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INFLUENCE OF HUMAN ACTIVITY ON POLLUTION OF THE WIEPRZA RIVER

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Abstract

The measurements of chemical components in water of Wieprza River showed that water of this river in 2002-2003 was characterised by the high purity. The average values of most indexes were contained in the ranges of standards for the first purity class. Nevertheless considerable increase of investigation parameters was observed in zone of sewage-treatment plant and uncontrolled waste dump. The part of flow downing pollutions were absorbed by peat soils. Kepice town bring into Wieprza River the load of organic matter miscalculating to BOD₅ average 133 kg O₂ d⁻¹ (85 t O₂ y⁻¹), the load of nitrogen 140 kg N d⁻¹ (51 t N y⁻¹) and phosphorus 18 kg P d⁻¹ (6.2 t P y⁻¹). However Wieprza River shows high self-purification ability. The level of investigation components in this river (4 km outside of the Kepice town) returned to the level which was 2 km before the town.

Key words: water, peat soil, river, chemical compositions

INTRODUCTION

The main reasons of waters pollution are: industrialization and urbanization increase, chemicalization of agriculture, the lack or not sufficient number of sewagetreatment plants by those waters and inappropriate use of polluted waters.

Beside economic utilization, the use of Pomeranian landscape for touristic and recreation purposes is the main source of impact on a quality of Pomeranian waters. It is reflected by the continuous increase of tourist activities in their various forms, permanent building and development of recreation centers. Among not numerous studies on the Middle Pomeranian rivers one should mention those studies on chemicalization of the Słupia River (Wilamski 1970, Friedrich and Wilamski 1985, Moczulska et al. 2006), the Parsęta River (Korzeniewski et al. 1961), Wieprza, Słupia and Parsęta Rivers (Moczulska and Korzeniewski 1976). The example of degradation of the Middle Pomerania's rivers is the Łupawa River (Korzeniewski et al. 1989). Geochemical examination in the northern Poland was conducted in a small degree. Czubiński and Szafer made a geobotanic regionalization of Pomerania (Augustowski 1977). Apart from the fact that many different types of peat and biotopes are present, the matter of peat soils was seldom touched.

The purpose of presented study was:

- to examine the transformation of chosen water pollution indexes in the Wieprza River,
- to define the influence of wastes stored in peat soils in Kepice area on environmental pollution.

AREA DESCRIPTION

Kepice region is situated in Słupsk district in the valley of the Wieprza River. Many arms of old river-bed make it possible to keep the high humidity of soils. The fact that Kepice town is situated in the Wieprza Valley is the reason of the underground waters high level. That fact is conducive to the development of marshy and peat flora. The agricultural activity is rather small. The studied peat soils are mainly used as permanent grassland.

Wood processing industry and a large "Kegar" tannery (existing till mid 90's) are the main representatives for industry on that area. Whilst tannering industry was developing in Kepice, impurities formed in production processes entered the Wieprza River (flowing through Kepice) and near situated soils. Wastes were transported to a "wild" waste dump located near Kepice town.

MATERIALS AND METHODS

The water samples from the Wieprza River and peat soils to be examined were taken from five specific places once a season in 2002-2003. Water samples were taken with a Ruttner's sampler. The peat soil was taken using soil drill Hiller type. Drillings were made in a 5 m distance from the river. Samples were 50 cm thick peat soil layer that were placed into hermetic containers. After homogenization samples were dried at 105°C temperature to constant mass in order to determine humidity.

Figure 1 presents the location of stations:

- Station 1 contained area directly by the Wieprza River and on the Wieprza River south from Kępice,
- Station 2 contained area next to the Wieprza River and on the Wieprza River near the former tannery,
- Station 3 contained area near the sewage-treatment plant and on the Wieprza River,
- Station 4 contained area directly next to the Wieprza River and on the Wieprza River north from Kępice,
- Station 5 was located in the northern part of the town, near uncontrolled waste dump.

Chemical analyse of water samples was made using methods given in Standard Methods (1992). The oxygen content in the studied water was examined by Winkler method and the water reaction using pH-meter. The organic matter content was determined through studying a biological oxygen demand. The suspended matter content was determined by gravimetric method. The concentration of nitrite nitrogen was determined by colorimetric method with sulphanicacid and naphthtyloamine, the concentration of nitrate nitrogen by colorimetric method with phenyldisulfonic acid and the concentration of ammonium nitrogen by colorimetric method with direct Nessler process.

