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*Original Research*

# Variability of Organic Carbon in Water and Sediments of the Odra River and Its Tributaries

**E. Niemirycz[1]*, J. Gozdek[2], D. Koszka-Maroń[3]**

[1]Institute of Meteorology and Water Management Maritime Branch, Department of Coastal Water Protection, ul. Jaśkowa Dolina 29, 80 – 286 Gdańsk, Poland
[2]Gdańsk University, Chemical Faculty, ul. Sobieskiego 18, 80-952 Gdańsk, Poland
[3]Polish Geological Institute Branch of Marine Geology, ul. Kościerska 5, 80-328 Gdańsk, Poland

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**Abstract**

This paper presents the results of tests for total organic carbon (TOC) and dissolved organic carbon (DOC) in water and sediments of the Odra River and its tributaries, collected in 1998-2000. TOC and DOC concentrations in tested samples were determined using the multi N-C analyser made by Analytik Jena/Instrument Development Company (IDC). More than 40% of waters from the Odra River and its tributaries were characterized by increased organic substances concentration levels according to Polish and German regulations (10-20 mgC $dm^{-3}$). TOC and DOC concentrations in water samples were in the range of 3.7-29.0 mgC $dm^{-3}$ and 2.5-16.3 mgC $dm^{-3}$, respectively, whereas TOC content in sediments varied between 1.4-176.0 mgC $g^{-1}$ d.m. Particulate organic carbon (POC) constituted about 20% of TOC in the tributaries and 37% in close-to-mouth water of the Odra River. Based on the obtained results, the temperature influence on the content of organic carbon in water samples was observed. The maximum TOC values were characteristic for spring–summer period, while the minimum ones for the autumn.

**Keywords:** TOC, DOC, POC, the Odra Basin, water flow, water temperature

## Introduction

Organic matter plays a major role in the aquatic system. It affects biogeochemical processes, nutrient cycling, biological availability, chemical transport and interactions. Organic matter content is typically measured as total organic carbon (TOC) and dissolved organic carbon (DOC), which are fundamental components of the carbon cycle. Organic matter in water consists of thousands of components, including macroscopic particles, colloids, dissolved macromolecules and specific compounds.

Measurements of biological (BOD) and chemical (COD) oxygen demand reveal the content of organic substances being suspectible to decomposition under specific conditions. And TOC measurement provides information on all organic substance content in water or sediments [2, 3]. Organic carbon content in river waters depends on the size of a water region, climate, flora surrounding the watercourse as well as the season of sample collection [4].

Literature data give the following values of TOC content in natural waters: in groundwaters–about 0.7 mgC $dm^{-3}$, in groundwaters with high amounts of humic substances–6-15 mgC $dm^{-3}$, in seas–about 2 mgC $dm^{-3}$ and in rivers and lakes–from a few to above 10 mgC $dm^{-3}$ [4].

Dissolved Organic Carbon is a parameter which includes active chemical matter with dispersed molecules smaller than 0.45 µm. They are mainly polymers of organic acids, being the elements of humic substances. DOC content in surface waters varies from 0.5 to 0.7 mgC $dm^{-3}$

*Corresponding author: e-mail: elzbieta.niemirycz@imgw.pl

in sea and groundwaters to above 30 mgC $dm^{-3}$ in waters from peat swamp. DOC is known to be a strong complexing agent for many toxic metals such as iron, copper, aluminum, zinc and mercury. DOC increases the weathering rate of minerals and solubility and consequently affects the mobility and transport of many metals and organic contaminants [5].

POC (Particulated Organic Carbon) and SOC (Suspended Organic Carbon) define organic carbon content in suspension. The suspension consists of detached fauna and flora elements, compounds and organic substances adsorbed on mud and clay. POC decomposition, associated with its content in water columns and sediments, plays an important role in river water quality such as decreasing dissolved oxygen concentration and increasing biochemical oxygen demand [6]. POC value is determined for the suspension obtained from water samples after filtration through a filter with pores of 45µm diameter. POC values depend on both the temperature and the season. Increases in river water pollution cause increases in the POC parameter [4, 7-9].

