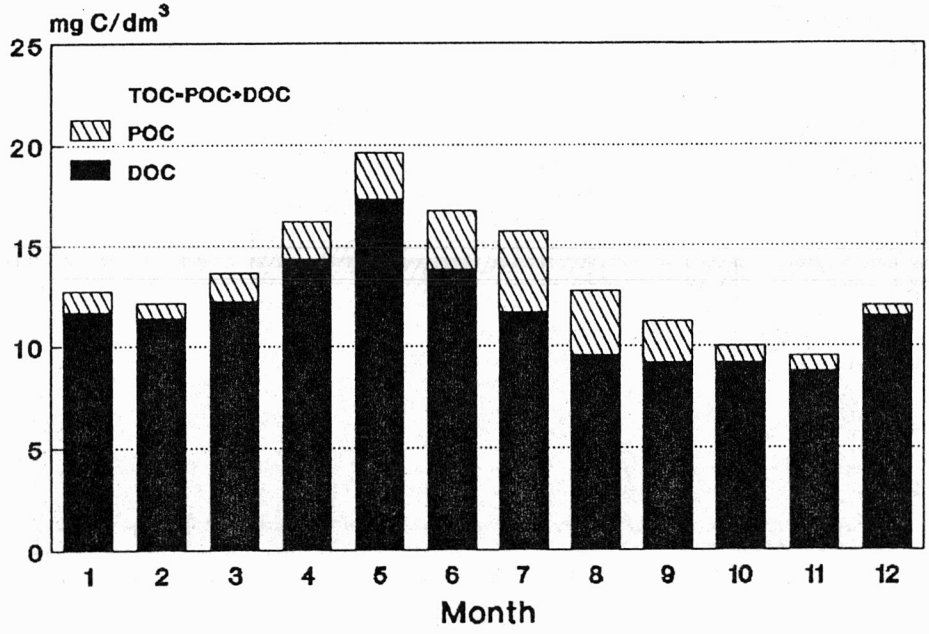

Fig. 3. Changes of DOC and POC in the Narew River (Pułtusk)

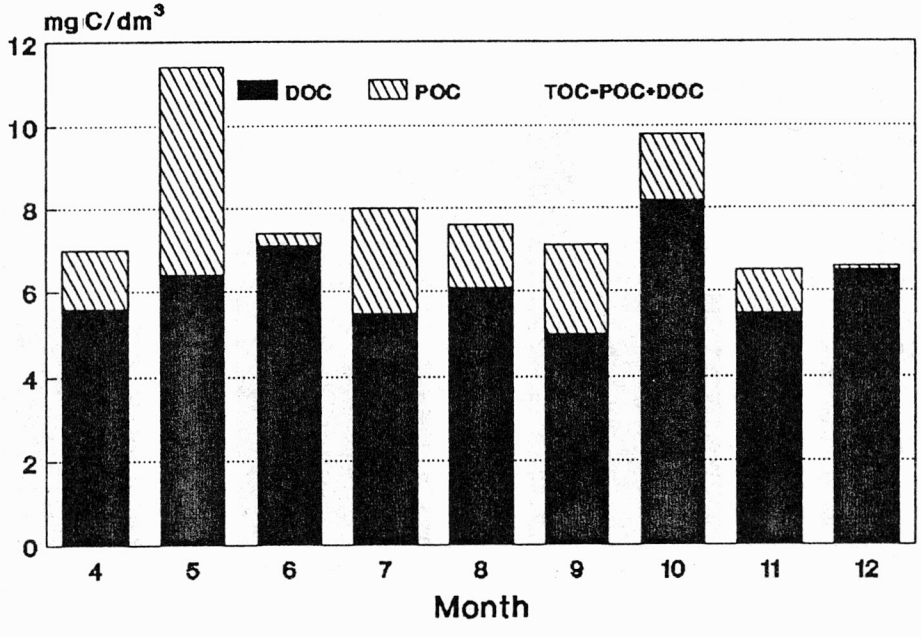

Fig. 4. Changes of DOC and POC in the Vistula River (Cracow)

