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The Attempts to Identify the Sources of the Emission of Phenol Compounds in the Upper Dunajec Catchment**

1. Structure and Nomenclature of Phenols

The name "phenols" is used to define the compounds formed by the substitution of one or more hydrogen atoms in benzene with hydroxyl groups. Thus in an aliphatic series they are equivalent to alcohols. Their molecules contain hydroxyl groups –OH directly connected with an aromatic radical of a chemical formula: C_6H_5OH; making one of the most burdensome components of wastewaters and occurring in the form of white crystalline solid.

1.1. Physical Properties of Phenols

The simplest phenols are liquids or solids with a low temperature of melting: 42.3°C. Their relatively high temperatures of boiling (181°C), are caused by inter-molecular hydrogen binds. Phenols are crystalline substances of a strong characteristic "sweet" smell. Phenol belongs to very toxic compounds, having germicidal properties and for a long time it was used as a popular disinfection product known as cresol. Nowadays, modern more effective, less dangerous and smelly products replaced phenol totally. Cresols have strong germicidal properties so they were used in disinfection (Lysol). Thymol, even stronger germicidal product, has been used in the dental treatment – to sterilize the cavities cleansed before filling. Stronger bactericidal properties of thymol result from its high lipophilicity – it permeates easier through cellular membranes than hydrophilic phenol.

To determine phenol index in surface waters and wastewaters, usually the following spectro-photometric methods are applied:
- spectro-photometric methods with 4-aminoantipyrine after distillation,
- the method of spectrophotometric determination phenol index with the application of tray tests.

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Spectro-Photometric Methods with 4-aminoantipyrine After Distillation

- The method of direct colorimetric measurement, allowing defining the value of the phenol index for phenol concentrations above 0.10 mg/l without earlier extraction with chloroform and with the application of phenol as a pattern.
- The method with the extraction with chloroform, which allows determining the phenol index with the accuracy of about to 0.002 mg/l to 0.10 mg/l with the application of phenol as a pattern [1].

The Method of Spectrophotometric Determination Phenol Index with the Application of Tray Tests

Phenol index is a number defining the concentration of various phenol compounds in water. The methods of determining the phenol index are defined by the international standard PN-ISO 6439 [6].

1.2. Sources of Phenol Compounds Emission

Phenol and its derivatives are widely spread in the environment. Naturally they are formed during the biodegradation of polymers containing aromatic rings such as lignin and tannins. They are synthesized by plants; make the components of root secretions of plants, as well as components of flower and fruit pigments. They also occur in the animal urine. The main source of phenol compounds of natural origin is the decomposition of organic matter. Dry grass, leaves as well as animal scavenge and faeces biodegrade releasing phenols, and this way posing threat to the environment. Phenol compounds get to waters with the surface flow, occurring during snow-melting or heavy rains [3, 4].

Definitely higher and more burdensome for the environment is the amount of phenols arising as the effect of human activities. Their main source is industry and agriculture, and phenol compounds get to the environment with (among others) wastewaters. The largest quantities of phenol compounds arise during the production of coke from hard coal – they are the main components of coal tar, obtained in this process. They are also released with industrial wastewaters from the plants of chemical industry, petrochemical plants, pharmaceutical industry, paper industry and textile industry. An important emitter of phenol compounds are industrial plants using phenol gums in insulation materials and particle boards, where phenol is made as a result of thermal decomposition of gums. Moreover, significant amounts of difficult to decompose substances, as well as toxic organic compounds, including phenols are contained in wastewaters originating from chemical industry, mainly producing dyes, pigments and varnishes [5]. Similar situation is in case of oil refineries. The threat of the contamination with phenol compounds is also posed by industry making products of rubber and plastics, because the final processes include fat removal, varnishing, painting and mechanical treatment, connected with the release of phenols. The source pollution of natural waters can also be landfills as well as irregularities in municipal wastewater management, including mainly unsealed septic tanks, or illegal releasing of untreated wastewaters directly to streams or rivers. An important source of pollution environment phenols and their derivatives is agriculture [6–8]. The most important in case of phenol-caused hazard is mineral and organic fertilization, particularly dangerous in case of heavy rains, when the precipitation could be absorbed by the soil [9–11]. The rains generate surface flows, taking artificial fertilizers, manure etc. get into waters. The treat is also connected with farming, and specifically with depositing faeces. The lack of proper seals of the objects designed to store the faeces can cause their leak to the drainage system, streams and rivers. The problem is also caused by scavenge and remains from slaughter, which unfortunately are not properly utilized. In table 1 the ways of elimination phenols from respective elements of environment are shown.