The elementary soil composition using works by Nowosielski (1974) and Lityński et al. (1962), pH – using potentiometric method in 1M KCl solution, the content of organic matter as a loss during roasting at 550°C temperature (the loss after roasting is surely agreed index estimating the content of organic matter) were determined in dried soil samples. The ash was determined using gravimetric method after roasting of samples and dissolving the residue in hydrochloric acid. Organic carbon was determined using dichromate method.

Calcium, magnesium, ferrum and aluminium were determined using complexical methods and chlorides using argentometric method.

Phosphate phosphorus was examined by colorimetrical method with ammonium molybdate and using ascorbic acid as a reducer, whilst total phosphorus was determined in the same way but after prior sample mineralization in the mixture of nitric acid (V) and hydrochloric acid (VII). In order to determine total nitrogen, the sample was mineralized using sulfuric (VI) and hydrochloric (VII) acids, and then nitrogen was determined by Kiejdahl method.

RESULTS AND DISCUSSION

The average dissolved oxygen content in all testing stations of Wieprza River was significant during the whole studied period and reached at the average 10.9 mg $O_2 I^{-1}$ (Tab. 1) and was involved in the range fixed for the first water purity class (6 mg $O_2 I^{-1}$). Korzeniewski et al. (1989) observed similar values in Łupawa River.

The average annual value of BOD₅ index was relatively small and reached 3.9 mg $O_2 I^{-1}$. Its value was in the first purity class (i.e. till 4 mg $O_2 I^{-1}$) along the whole studied length of the Wieprza River. It exceeded the value 4.0 mg $O_2 I^{-1}$ only at station 3 behind the sewage-treatment plant. At that station as well, the highest $ChOD_{Cr}$ values (21.3 mg $O_2 I^{-1}$) were observed (Tab. 1). Similar levels of BOD₅ index were given for Słupia River by Moczulska et al. (2006) in 2003, and for Łupawa River by Korzeniewski et al. (1989). Twice greater values for that index were observed in Bukowina River (Trojanowska 1996) and Charstnica River (Trojanowska et al. 1996). The changes of average values of water reaction (pH) in front of and behind Kępice along the Wieprza River in 2002-2003 did not show considerable differences, with the average pH value at the level 7.8 (Tab. 1). The water reaction changed in the range assigned for the first purity class (7.1 – 8.4).

Table 1

Parameters	Stations					x*	v	v	S
	1	2	3	4	5	Α.	x _{min}	x _{max}	5
Colour (mgPt l ⁻¹)	30	25	30	28	30	29	20	40	8.2
pН	7.8	7.7	7.9	7.8	7.8	7.8	7.2	8.3	0.46
O_2 (mgO ₂ l ⁻¹)	11.2	10.6	10.7	11.2	11.0	10.9	9.8	12.9	0.93
BOD ₅ (mgO ₂ l^{-1})	3.5	3.8	4.5	4.0	3.9	3.9	3.1	5.3	0.81
ChOD (mgO ₂ l^{-1})	20.1	19.4	21.3	20.9	21.0	20.5	17.4	24.3	3.0
T-N $(mgN l^{-1})$	2.09	2.21	2.47	2.40	2.35	2.30	1.83	2.74	0.41
$NO_3-N (mgN l^{-1})$	1.07	1.09	1.13	1.17	1.16	1.12	0.92	1.30	0.18
NO_2 -N (mgN l ⁻¹)	0.014	0.014	0.015	0.015	0.016	0.015	0.010	0.021	0.04
NH_4 -N (mgN l ⁻¹)	0.050	0.056	0.064	0.060	0.056	0.055	0.038	0.081	0.015
T-P $(mgP l^{-1})$	0.129	0.158	0.178	0.169	0.163	0.160	0,102	0.205	0.040
PO_4 -P (mgP l ⁻¹)	0.069	0.078	0.080	0.079	0.078	0.076	0.035	0.108	0.031
Susp. (mg l^{-1})	12	14	16	17	19	16	8	23	6.2
$CaCO_3 (mg l^{-1})$	167.7	170.8	170.0	168.0	167.9	168.9	137.7	199.2	29.6
SO_4 (mg l ⁻¹)	24.7	30.2	31.9	31.0	32.6	30.1	18.8	36.8	6.2
Cl $(mg l^{-1})$	8.1	10.3	12.3	10.8	10.6	10.4	4.5	16.1	5.5
Ca $(mg l^{-1})$	49.8	51.7	50.3	50.9	49.9	50.5	30.9	70.4	19.4
Mg $(mg l^{-1})$	3.9	5.1	4.9	4.7	4.5	4.6	2.6	5.8	1.1
Fe (mg l^{-1})	0.39	0.40	0.41	0.39	0.40	0.40	0.24	0.63	0.13
Mn $(mg l^{-1})$	0.083	0.113	0.121	0.110	0.098	0.104	0.061	0.132	0.026