In accordance with Polish legislation [10], TOC boundary values for particular surface water quality classes are the following: 5 mgC $dm^{-3}$ (I class), 10 mgC $dm^{-3}$ (II class), 15 mgC $dm^{-3}$ (III class), 20 mgC $dm^{-3}$ (IV class) and > 20 mgC $dm^{-3}$ (V class). And in accordance with German legislation (LAWA 1998) regarding TOC content, the following surface water quality classes exist: ≤ 2 mgC $dm^{-3}$ (I class), ≤ 3 mgC $dm^{-3}$ (I-II class), ≤ 5 mgC $dm^{-3}$ (II class), ≤ 10 mgC $dm^{-3}$ (II-III class), ≤ 20 mgC $dm^{-3}$ (III class), ≤ 40 mgC $dm^{-3}$ (III-IV) and > 40 mgC $dm^{-3}$ (IV class).

Determination of organic carbon is used to identify the presence of organic substances in sediments. The content of organic carbon depends on geographical location, pollutants entering rivers and layer depth of tested sediments. Sediment content is different for flowing waters and lakes.

This paper presents evaluation of TOC, DOC and POC content in waters as well as TOC content in sediments of the Odra Basin in 1998–2000. TOC results for waters were compared with these for close-to-mouth section of the Odra River in 1995–2000 obtained in the framework of National Environmental Monitoring activities [11]. Also, the relation between the temperature, water flow and TOC, DOC content in water samples from the Odra River and its tributaries were defined.

## Materials

In 1998–2000 in the the Odra Basin four expeditions were organised to collect water (n=82) and bottom sediment (n=73) samples. In 1998 samples were collected twice, in May and November. The next years (1999 and 2000) samples were collected only in the spring. 14 research section areas located along the main Odra watercourse, close-to-mouth sections of its 6 main tributaries and 3 sections along the main Odra River tributary – the Warta River watercourse were selected (Table 1).

## Methods

Water samples were collected from the subsurface, with no air bubbles, directly to dark glass vessels. They were stored at +4°C. Sediment samples were collected from the surface using a scoop and stored at –20°C.

TOC and DOC determination in water samples and TOC determination in sediment samples were performed using the multi N-C analyser made by the Analytic Jena/ Instrument Development Company (IDC).

TOC and DOC content in water samples was determined according to the Polish Standard [1]. Tested samples were acidified with phosphoric acid (V) to about pH 2, then carbon dioxide from inorganic compounds was removed by flowing nitrogen through the sample (about 20 min.). Such prepared samples were incinerated in the presence of a catalyst ($Ce_5O_2$) at 850°C in the oxygen atmosphere. The formed carbon dioxide was determined quantitatively using the infrared spectrophotometric method. DOC was determined after filtrating water samples through a filter paper with pore diameter of 0.45µm. The solutions were analyzed as alone.

POC values were calculated by substracting obtained TOC and DOC results. (POC=TOC-DOC).

TOC content in sediments was determined in accordance with the instruction for the multi N-C analyzer. About 1 g of sediments (lyophilized, screened through a sieve of 2 mm and grinned in a ball-grinder), 10 ml of water and 2.5 ml of 25% HCl were put into a crucible. Then they were all mixed in an ultrasonic bath for 5 minutes and heated in a sand bath to 75°C for about 12 hours until the solid mass was obtained. Such a prepared sample was rehomogenized. The mixture (about 100-1000 mg) underwent pyrolysis at 1100°C in the oxygen atmosphere – in the presence of a catalyst (cerium dioxide). The formed carbon dioxide was determined quantitatively using the infrared spectrophotometric method. Determination of TOC content in a standard ($CaCO_3$) allowed us to evaluate the credibility and accuracy of this method.

Water temperature was determined while collecting samples using the MultiLine F/SET-3 measurement set made by the WTW company.

Water flow in the Odra River and its tributaries was measured and results compiled within statutory works of the Institute of Meteorology and Water Management.