Table 1. The time of the elimination of phenol contamination from respective parts of the environment

Place	Kind	Elimination half life
air	photo-oxidation	14 hours
water (at the surface)	photolysis	176 hours
water (depth 1m)	photolysis	19 days

2. The Characteristics of the Upper Dunajec Catchment

2.1. The Upper Dunajec Catchment (Fig. 1)

The Dunajec is a typically mountainous river in the southern Poland. The surface of the catchment is 6804 km^2, including 4854.1 km^2 in Poland, and 1949.9 km^2 in Slovakia (while 1594.1 km^2 make the catchment of Poprad, and 355.8 km^2 – the catchment of the Dunajec proper). The length of Dunajec is 274 km (with Czarny Dunajec). It flows through Podhale, Pieniny, West Beskidy, Pogórze Środkowobeskidzkie and the Sandomierz Valley. There are two sets of water reservoirs at the Dunajec river: in the region of Czorsztyn – the reservoirs of Czorsztyn and Sromowce Wyżne and in the region of – the reservoirs of Rożnów and Czchów. The springs of Dunajec are in the Carpatia and West Tatra mounteins. They make streams: Siwa Woda and Kirowa Woda, which form Czarny Dunajec while streams Zakopianka and Poroniec make Biały Dunajec. Czarny Dunajec joins Biały Dunajec in the town of Nowy Targ, the so-called Samorody area and from this point the river Dunajec begins. Between 154.0 a 171.0 km Dunajec makes the state border with Slovakia. After the fusion of the spring streams Dunajec flows eastwards in a wide valley through the Nowy Targ Valley (Orawa-Nowy Targ Trough). Behind Dębno the river flows to the Czorsztyn Lake, which ends with the dam in Niedzica. In the south from the dam there is another reservoir – the Sromowce Lake 1.5 km long – ending at the dam in the Sromowce Wyżne. Then Dunajec, as a border river goes to the Pieniny Proper, through which it goes as a very sinuous and narrow gorge, surrounded by tall walls. Its main part starts not far from Sromowce Niżne, under the Trzy Korony and ends in Szczawnica. Between Leśnica and Szczawnica the state border turns towards the Małe Pieniny. Behind Szczawnicą the river separates two mountain groups – Pieniny and Beskid Sądecki and goes northwards leaving the Pieniny in Krościenko. Then, starting from Krościenko to the area of Zabrzeże, it makes the border between the Gorce and Beskid Sądecki. Between the Gorce range of Lubań, and Beskid Sądecki there is a small locality Tylmanowa, through which the Ochotnica stream is running, being the tributary to the Dunajec River.

Fig. 1. The Upper Dunajec Catchment

The most important tributaries of the Upper Dunajec are:

- Biały Dunajec – a river running through the Tatra Mountains and the Podhale region is the right tributary of the Dunajec. Its length is 31 km and the catchment area – 224 km^2. It goes through the West Tatras as Małołącki Potok, then Cicha Woda and Zakopianka, which joins Poroniec and makes Biały Dunajec.
- Czarny Dunajec – another river in southern Poland. Its length is 48 km, and the surface of the catchment is 456 km^2. It is formed in Roztoki from the fusion of two small streams: Siwa Woda and Kirowa Woda. In Nowy Targ it joins Biały Dunajec.
- Białka – a river making right tributary of the length 41 km (with the spring stream Biała Woda) the area of the Białka catchment is 230 km^2. Its springs are in the High Tatras, it is formed from the fusion between Rybi Potok and Biała Woda. It goes to the Czorsztyn Reservoir.
- Bystra Woda – a small stream, arising from the fusion of many streams flowing from the valleys situated in the fan shape, developing in the Bystra Valley in the West Tatras. After leaving the Tatras the stream goes through Zakopane, where it joins Cicha Woda forming the Zakopianka River, which is a tributary of Biały Dunajec.