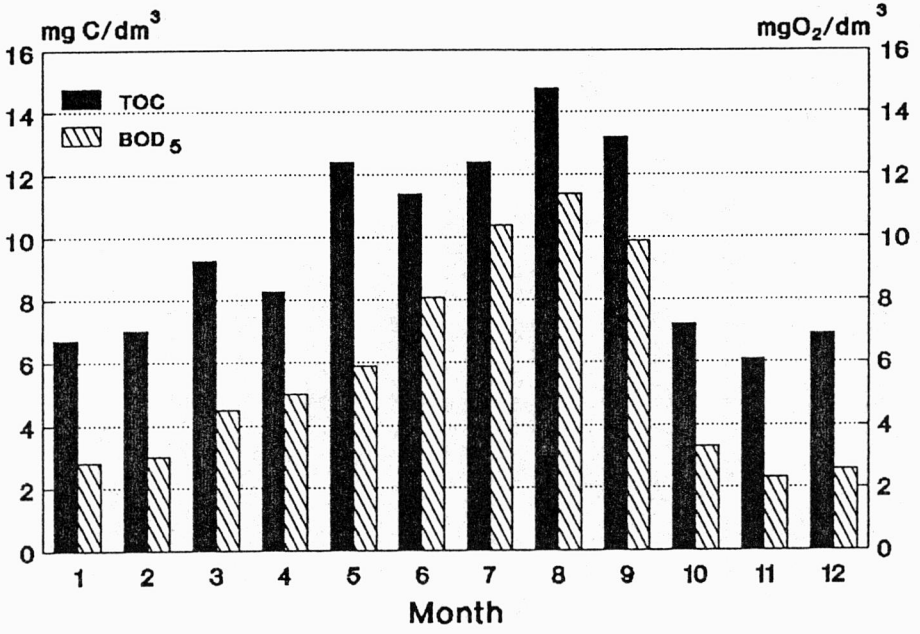

Fig. 5. Changes of TOC and BOD_5 in the Vistula River (Warsaw)

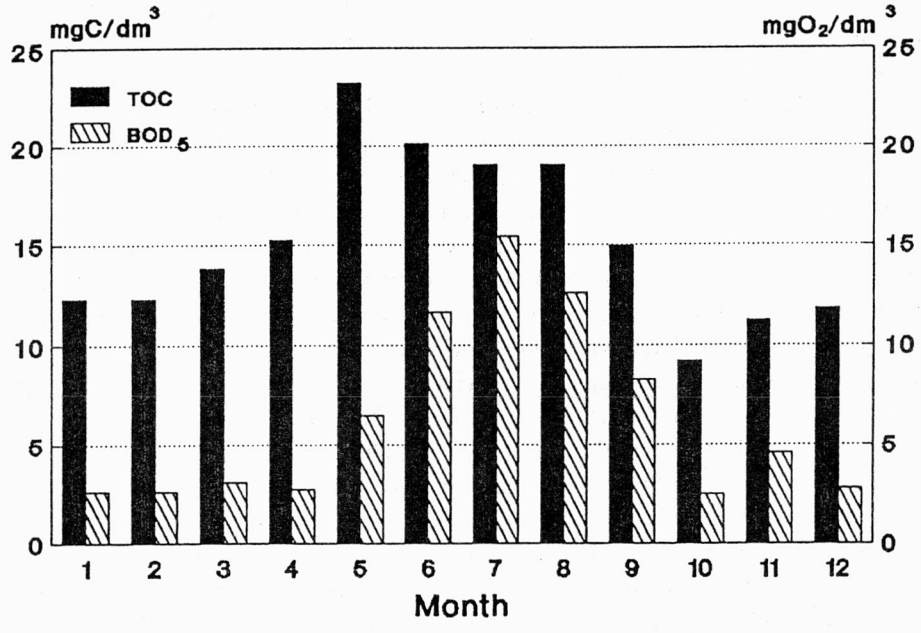

Fig. 6. Changes of TOC and BOD_5 in the Bug River (Wyszków)

