Maciej Michałowski*

The Occurrence of Phenol Compounds in the Upper Part of the Raba River and the Analysis of Their Sources**

1. Introduction

Surface waters, when used as the source of drinking water for people should meet high quality standards and correspond to the 1st class of purity for inland surface waters.

Krakow is supplied with drinking water that in 97 percent comes from surface waters.

Water supply stations for Krakow are located on the rivers of Raba – the Dobczyce reservoir, Rudawa, Dłubnia and Sanka. The basic function of the Dobczyce reservoir on Raba is ensuring the water supply for Krakow. A real threat for the purity of waters in the reservoir are pollutants introduced directly by the Raba river, as well as the processes of eutrofication in the reservoir [1].

2. The Characteristic of the Study Area

The Raba river goes through the Małopolska Province, its spring area is on the altitude of 785 m a.s.l. It goes through the West Beskidy, Pogórze Zachodniobeskidzkie and the western part of the Sandomierska Valley. It goes through the following localities: Bochnia, Myślenice, Rabka, Raba Niżna, Raba Wyżna, Chabówka, Mszana Dolna, Gdów and Dobczyce, where the reservoir is located. Due to the length of the river, which is 131.9 km and the surface of the catchment: 1537.1 km^2 Raba is regarded a small river.

* Faculty of Fuels and Energy, AGH University of Science and Technology, Krakow
** The paper was financed from the grant of the AGH no. 10.10.150.961

The most important tributaries of the Raba river, above the reservoir are:
- left-bank tributaries:
  - **Poniczanka** – length 10.0 km, getting in the locality of Rabka in 114 km of the Raba river, the springs of this tributary are on the altitude of 920.0 a.s.l.;
  - **Lubieńka** – of the catchment of 47 km^2;
  - **Krzoczonówka** – of the catchment of 92.2 km^2 and length 17 km;
  - **Trzebunia-** of the catchment of 32.8 km^2;
- right-bank tributaries:
  - **Mszanka** – at the 20 km of the Raba river, its length is about 17 km, and its tributaries are: Koninka and Konina, which are the most water abundant tributaries in the whole Raba catchment.
  - **Kasinka** – of the catchment of 49.6 km^2.

The catchment of the Raba river is characterized by a relatively large altitude differentiation. About 31% of the area is between 250–500 m a.s.l., 48% ranges from 500 to 700 m a.s.l., 20% is betweem 700–1000 m a.s.l., and 1% make the areas above 1000 m a.s.l. Below the locality of Rokiciny the Raba river is not a mountain stream any more. In the Mszana Dolna valley the riverbed width is 20–30 m. Below the reservoir Raba flows through the Pogórze Wielickie to the Raba mouth to the Vistula in the western part of the Sandomierz Lowland. The most important tributaries below the reservoir are: the stream of Krzyworzeka of the catchment of 77 km^2 and Stradomka, the biggest tributary of the Raba, catchment of 368 km^2.

The geomorphology of the studied area is within the covers of the Quaternary formations and the bed of the Carpathian flysch rocks (sandstones and tiles, with a small participation of other formations). The mean annual temperature for the whole area ranges 2.7–7.9°C. From the data of many years it was found that the minimal precipitation was in February and maximal in July. In the studied area mean temperatures and summary precipitations are very differentiated, which is caused by local morphological conditions. Agricultural areas make 54% of the whole are and forests make 44%. In the structure of agricultural areas the arable land takes 44.1% and green areas – 8.6%. The structure of agricultural use of the study area shows its lack of compatibility with environmental conditions of the area – with too large amount of arable land and too small participation of green areas.

3. The Sources of the Raba River Pollution

The chemical composition of pollutants is formed by natural factors, e.g. the leaching of substances from soils and rocks, development and death of aquatic organisms and anthropogenic factors. Anthropogenic pollutants of the surface wa-

ters of the Raba river come from point and surface pollution sources. They are the result of: urbanization, industrialization and agriculture. The most frequent anthropogenic pollutants are: pesticides, surface-active substances, aromatic hydrocarbons, phenols, chloral derivatives of biphenyls and heavy metals, mainly: lead, copper, chromium, cadmium, mercury and zinc [2].

The sources of point pollution are mainly the releases of raw sewage, as well as insufficiently treated wastewater, released through municipal output pipes, from the sewerage-equipped areas, arising as a result of municipal activities of humans and industrial, i.e. released from industry or commercial enterprises other than municipal wastewater or polluted precipitation water washed out from the roads (e.g. the main road Kraków-Zakopane). Municipal wastewater come from households and contain urine, faeces, kitchen wastes and detergents. They release organic matter and dissolved mineral substances in the form of nitrates and phosphates into rivers and reservoirs [3].