## Discussion of Results

Fig. 1 shows the range of TOC and DOC concentration values in water samples from the Odra River and its tributaries (minimum and maximum values, quartiles and arithmetic mean values), collected in 1998–2000. Values of organic carbon concentration changed in the narrowest range in 1999 (Fig. 1a, 1b). Higher variability was observed for water samples collected in May 1998 for TOC and 2000 for DOC, when minimum and maximum values were in the range of 3.7-29.0 mgC dm$^{-3}$ and 2.5-16.3 mgC dm$^{-3}$, respectively.

The obtained DOC concentration values were twice as high as those for European rivers, but they were the same as ranges in other Polish rivers (Table 2). Both anthropogenic pollution of Polish rivers and their natural hydrochemical background may affect these high concentration values [9].

Fig. 2 shows the mean concentration values of TOC in waters from the Odra River and its tributaries in 1998-2000. The maximum values were in the range of 10-20 mgC dm$^{-3}$. They were characteristic for right–bank Odra River tributaries (Barycz, Obrzyca, Warta) and waters from the Odra River close-to-mouth section (Mescherin and Widuchowa).

According to Polish and German regulations, more than 40% of analyzed water samples from the Odra Basin can be treated as waters with increased organic substance concentration levels [10, 12]. In the research period the values above 15 mgC dm$^{-3}$ were observed only occasionally (7 times). Due to these values the water samples did not fufill the requirements for surface waters for consumption purposes [13].

Seasonal variability in TOC and DOC content in water samples from the Odra River and its tributaries, connected

Table l. Localization of sampling points.

| No | Sampling point | km of river course | May 1998 | November 1998 | June 1999 | May/June 2000 |
|---|---|---|---|---|---|---|
| Odra River | | | | | | |
| 1. | Opole – Groszowice | 144 | - | - | w, s | w, s |
| 2. | Bytom Odrzański | 416 | w, s | w, s | w, s | w, s |
| 3. | Krosno Odrzańskie | 516 | w, s | w, s | w, s | w, s |
| 4. | Frankfurt (Słubice | 584 | w, s | w | w, s | w, s |
| 5. | Kietz (Kostrzyn | 617.6 | w, s | w | w, s | w, s |
| 6. | Czelin | 640 | - | - | w, s | w, s |
| 7. | Widuchowa | 701 | w | w, s | w, s | w, s |
| 8. | Mescherin | 715 | w, s | w, s | w, s | w, s |
| 9. | Gryfino | 719 | w, s | w, s | w, s | w, s |
| 10. | Podjuchy | 730 | w, s | w | w, s | w, s |
| 11. | Szczecin | 740 | w, s | - | w, s | w, s |
| 12. | Police | 760 | s | s | w, s | w, s |
| 13. | Roztoka Odrzańska | 761.9 | w, s | w, s | w, s | w, s |
| 14. | Świna – Świnoujście | | w | - | - | - |
| Odra tributaries | | | | | | |
| 15. | Kaczawa | 315.9 | w, s | w, s | w, s | w, s |
| 16. | Barycz | 378.1 | w, s | w, s | w, s | w, s |
| 17. | Obrzyca | 469.4 | w, s | w, s | w, s | w, s |
| 18. | Bóbr | 516.2 | w, s | w | w | w |
| 19. | Nysa Łużycka | 542.4 | w | w, s | w | w, s |
| 20. | Warta | 615 | w, s | w | w, s | w, s |
| Warta River | | | | | | |
| 21. | Zawiercie | 801 | w, s | w, s | w, s | w, s |
| 22. | Poznań – Czapury | 243.6 | w, s | w, s | w, s | w, s |
| 23. | Gorzów Wielkopolski – Świerkocin | 56.4 | w, s | w, s | w, s | w, s |