2.2. The Characteristics of the Catchment – Structure of the Land Management

The area of the Upper Dunajec catchment is situated within different spatial formations, characteristic for regional units. According to the physical geographic division of Poland by J. Kondracki and A. Richling the area of the studied catchment is situated in the following sub-provinces “External West Carpathia” and “Central West Carpathia”. Sub-provinces are divided into smaller regional units. The base for such a division is the difference in the type of relief, as well as spatial distribution of convex and concave forms. In the area of the Upper Dunajec catchment smaller units are differentiated, such as the following macroregions: “West Beskidy”, “Orawa – Podhale Trough” and “the Tatra Chain”. The climate of the Upper Dunajec catchment is considerably harsh. Particular parts of the catchment significantly vary in terms of the climate, which depends, among others, on the altitude above the sea level. In case of Nowy Targ (where the Dunajec starts) the harshness of the climate is typical of large mountain valleys, situated among high mountain massifs. In the area of the Upper Dunajec catchment strong winds blow often. There is a distinct influence of the Halny foehn wind, causing warming and quick melting of snow. The precipitation in the Upper Dunajec catchment is strictly linked with the relief. Mean annual precipitation ranges from 800 mm to

1100 mm, the highest precipitation is in summer months (June, July) and the smallest in winter (January, February). Soil environment in the area of the Upper Dunajec catchment is differentiated. This can be a result of several factors, including diversity of geological structure, topographic diversity connected with the inclinations and the altitude, as well as the richness of vegetation and variability of anthropogenic factors. The defined type or soils in a given area is a result of the relationship between the rock bed, climate, relief and vegetation. On the flysh bed of the Upper Dunajec catchment the soils of different properties are formed. They make typical for such mountain areas soil mosaics. As a result of human activities, the soils in a large part of the areas of the Dunajec and Białka catchment are transformed from typical forest soils into soils highly degraded by agriculture or pastures. Most soils of the Upper Dunajec catchment belong to mountainous soils, made of flysh rocks. There are two kinds of soils: shallow clay soils and medium depth clay soils. They are usually classified in class IV and V. shallow clay soils are also called skeleton soils and occur in the highest parts of the mountains, playing important hydrologic role because of their high retention abilities. The other among the mentioned soils are the most widely spread. They are acid soils moderately rich in humus, potassium and magnesium, and poor in possible to assimilate phosphorus [12–15]. The Upper Dunajec Catchment includes two districts: Nowy Targ and Tatra. The structure of land use in the catchment area is presented in table 2 [16–18].

Table 2. The structure of land use in the Upper Dunajec catchment

Lp.	Area	The district of Nowy Targ (percentage of the district total area)	The district of Tatra (percentage of the district total area)
1	arable land	54.5	38.5
2	forests and forest-type land	37.2	48.2
3	other grounds and infertile land	8.3	13.3

3. Defining the Emission Sources for Phenol Compounds Based on the Analysis of the Area

In the Upper Dunajec catchment there are industrial objects posing threat to the environment by the emission of dangerous substances, including phenols. They include:

- "Chemeko" – Elżbieta Kniotek, Nowy Targ;
- "Gumplast – Podhale sp. z o.o., Nowy Targ;
- "Awastek Gospodarka Odpadami" (Awastek Waste Management) – Alina Poray-Zbrozek, Nowy Targ;

- "Garbarnia Sc. Nowotarskie Zakłady Skórzane" (Tanning – the Nowy Targ Leather Industry) – Andrzej Rajski Marek, Nowy Targ;
- "Dafo Plastics sp. z o.o. – Nowy Targ;
- "Zakład garbarski LEJA" (Tanning Industry LEJA) – Leja Jakub, Nowy Targ;
- "Zakład garbarski" (Tanning Industry) – Krauzowicz Andrzej, Nowy Targ.

Wastewaters from these industries can significantly contribute to the pollution of the Dunajec waters, as well as the wastewaters coming from the plants dealing with deposition and utilization of wastes. Some of the companies dealing with waste removal are:

- Przedsiębiorstwo Usług Komunalnych (the Enterprise of Municipal Services) "EMPOL",
- Przedsiębiorstwo Produkcyjno-Handlowe (Production and Trade Enterprise) "ITAL-BIKE" Sp. z o.o.