Chemical characteristics of water in Wieprza River (1-5 – stations, x* – mean value, S – standard deviation)

The suspended matter content in that river in the studied section did not show significant differences and varied in the range of average values from 12 to 19 mg Γ^1 with average value 16 mg Γ^1 (Tab. 1). Just it was contained in the first purity class. Similar results were obtained by Korzeniewski et al. (1989) in Łupawa River. However yet Trojanowska (1996) observed in water of Bukowina River three times higher content of the suspended matter.

Along the stream of the river the concentration of ammonium compounds (NH₄-N) increased from 0.050 mg N Γ^1 at station 1 to 0.064 mg N Γ^1 at station 3 and then decreased to 0.056 mg N Γ^1 at station 5 (Tab. 1). The average concentration of that component in the studied period was 0.055 mg N Γ^1 . Similar levels of that parameter were given in the cose of Słupia River water by Moczulska et al. (2006). Four time greater the ammonium nitrogen content were confirmed in Łupawa River (Korzeniewski et al. 1989), and in Charstnica River (Trojanowska et al. 1996). The average annual ammonium nitrogen content at all stations in water of Wieprza River was significantly lower than the admissible value for the first class purity waters

(i.e. below 1.0 mg N I^{-1}). The nitrate (NO₃-N) content was also in the first purity class (i.e. below 1.5 mg N I^{-1}) and reached at the average 1.12 mg N I^{-1} . Lower concentrations of that form of nitrogen were observed in Słupia River water (Moczulska et al. 2006), and in Charstnica River (Trojanowska et al. 1996), and in Bukowina River (Trojanowska 1996).

The participation of ammonium nitrogen, nitrate nitrogen and nitrite nitrogen (NO₂-N) in total nitrogen (T-N) changed along the river. Inorganic nitrogen (54.3% of total nitrogen) prevailed in front of Kępice town (st. 1), whilst behind the town (st. 3) inorganic nitrogen reached only 48.3% of total nitrogen. The average total nitrogen concentration in the studied river was 2.30 mg N I⁻¹. The increased amount of total nitrogen (2.47 mg N I⁻¹) on station 3 was probably caused by the near neighbourhood of sedimentation clarifier from the urban sewage-treatment plant. The average total nitrogen concentration (2.35 mg N I⁻¹) descended along the river at station 5 (situated the farthest north form the town). The participation of inorganic nitrogen increased (52.4% of total nitrogen).

The average phosphate phosphorus (PO₄-P) concentration in the Wieprza River was 0.076 mg P Γ^1 (Tab. 1). The concentration of that component did not exceed the admissible value for the first purity class. The phosphates concentration increased from 0.069 mg P Γ^1 at station 1 to 0.080 mg P Γ^1 at station 3 (after the river passed the town), analogous to nitrogen compounds, the concentration of that component at the studied sector of the river reached the maximum value. Wieprza River waters contained similar phosphate phosphorus quantites as Shupia River waters (Moczulska et al. 2006). However yet obtained values of phosphates concentration in Łupawa River and Charstnica River were several higher then those in Wieprza River.

The average content of total phosphorus (T-P) in the studied period oscillated between 0.129 mg P Γ^1 in front of the town at station 1 and 0.178 mg P Γ^1 at station 3 by the sewage-treatment plant (Tab. 1). The participation of phosphates in total phosphorus (47.5%) decreased along the river. The largest participation was observed at station 1 – 53.5% and the smallest at station 3 – 44.9%. Just in that sector of the river, organic forms dominated among phosphorus compounds.

The literature concerning other rivers on the Middle Pomerania referred mainly to the lower sector of rivers (Zaręba 1998). In that sector the concentration of phosphorus compounds in the Łupawa River (0.185 mg P I^{-1}), in the Słupia River (0.237 mg P I^{-1}) and in the Łeba River (0.203 mg P I^{-1}) was hilder than in the Wieprza River (0.159 mg P I^{-1}).