Important objects releasing municipal wastewater to the waters of the Raba river above the Dobczyce reservoir are:

- municipal wastewater treatment stations of the towns of Rabka-Zdrój, Mszana Dolna and Myślenice;
- The House of Social Welfare and the inn "Czarny Lew" in Pcim, as well as the Voluntary Fire Brigade in Stróża;
- holiday resorts, schools, kindergartens, medical centres;
- small local municipal wastewater treatment stations (Raba Niżna, Pcim).

Surface pollution come from surface washout and erosion of soils from agricultural areas, forest lands and urban areas not equipped with sewerage systems. Agricultural use of catchment, permeability of soils, supplying surface waters with shallow ground waters and forestation affect surface washout significantly. Together with infiltrating precipitation, atmospheric pollutants get into the waters of the reservoir and Raba river.

Pollutants coming from agriculture contain large quantities of biogens, mainly coming from:

- mineral fertilizers
- manure,
- vegetation remains from the crops,
- municipal wastewater.

Nitrates and phosphates coming from mineral fertilizers cause oxygen deficit in water, due to the excessive development of algae. A visible effect of this phenomenon manifests as a so-called algae bloom [4].

Surface pollutants are difficult to identify and their effect on water quality is not immediate, unlike in point pollution.

4. Physicochemical Analysis of the Raba Water

In the framework of the studied topic the following tasks were carried out:
- the methods of sampling were found and the place of sampling was determined,
- samplings were carried out in July and October 2008,
- the sources of pollutants emission in the upper part of the Raba river were identified,
- water samples from the river and selected tributaries were taken,
- the phenol index of the studied samples was determined.

4.1. Methods of Water Sampling

Water

The samples were collected in 12 points, 2 in the middle of the river flow and 2 near the each of the river banks. Altogether 48 samplings were made. The samples were put into glass bottles of 1 litre volume. The sampling procedure was according to standards containing directives referring to programmes and techniques of sampling surface fluvial waters. Places of water sampling are presented in figure 1.

Determination of phenol index in water

The principle of determining phenol index in the applied method is based on the formation of yellow complex with 4-nitroaniline and photometric analysis with the application of tray tests [5, 6]. Tray test allow the determination in the range of the measurements from 0.05 to 5 mg/l, with an easy possibility to exchange this range by dissolving. The highest accuracy and sensitivity of the applied method allowed exact analysis of the samples. The analysis in water samples was carried out with a spectrophotometric method, with tray tests and using spectrophotometer DR 3800 sc VIS of HACH LANGE.

5. Results

As a result of the carried out analyses the values of phenol index in water samples of the Raba river were obtained. Their statistical analysis was presented in table 1.