Unfortunately, despite organized waste disposal, big problems in the catchment are unauthorised landfills, which can make a source of large quantities of phenol compounds. The area of catchment is mainly a recreational area. Unauthorised landfills are usually formed in the areas neighbouring to holiday resorts, near forests and recreational areas, as well as mountain streams often visited by the residents and tourists [19, 20]. Phenols contained in wastewaters can disturb the processes of their biological purification. Already the concentration of phenol in wastewaters above 200 $g \cdot m^{-3}$ inhibits this process. Unsatisfactorily purified wastewaters get to the points of water supply, polluting them with different harmful substances, also toxic ones, including phenols [21, 22]. In the rivers there are the processes of self-purification, which are very sensitive to the content of phenols. In surface waters phenols are subdued to mineralization within 3–4 days, and this process is definitely easier and faster, when water contains other organic pollutants, this way being a good feed for biological organisms. This process gets much slower at the temperature of 10°C, an is fully stopped at the temperature of 4°C, which explains why the problems with phenols become more acute in winter [23, 24]. Disorganised water and waste water management makes the situation when much wastewater gets directly to the water supply system, without being purified, because of so-called illegal releases. Such wastewaters definitely cause water pollution. In the studied area of the Upper Dunajec catchment, there are unfortunately many localities not included into the sewer system, and those with sewer system are not covered by this in 100%. The example can be (among others) the communities of: Poronin, Biały Dunajec, or Czorsztyn. Taking into account the percentage of covering the community into the sewer system the situation is the following: Poronin – 54% under the sewer system, Biały Dunajec – 38%, Czorsztyn – as much as 75%. However, analysing individual localities in these communities, it turns out that in many cases there is no sewer system at all. For example this is the case of: Bustryk, Nowe Bystre (Poronin Community), villages: Leszczyny, Sierockie and Gliczarów Dolny (Biały Dunajec Community). In the case of the community of Czorsztyn, it could look as if the situation was not that bad, because it is connected to the system in 75%. Unfortunately, also in this community there are localities without sewer system, e.g. Huba.

4. The Methods of Determining Phenol Compounds

The sampling of water for the analysis was carried out according to Polish standards. The series of samples were taken in the horizontal profile on the average depth of about 20–50 cm below the water surface. The analysis of samples was carried out within 24 hours from the date of sampling [25, 26]. The analysis of the content of phenol and its derivatives in water samples was done with a spectrophotometric method, using tray tests NANOCOLOR® and spectrophotometer XION500 by HACH LANGE.

4.1. The Location of Sampling Points in the Map

The maps below (Figs 2, 3) present distribution of sampling points. In the tables 3 and 4 the results measurements are shown.

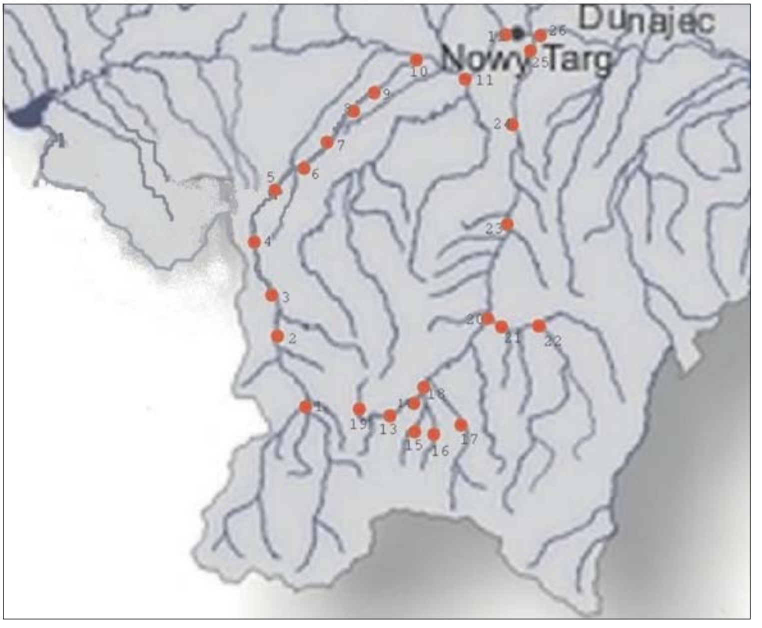

Fig. 2. The places of taking samples on 15.04.2009, 12.09.2009 and 15.06.2009

Fig. 3. The places of sampling on 17.04.2009, 15.09.2009 and 17.06.2009

5. Results

5.1. The Results from the Analyses

The results from the analyses were presented in tables 3 and 4 and at figures 4–12.

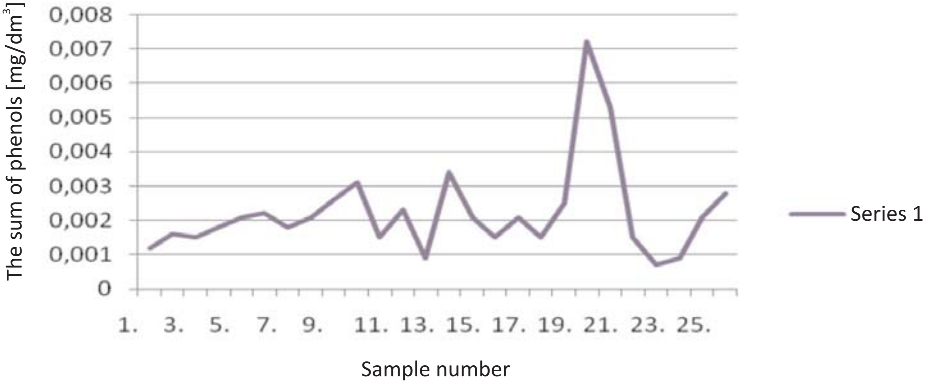

Fig. 4. The content of phenol compounds in the samples analysed on 15.04.2009

Table 3. Results of the measurements of 15.04.2009, 12.09.2009 and 15.06.2010 (according to figure 2)