The similar situation was observed in the case of a nitrogen compounds concentration: Wieprza – 2.26 mg N l⁻¹, Łupawa – 2.41 mg N l⁻¹, Łeba – 2.47 mg N l⁻¹ and Słupia – 2.61 mg N l⁻¹. The concentration of nitrogen inorganic forms, particularly nitrates, was compared with the Wieprza River and reached 1.18 mg N l⁻¹, in the Łupawa River – 1.39 mg N l⁻¹, in the Łeba River – 1.19 mg N l⁻¹ and in the Słupia River – 1.22 mg N l⁻¹.

The content of chloride ions (Cl) oscillated between 4.5 and 16.1 mg Γ^1 (Tab. 1). The concentration of calcium ions (Ca) ranged from 30.9 to 70.4 mg Γ^1 and magnesium ions (Mg) from 2.6 to 5.8 mg Γ^1 . The concentration of total ferrum (Fe) in the Wieprza River was at the same level and reached 0.40 mg Γ^1 . The changes of man-

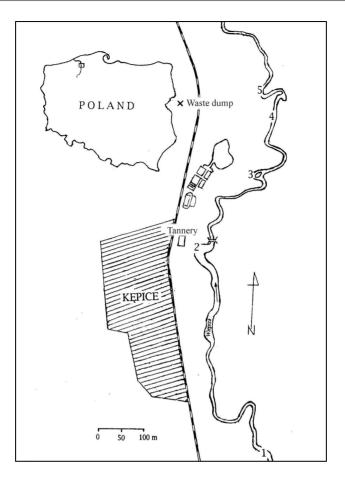


Fig. 1. Location of the sampling stations in the Wieprza River

ganese ions (Mn) content oscillated between 0.061 at station 1 and 0.132 mg Γ^1 at station 3.

The values of some components existing above (st. 1) and below (st. 5) the town were compared in order to determine the influence of the town and surroundings on the purity of the Wieprza River. The measurements of water flow speed showed that all pollution components rose their value (Tab. 1) after the Wieprza River passed Kępice town. That town supplied the Wieprza River at the average with: organic matter in terms of $BOD_5 - 133 \text{ kg O}_2 \text{ d}^{-1}$, that means 85 t $O_2 \text{ y}^{-1}$, respectively total nitrogen $- 140 \text{ kg N d}^{-1}$, that means 51 t N y⁻¹ and total phosphorus $- 18 \text{ kg P d}^{-1}$, that means 6.18 t P y^{-1} .

The physico-chemical soil composition was defined in order to determine if, and in what degree, the pollution adsorbed on peat soils influences the water quality in the Wieprza River.

The soil reaction is the essential factor of the soil. It influences the speed of nutrients liberation in the weathering process, the solubility of many soil components and the quantity of nutrient ions stored in the sorption complex (Gorham 1987).

The distinctive feature of studied peat soils is their considerably high acidifying in the surface layer (from 0.0 to 0.5 m) from pH 3.4 (average) at station 4 to pH 4.1 at station 2 (Tab. 2). Such pH values show that they belong to high acid soils. The only place where peat soil pH was relatively high and reached 8.2 was station 5 near uncontrolled waste dump. The similar pH value was observed on peat land near the village Bagno-Puławy with pH – 6.1 (Maksimow 1959).

On the one hand organic acids arising during organic matter decay and on the other hand low contents of base-forming elements such as: calcium (average values: $3.3-9.8 \text{ mg g}^{-1}$ d.w.), magnesium (0.32-0.68 mg g⁻¹ d.w.) influence on the low pH values. Those values are comparable with reactions of peat soils from Protection Area in Kluki in the Słowiński National Park, where soil pH value varies between 3.1 to 4.6 (Tobolski et al. 1997). But they are higher from considerably acidified soils from villages Krakulice and Karwińskie Błota with soil pH values reaching 2.8 pH (Trojanowski and Parzych 2005).

High pH value at station 5 may be the result of higher content of base-forming elements, such as calcium (9.8 mg g^{-1} d.w.) and magnesium (0.68 mg g^{-1} d.w.) at that station. The uncontrolled waste dump is situated near that station. When "Kegar" tannery run their production, waste products were stored on that waste dump.