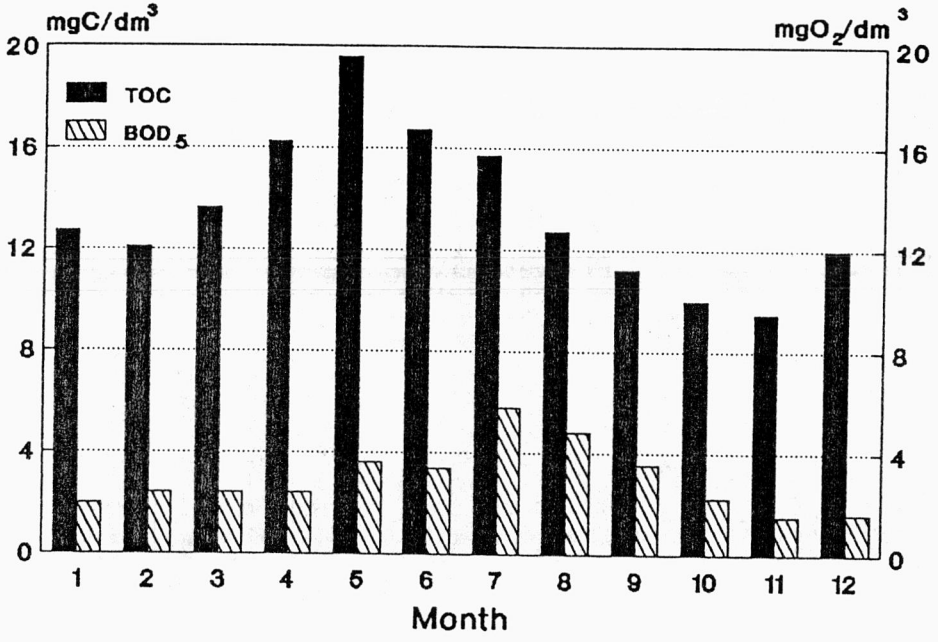

Fig. 7. Changes of TOC and BOD_5 in the Narew River (Pułtusk)

Both rivers are polluted with organic compounds and hence eutrophic. The highest value of TOC, i.e. 23.2 mg C/dm^3, was measured in the Bug River, and the lowest value, i.e. 6.1 mg C/dm^3, in the Vistula River in Warsaw. The TOC values in rivers varied with time, always being the highest in warm periods (figures 1–4). It could be partly explained by algae growth.

A high correlation between TOC and BOD_5 could be observed (figures 5–7). The ratio of BOD_5 to TOC for the Vistula River in Warsaw was equal to 0.6 (mean), in the Bug River – 0.4, and in the Narew River – 0.2. The highest COD-Cr/TOC ratio was in the Vistula River (mean value, 3.5) and the lowest – in the Narew River (mean value, 2.7) (table 8). This proved that organic compounds occurred in waters. The Narew River water contains less biodegradable organic substances compared to the Vistula water. Percent of biodegradable compounds is higher in growing season (June–August) than in other months, which can be correlated with growth of water organisms.

The variation in dissolved organic carbon (DOC) and particulate organic carbon (POC) was more pronounced than that in TOC. DOC reached the highest value in the Narew (87% of TOC), slightly lower in the Bug (73% of TOC), and the lowest in the Vistula in Warsaw (60% of TOC). An inverse relationship was found for POC, which was the highest in the Vistula in Warsaw (40% of TOC), and the lowest in the Narew (13% of TOC). This phenomenon was correlated with the content of suspended solids, the highest in the Vistula, and the lowest in the Narew. There was a high correlation between the content of suspended solids and POC. The ratio of POC to SS was as follows: for the Vistula 0.11

(mean), for the Bug 0.15 and for the Narew 0.30 (table 8). The highest concentrations of POC and SS were measured in summer (June, July, August).

7. CONCLUSIONS

- Organic carbon is considered to be a very important parameter, as it gives full information about pollution of water with organics.
- The values of TOC in Polish rivers (especially in the Bug and the Narew) were higher than in a few selected rivers in the world.
- The values of TOC in Polish rivers examined increase in summer. This can be connected with the growth of algae in warm periods. Usually the POC values were also higher in warm periods. The DOC values were more stable.
- The ratio of TOC to BOD_5 gives a valuable information on biodegradability of organic compounds in water.
- In many European countries, there are strict rules regulating the concentration of organic carbon in various quality classes of surface water. In Poland, there is no such a regulation. The authors of this paper propose the values of permissible TOC concentration for three classes of surface water quality, according to the actual classification [16].

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FORMY NIEORGANICZNEGO I ORGANICZNEGO WĘGLA W WODACH ZLEWNI WISŁY

Ciągle rośnie zainteresowanie zawartością organicznego węgla w wodzie. Bardzo często mierzy się więc całkowite stężenie węgla organicznego i stężenie rozpuszczonego w wodzie węgla organicznego. Zgodnie z regulacjami prawnymi przyjętymi w różnych państwach należy ograniczyć zawartość całkowitego i rozpuszczonego węgla organicznego. Po dokonaniu przeglądu tych regulacji zaproponowano, aby do polskiego ustawodawstwa wprowadzić całkowitą zawartość węgla organicznego. W artykule poinformowano o zawartości węgla organicznego w wielu wodach powierzchniowych na świecie. Przedstawiono też wyniki jednorocznych pomiarów zawartości nieorganicznego węgla (19,1–53,6 mg C/dm^3), całkowitego węgla organicznego (6,1–23,2 mg C/dm^3), rozpuszczonego węgla organicznego (4,6–20,6 mg C/dm^3) i pyłowego węgla organicznego (0,1–9,9 mg C/dm^3) w takich polskich rzekach, jak: Wisła, Bug i Narew. Omówiono korelacje między BZT_5 a całkowitą zawartością węgla i $CHZT_{Cr}$ oraz między całkowitą zawartością węgla organicznego a zawiesinami. Najwyższe stężenie organicznego węgla zmierzono w ciepłych porach roku.