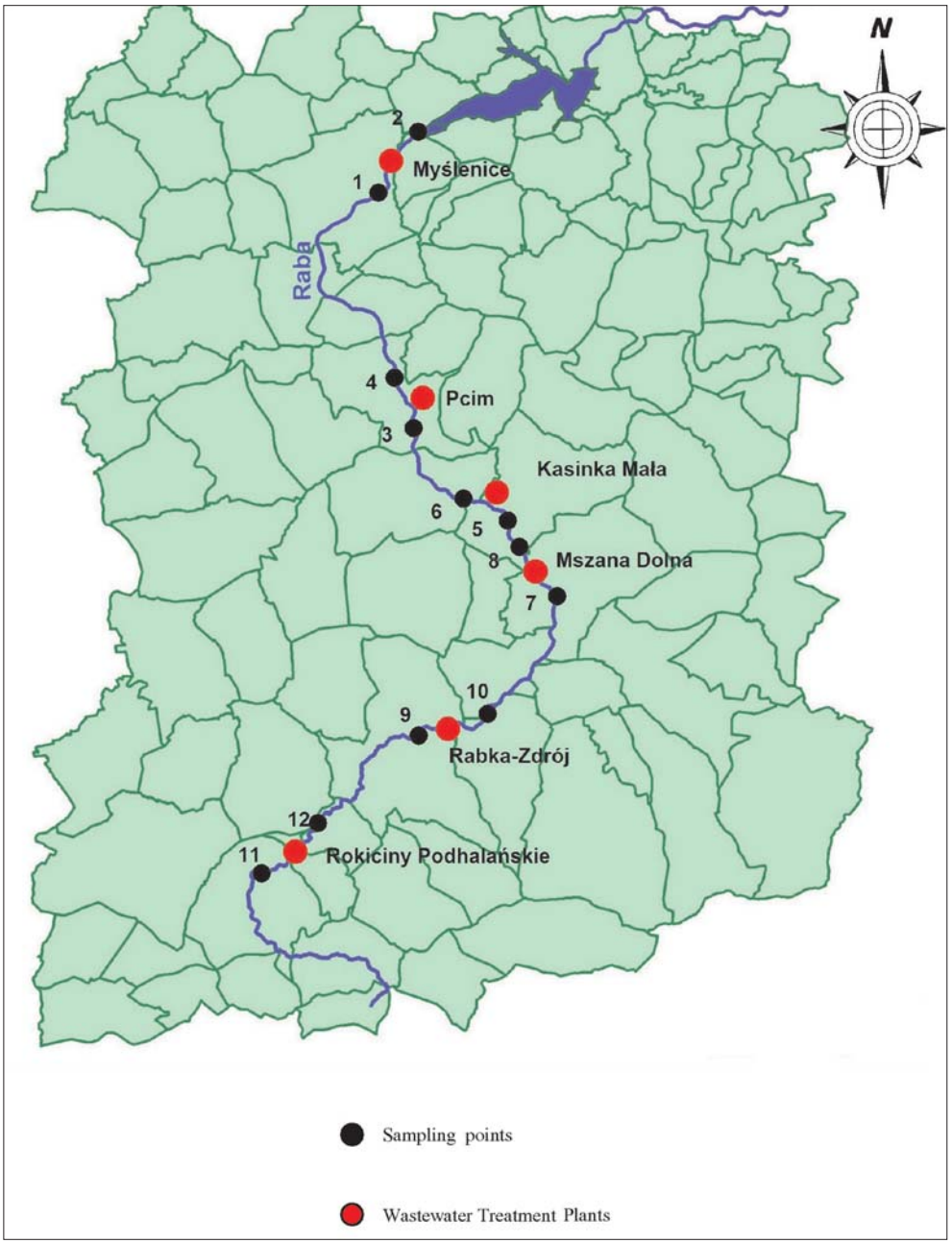

Fig. 1. Places of water sampling on the Raba river

Table 1. The results of the analysis of phenol compounds in the Raba river

No.	Place of sampling	Sum of phenols [mg/dm^3]				Mean sum of phenols [mg/dm^3]
		Sample no. 1	Sample no. 2	Sample no. 3	Sample no. 4	
1	Above the wastewater treatment station of Myślenice	0,00095	0.00095	0.00097	0.00096	0.00096
2	Below the wastewater treatment station of Myślenice	0.00073	0.0016	0.00071	0.00073	0.00094
3	Above the wastewater treatment station of Pcim	0.00084	0.00084	0.00083	0.0017	0.00105
4	Below the wastewater treatment station of Pcim	0.00078	0.0017	0.0017	0.00079	0.00124
5	Above the wastewater treatment station of Kasinka Mała	0.00085	0.00086	0.00086	0.00086	0.00086
6	Below the wastewater treatment station of Kasinka Mała	0.00076	0.00074	0.00074	0.00073	0.00074
7	Above the wastewater treatment station of Mszana Dolna	0.00266	0.00267	0.00268	0.00266	0.00267
8	Below the wastewater treatment station of Mszana Dolna	0.00191	0.00192	0.00191	0.00191	0.00191
9	Above the wastewater treatment station of Rabka Zdrój	0.00101	0.00102	0.00102	0.00103	0.00102
10	Below the wastewater treatment station of Rabka Zdrój	0.00094	0.00095	0.00094	0.00094	0.00094
11	Above the wastewater treatment station of Rokiciny Podhalańskie	0.00146	0.00147	0.00147	0.00144	0.00146
12	Below the wastewater treatment station of Rokiciny Podhalańskie	0.00139	0.00139	0.00137	0.00136	0.00138

Table 2. Statistical values of phenol index parameters in the water of the Raba river [mg/dm^3]

Statistical Parameters	Water
Number of Samples	48
Minimum	0.00071
Maximum	0.00268
Arithmetic Mean	0.001291
Median	0.00099
Standard Deviation	0.0006

The concentrations of phenol index ranged from 0.00071 to 0.00268 mg/dm^3. Mean content of phenol index was 0.00129 mg/dm^3. The highest value was found in the measurement point of Mszana Dolna, the lowest contents were below the wastewater treatment station in Myślenice. The concentrations of phenol index in water samples did not exceed the maximum accepted values for the 1st and 2nd purity class of waters given in the Enactment of the Minister of Enviroment (tab. 2). The analyses were referring to a relatively short period of studies. In a longer period of the monitoring in various seasons it would probably be possible to find a wider range of phenol index values.