Hydrogen ions have an important role in the soil acidity. They have a large influence on soil chemical and biological properties. Soils with high exchangeable acidity (unsaturated sorption soils) have large absorptive properties because acid humus works as protective colloid and is conducive to leaching of other colloids inside profile (Kowda 1984, Turski 1986). The highest values of exchangeable acidity (1.04 cmol kg⁻¹) were observed in peat soils at station 4 with the largest content of organic matter. In turn peat with low organic matter (st. 5) has the lowest exchangeable acidity value (0.68 cmol kg⁻¹). The determination of the exchangeable acidity gives information about the quantity of movable ions H⁺ and Al³⁺ and their participation in hydrolytic acidity. The hydrolytic acidity values varied between 5.1 cmol kg⁻¹ at station 5 and 12.7 cmol kg⁻¹ at station 2.

The studied layers of the peat soils are characterized by very high organic matter values (the loss on incineration – average from 761 mg g⁻¹ d.w. to 920 mg g⁻¹ d.w.). It is caused by decomposition of peat flora. The highest content of organic matter was noted at stations 2 (919 mg g⁻¹ d.w.) and 4 (920 mg g⁻¹ d.w.). That result is comparable with peat soils from a village Biedkowo (918 mg g⁻¹ d.w.) (Maksimow 1959). The lowest content of organic matter was observed at station 5 (761 mg g⁻¹ d.w.) The similar content of organic matter was observed in peat soils near villages Bielawa and Błonie Topola, reaching respectively 866 mg g⁻¹ d.w. and 874 mg g⁻¹ d.w. (Maksimow 1959).

The very high loss on incineration underline the low silica content (average from 69 mg g⁻¹ d.w. at station 2 to 143 mg g⁻¹ d.w. at station 5) and the high organic carbon content (average 419-502 mg g⁻¹ d.w.). Peat soils at stations 2 and 4 (at average 501 mg g⁻¹ d.w.) were the richest with that component.

Table 2

Domonstans	Stations								
Parameters	1	2	3	4	5	х*	x _{min}	x _{max}	S
Mat. org. (mg g ⁻¹ d.w.)	885	919	869	920	761	871	628	997	113
C_{org} (mg g ⁻¹ d.w.)	482	502	473	500	419	475	308	625	151
CaO (mg g ⁻¹ d.w.)	4.1	5.9	6.8	3.3	9.8	6.0	2.5	12.5	3.2
MgO (mg g ⁻¹ d.w.)	0.32	0.61	0.59	0.53	0.68	0.55	0.23	0.89	0.31
$Fe_2O_3 (mg g^{-1} d.w.)$	1.06	1.21	0.91	0.92	0.83	0.99	0.52	1.48	0.42
$Al_2O_3 (mg g^{-1} d.w.)$	0.51	0.88	0.62	0.73	1.22	0.79	0.24	1.50	0.53
MnO (mg g ⁻¹ d.w.)	014	0.32	0.41	0.21	0.28	0.27	0.08	0.65	0.18
CO_3^{-2} (mg g ⁻¹ d.w.)	5.2	7.3	8.2	3.5	9.3	6.	1.7	11.6	4.6
$SiO_2 + z (mg g^{-1} d.w.)$	134	104	143	69	187	127	38	216	83
рН	3.9	4.1	3.7	3.4	8.2	4.7	3.1	8.8	2.4
N-NH ₄ (mg g ⁻¹ d.w.)	0.036	0.034	0.155	0.044	0.092	0.072	0.018	0.169	0.051
T-N (mg g^{-1} d.w.)	13.4	15.3	20.8	18.8	17.2	17.1	9.1	25.2	1.6
T-P (mg g^{-1} d.w.)	3.2	4.5	7.1	6.1	5.6	5.3	1.1	9.6	0.5
Cl^{-} (mg g ⁻¹ d.w.)	0.072	0.081	0.150	0.084	0.192	0.116	0.041	0.247	0.052
H _a (cmol kg ⁻¹ w.w.)	0.84	0.89	0.74	1.04	0.68	0.84	0.43	1.27	0.35
H_h (cmol kg ⁻¹ w.w.)	11.5	12.7	5.4	9.9	5.1	8.9	2.5	15.1	5.4

Chemical characteristics of peat soils located near Wieprza River (x^* – total mean value, S – standard deviation, H_a – exchangeable acidity, H_h – hydrolytic acidity)

Chloride anion is not sorbed exchangeable (exceptionally in minimum degree by humus) and therefore it is washed out very fast from the upper soil layers or taken by the plant. In small doses, chloride anions increase protoplasma release and at the same time decrease a transpiration and improve the plant water balance (Roguski 1973). Moreover they increase the protein content in the plant. The admissible critical contents of chloride ions are very small and different for various plants. According to Chapman (1961) the content of chloride anions should not exceed 0.1 mg g⁻¹. They have toxic properties for larger concentrations.