w-water, s-sediments, – no samples

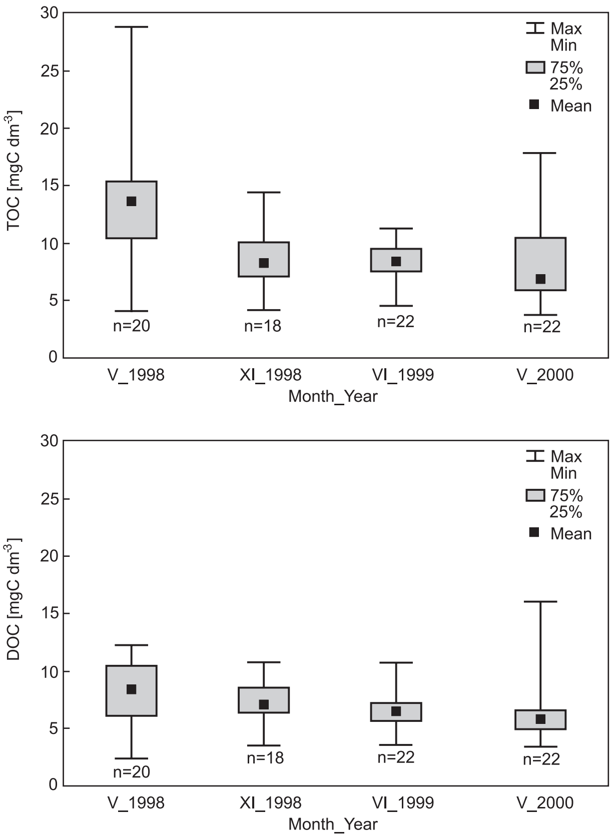


Fig. 1. TOC and DOC concentrations in water samples Odra River and its tributaries in 1998-2000. (data from 23 sampling points – see Table 1).

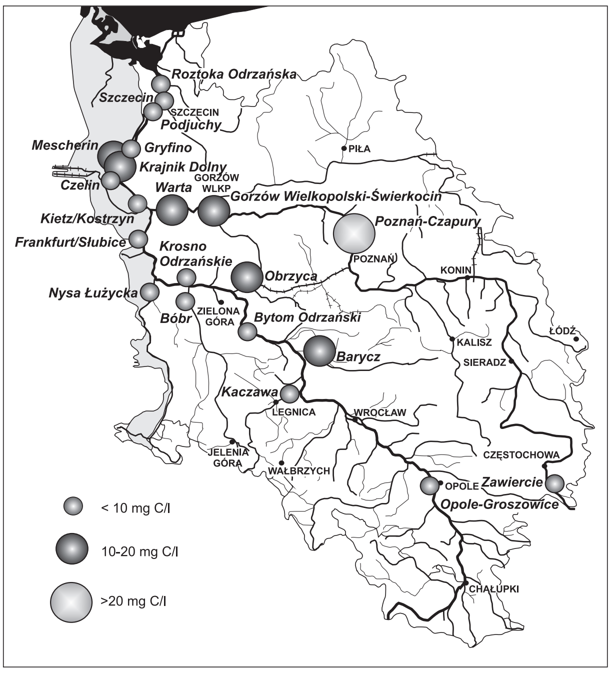


Fig. 2. Mean TOC concentration in waters of the Odra river and its tributaries in 1998-2000.

with a biological cycle, resulted in concentration levels observed in May and November 1998 (Fig. 1). Mean TOC values in May and November 1998 were 12.8 mgC dm$^{-3}$ and 8.6 mgC dm$^{-3}$ respectively. The obtained results were compared to the data for the Odra River section in Krajnik Dolny carried out within the framework of National Environmental Monitoring in 1995–2000 [11]. The results show there was an increase in TOC concentration in spring/summer period in comparison to autumn/winter months (Fig. 3). Similar seasonal changes in TOC concentrations in waters were observed for the Verde River by Parks and Baker (USA, 1997). In winter, TOC values were about 1-3 mgC dm$^{-3}$ on average, whereas in summer they increased even to 30mg C dm$^{-3}$ [14]. The increase in TOC concentration in summer months can be influenced by more active biological life in rivers that are enriched with many nutritious substances [9].

A similar relation was observed between mean monthly TOC concentration and mean monthly water temperature in the Odra River section in Krajnik Dolny (1995-2000) ($R^2$=0.5) (Fig. 4).