6. Closing Remarks and Conclusions

Precise definition of the sources of the emission of phenol compounds into the waters of Raba was relatively difficult due to the fact, that large emitters of these pollutants were not identified. The main, most representative sources were releases of municipal-household wastewater and surface pollution sources of different kind. Surface sources of pollutants usually come from agricultural areas, where some amounts of phenol compounds are washed out from mineral fertilizers and pesticides [7]. The identification of the source of surface pollutants from the catchment, as a result of the atmospheric pollution coming with precipitation and agricultural use, including farming, can only be a rough assumption, because in the catchment there are many sources the surface form of which causes difficulties in the estimation of their scale. Another source of the phenol pollution threat to the waters of Raba is an international road E-7, where traffic in the direction of Zakopane and Slovakia is very intense. This road has been being rebuilt into an express road for many years. The section from Lubień to Myślenice has already

been equipped in rain-sewage system and devices for mechanic treatment of the first wave of rain waters flowing from the motorway. However, so far, despite immense traffic on this route – rain water has not been treated. Only the central areas of Rabka Zdrój and Myślenice have rain sewerage system included to the collectors of municipal sewerage system and to wastewater treatment.

Limit values of the quality indicators for surface waters and phenol index, defined in the Enactment of the Minister of Environment, are shown in table 3, experimentally established values are presented in figure 2.

Table 3. Limit water quality indicators in five classes of water purity

Water Purity Class	Phenol Index [mg/ dm^3]
I	0.001
II	0.005
III	0.01
IV	0.05
V	> 0.05

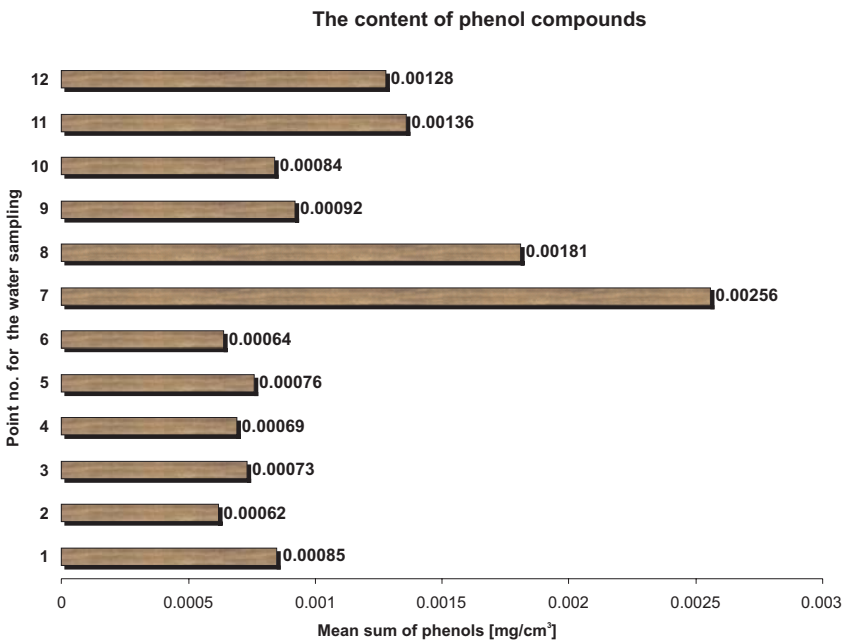

Fig. 1. The values of the sum of phenols obtained as a result of the carried out studies

According to the enactment by the Minister of Environment, referring to limit values for phenol index, the quality of the analysed samples can mainly be referred as class I of water purity [8]. The exceptions are samples taken in the vicinity of wastewater treatment stations of Mszana Dolna and Rokiciny Podhalańskie where the water fall into class II of purity [9, 10]. In the case of the wastewater treatment station of Mszana Dolna, the elevated level of phenols in this area could be caused by an illegal wastewater release point, located above the wastewater treatment station. The results were obtained from the samples taken in July and October 2008. They indicate that intensified construction works at the section Lubień – Rabka and road junction in the vicinity of Lubień can cause an increased pollution of Raba and its tributaries with this group of toxic substances. Raba is a mountainous river taking water from rain, snow and groundwater. The water level is very changeable, low in autumn and high in spring and summer, thus in 2009 the analyses of phenol pollution are planned in spring and summer, when the flow of waters is significantly more intensive.

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