The average content of chloride ions in the surface layer of those peat soils of 0.0--0.5 m was the highest in samples at station $5 - 0.192 \text{ mg g}^{-1}$ d.w. and station $3 - 0.15 \text{ mg g}^{-1}$ d.w. Peat from Kluki and Krokulice (Trojanowski et al. 2000) also have the large content of chlorides, the sea neighbourhood is the reason for their large content. The high chloride ions concentration at station 5 may be caused by anthropogenic pollution.

At both stations the highest concentrations of ammonium ions were also observed (Tab. 2). The concentration of ammonium ions was highest at station $3 - 154.8 \ \mu g \ N g^{-1} d.w.$

The studied peat soils at those stations were characterized by the high content of total nitrogen at the average 17.1 mg P g⁻¹ d.w. and total phosphorus at the average 5.3 mg P g⁻¹ d.w. Peat soils at station 3 near the waste clarifier have the highest value of total nitrogen (20.8 mg N g⁻¹ d.w.).

CONCLUSIONS

- In 2002 and 2003 the Wieprza River was characterized by the high water purity. The average values of most indexes were contained in the ranges of standards for the first purity class. Hydrochemical investigations carried out in last years clearly showed that the out of order sewage-treatment plant and uncontrolled waste dump have a negative impact on the water quality in the Wieprza River. Probably the water from the pollution clarifier without any purifying flows into the river. The increased indexes of water purity at station near the clarifier confirm that situation.
- The self-purification process is observed in the water of the Wieprza River along its stream.
- The increased concentration of nitrogen and phosphorus compounds in the Wieprza River during its flow through Kepice town confirms that Kepice town is one of the most essential sources of sewage flowing into the Wieprza River.
- The highest values of exchangeable acidity (1.04 cmol kg⁻¹ in the layer 0.0-0.5 m) were observed in peat soils at station 4, with the largest content of organic matter. Peat with the smallest content of organic matter (st. 5) have the lowest value of exchangeable acidity (0.68 cmol kg⁻¹).
- The studied peat soils at stations 3 and 5 were characterized by the high content of total nitrogen at the average 17.1 mg g⁻¹ d.w. and total phosphorus at the average 5.3 mg g⁻¹ d.w.).
- The increased content of chloride ions in the studied peat soils at station 3 and 5 confirms the distinct influence of the sewage-treatment plant and waste dump.

To maintain the good water quality in the Wieprza River one ought to order the water sewage disposal in Kepice and properly protect the waste dump.

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WPŁYW ANTROPOGENICZNY NA ZANIECZYSZCZENIE RZEKI WIEPRZY

Streszczenie

Określenie składu chemicznego wody w rzece Wieprzy pozwoliło stwierdzić, że wody tej rzeki charakteryzują się dużą czystością. Większość analizowanych składników mieściła się w granicach norm dla I klasy czystości. Niemniej jednak w rejonie oczyszczalni ścieków i niekontrolowanego wysypiska odpadów obserwowano znaczny wzrost badanych parametrów. Badania gleb torfowych wykazały, że część spływających ku rzece zanieczyszczeń jest absorbowana przez te gleby. Oszacowano, że miasto Kępice, przez które przepływa rzeka Wieprza, wprowadza do niej ładunek materii organicznej, w przeliczeniu na BZT₅, średnio 133 kg O₂ d⁻¹ (85 t O₂ r⁻¹), ładunek azotu 140 kg N d⁻¹ (51 t N r⁻¹) i fosforu 18 kg P d⁻¹ (6,2 t P r⁻¹). Jednak rzeka Wieprza wykazuje duże zdolności samooczyszczające, ponieważ około 4 km za miastem poziom badanych składników wody powraca do wartości, jakimi charakteryzowały się wody tej rzeki 2 km przed miastem.