The increase of TOC concentrations with the increase of temperature was noted for some British riv-

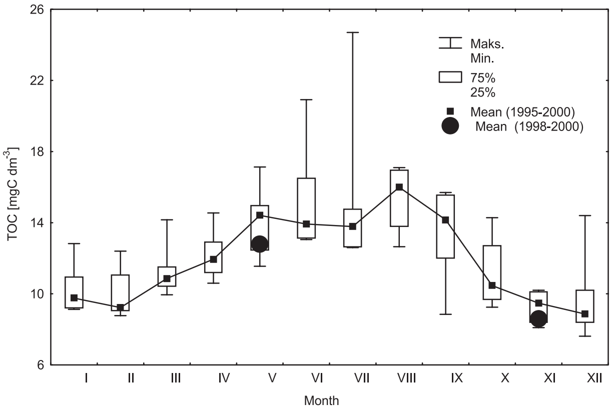


Fig. 3. Seasonal variability of TOC mean concentrations in waters in the close-to-mouth section of the Odra River in Krajnik Dolny (960 km) in 1995-2000 and the Odra Basin in 1998-2000.

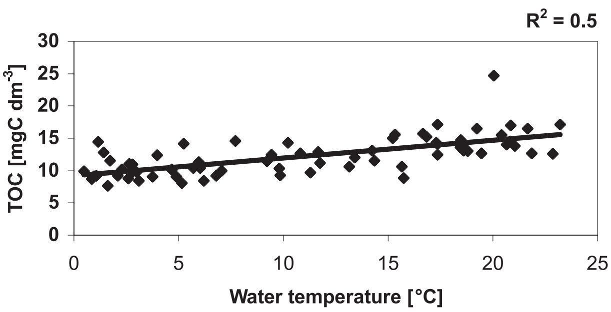


Fig. 4. Relation between TOC mean monthly concentrations in waters and mean monthly water temperature in close-to-mouth section of the Odra River in Krajnik Dolny (690 km) in 1995–2000.

Table 2. DOC and TOC values in world river waters.

| Continent | River | | Year | DOC [mgC dm$^{-3}$] | TOC [mgC dm$^{-3}$] | Literature |
|---|---|---|---|---|---|---|
| Europe | Odra Basin | | 1998-2000 | 2.5 – 16.3 | 3.7 – 29.0 | own research |
| | Odra (Chałupki) | | 1994 | | 6.0 – 13.0 | Siepak, 1999 |
| | Odra (Wrocław) | | | | 5.5 – 13.0 | |
| | Odra (Krajnik Dolny) | | | | 7.8 – 23.8 | |
| | Warta (Poznań) | | | | 10.3 – 20.7 | |
| | Bug (Warszawa) | | | | 6.2 – 28.9 | |
| | Narew (Półtusk) | | | | 6.7 – 23.0 | |
| | Wisła (Warszawa) | | | | 4.2 – 18.2 | |
| | Wisła (Kraków) | | | | 5.8 – 11.2 | |
| | Wisła | close-to-mouth section | 1985-1993 | | 21.1 | Niemirycz, 1985-2001 |
| | Odra | | 1990-2000 | | 11.4 | |
| | Ina | | | | 12.1 | |
| | Rega | | | | 10.4 | |
| | Parsęta | | 1990-1992 | | 11.0 | |
| | Grabowa | | | | 5.7 | |
| | Wieprza | | | | 7.5 | |
| | Słupia | | | | 10.1 | |
| | Łupawa | | | | 6.6 | |
| | Łeba | | | | 10.8 | |
| | Reda | | 1991-1993 | | 14.4 | |
| | Pasłęka | | 1990-1992 | | 12.1 | |
| | Ner | | 1997 | 13.4 – 86.0 | | Bojakowska, 1998 |
| | | | 1998 | 8.6– 28.0 | | |
| | Loire | | | 3.5 | 5.5 | Thurman, 1986 |
| | Rhine | | | 5.5 | 8.5 | |
| | Garonne | | | 3.2 | 5.7 | |
| | Danube | | | 5.8 | | |
| | Seine | | | 2.4 | | |
| | Tage | | | 2.2 | | |
| | Mura | | 1990-1998 | 1.8 – 8.1 | | Brodnjah-Voncina, 2002 |
| East Europe and Asia | 12 Russian rivers flowing into the Arctic Ocean | | 1994-1995 | 2.8 – 12.1 | 3.1 – 13.9 | Lobbes, 2000 |
| Asia | China | | | | 1.0 – 10.0 | Tao, 1998 |
| | Japan | | 1994-1996 | | 1.5 – 3.3 | Imai et al., 2001 |
| | Yangtze | | | 7.0 | | Thurman, 1986 |
| | Brahmaputra | | | 5.0 (1 – 29) | | |
| | Indus | | | 5.0 (1 – 40) | | |
| South America | Orinoko | | | 5.0 | 6.0 | |
| | Amazon | | | 5.0 | 10.0 | |
| | Rio Negro | | | 8.0 | 11.0 | |
| North America | Mississippi | | | 3.5 | 7.5 | |
| | Missouri | | | 4.5 | 24.5 | |
| | Saskatchewan | | | 9.0 | 11.0 | |

ers. On the basis of monitoring data from 18 months, the distinct relation between DOC concentration level in water and temperature was observed. The water temperature was a major factor and it enabled us to define the relation between DOC and water flow in the Humber rivers [15].

There was no relationship between mean monthly TOC values and mean monthly water flows in the Odra River section in Krajnik Dolny (1995–2000) (Fig. 5).

In the shorter period of 1998-2000 (the Odra Basin) only in selected close-to-mouth sections of the Odra river

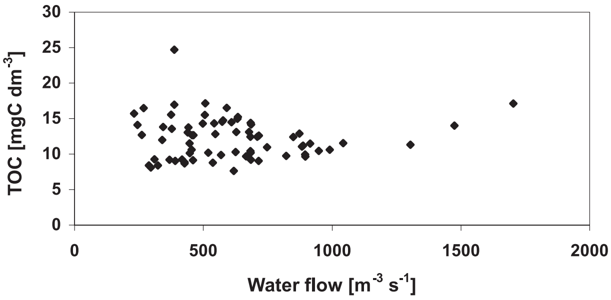


Fig. 5. Mean monthly TOC concentration levels in waters in relation to mean monthly water flows in close-to-mouth section of the Odra river in Krajnik Dolny (690 km) in 1995-2000.

tributaries (Kaczawa, Warta, Bóbr) was the relationship between TOC and DOC values and water flow (measured in the same day as the samples were collected) observed (Figs. 6a and 6b).

Dissolved Organic Carbon (DOC) constituted a major fraction of total organic carbon content in the Odra River and its tributaries in 1998-2000. The mean organic carbon percentage content (POC) in suspended particles was below 35% of TOC value in close-to-mouth section of the Odra River, and about 20% in close-to-mouth sections of its tributaries (Fig. 7). Similar values were observed for the Amazon River and its tributaries as the POC content was in the range of 20-40% of TOC content. Exchange between the fraction (TOC, DOC) is important for some phenomena such as metal transport by organic matter because this kind of transport and molecular mass distribution of associated metals to organic matter are closely connected with the size of the organic material [16].

The extreme values and the range of TOC concentration levels in bottom sediment samples collected from the Odra Basin in 1998-2000 were decreasing in the analyzed period (Fig. 8). Similarly, the mean arithmetic values of TOC were decreasing each year and were equal to 63 mgC $g^{-1}$s.m. (1998, n=32), 49 mgC $g^{-1}$s.m. (1999, n=20) and 29 mgC $g^{-1}$s.m. (2000, n=21) respectively, where (n) is the number of samples. Decrease of TOC concentration levels in sediment samples is probably connected with de-

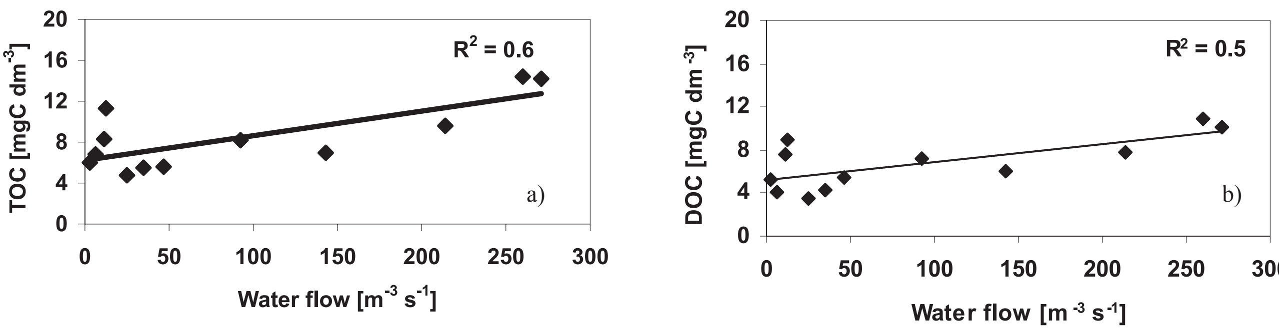


Fig. 6. Relationships between TOC (a) and DOC (b) concentration levels in water samples and water flows in close-to-mouth sections of the Odra River in 1998–2000.

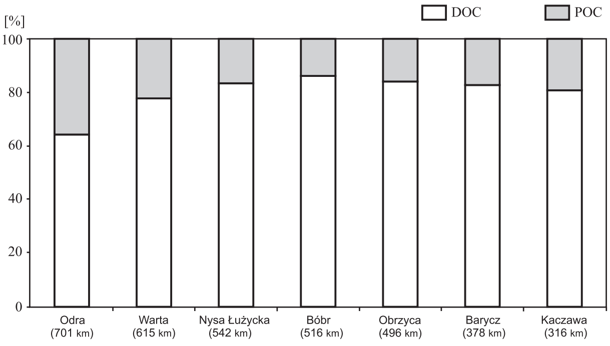


Fig. 7. The portion of the DOC and POC mean values in close-to-mouth sections of the Odra River and its tributaries in 1998–2000.

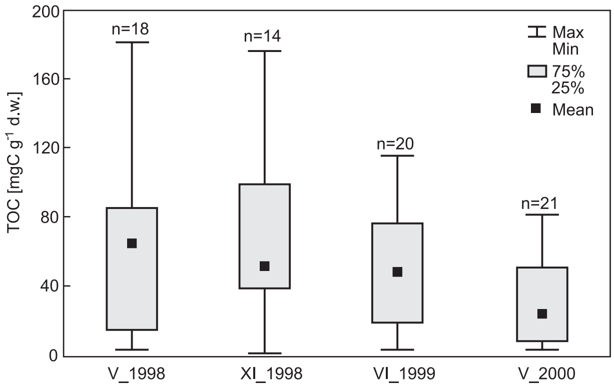


Fig. 8. TOC concentrations in bottom sediments of the Odra River and its tributaries in 1998-2000. (data from 23 sampling points – see Table 1).

creasing pollutants in river sediments after an enormous flood in the Odra Basin in 1997.

These results are higher than those obtained in the tests conducted by the Polish Geological Institute, in which TOC content in bottom sediments in Polish rivers fluctuated from about 2 to 119 mgC $g^{-1}$s.m., and the mean value was 19 mgC $g^{-1}$ s.m. [17].

The analysis of organic carbon distribution in bottom sediment-water pattern showed that TOC content in the bottom sediments is more than 4,000 times higher than in water for the Odra Basin in 1998-2000.

## Summary

- In accordance with Polish and German legislation, about 40% of tested water samples from the Odra Basin can be qualified as those loaded with organic substances exceeding standards. The highest TOC concentrations were observed in close-to-mouth sections of right-bank tributaries of the Odra River and in waters from close-to-mouth section of the Odra watercourse (701 and 715 km). On average, higher TOC concentrations in the Odra River and its tributaries in comparison with other bigger European rivers indicate that the majority of pollutants are anthropogenic.
- TOC and DOC concentration levels in river waters change seasonally; the relationship between TOC concentration and water temperature was observed.
- It was not possible to define the relationships between TOC and DOC concentration levels and water flow in rivers for the majority of measuring points. Only in measuring points located in close-to-mouth areas of some tributaries of the Odra River was this observed.
- Dissolved Organic Carbon (DOC) constituted the main fraction (63-85%) of TOC in analyzed water samples.
- Organic carbon content in bottom sediments of the Odra Basin is more than 4,000 higher than in water, which confirms the significant accumulation of organic matter in bottom sediments.

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