Sample no.	Stream name	Place of sampling	Sum of phenols [mg/ dm³]			Water temperature [°C]			Class		
			15.04. 2009	12.09. 2009	15.06. 2010	15.04. 2009	12.09. 2009	15.06. 2010	15.04. 2009	12.09. 2009	15.06. 2010
1	Czarny Dunajec	Siwa Polana	0.0012	–	0.0031	5.2	–	12.8	2	–	2
2		Witów – stream gauge Kojsówka	0.0016	–	0.0034	4.5	–	12	2	–	2
3		Chochołów	0.0015	–	0.0052	5.4	–	12.5	2	–	3
4		Koniówka – stream gauge	0.0018	–	0.0068	5.1	–	12.8	2	–	3
5		Podczerwone	0.0021	–	0.0074	4.3	–	13	2	–	3
6		Czarny Dunajec	0.0022	–	0.0082	4.9	–	13.5	2	–	3
7		Wróblówka	0.0018	–	0.0091	5.2	–	12	2	–	3
8		Długopole	0.0021	–	0.0087	4.5	–	12.5	2	–	3
9		Krauszów	0.0026	–	0.0075	4.9	–	12	2	–	3
10		Ludźmierz	0.0031	–	0.0085	4.5	–	13.1	2	–	3
11		Nowy Targ – stream gauge	0.0015	–	0.0092	7.1	–	13.5	2	–	3
12		Nowy Targ – mouth to the Dunajec river	0.0023	–	0.0084	6.7	–	12.4	2	–	3

13	Bystra Woda	Bystra Woda – above the water-taking pump for Zakopane	0.0009	–	0.0042	6	–	10	1	–	2
14	Cicha Woda	Gronik	0.0034	–	0.0051	6.2	–	11.5	2	–	3
15	Cicha Woda	Zakopane Harenda	0.0021	–	0.0054	7.1	–	12	2	–	3
16	Stream Młyńska	Zakopane	0.0015	–	0.0062	6.1	–	12.2	2	–	3
17	Potok Olczyski	Zakopane	0.0021	–	0.0042	5.8	–	11.5	2	–	2
18	Biały Potok	Zakopane	0.0015	–	0.0051	5.9	–	12.1	2	–	3
19	Kościeliski Potok	Kościelisko	0.0025	–	0.0052	6.2	–	11.5	2	–	3
20	Biały Dunajec	Poronin	0.0072	0.0062	0.0241	5.5	9.2	11.2	3	3	4
21	Poroniec	Poronin – below the mouth to Biały Dunajec	0.0053	0.0056	0.0086	5.2	8.2	11.8	3	3	3
22	Cichowiańska Woda	Małe Ciche	0.0015	0.0021	0.0052	4.5	7.5	11.5	2	2	3
23	Biały Dunajec	Biały Dunajec	0.0007	0.0032	0.0058	5.8	10.2	12.2	1	2	3
24		Szaflary	0.0009	0.0035	0.0086	6.7	10.5	12.5	1	2	3
25		Nowy Targ – the mouth to Dunajec	0.0021	0.0042	0.0089	5.1	11	12.2	2	2	3
26	Dunajec	Nowy Targ – joining Czarny Dunajec and Biały Dunajec	0.0028	0.0032	0.0092	5.5	11.5	13.1	2	2	3

Table 4. Results of the measurements of 17.04.2009, 15.09.2009 and 17.06.2010 (according to figure 3)

Sample no.	Stream name	Place of sampling	Sum of phenols [mg/ dm³]			Water temperature [°C]			Class		
			17.04. 2009	15.09. 2009	17.06. 2010	17.04. 2009	15.09. 2009	17.06. 2010	17.04. 2009	15.09. 2009	17.06. 2010
1	Jaworinka	Jurgów	0.0021	0.0012	0.0062	6.2	10	12.2	2	2	3
2	Odewsiański Potok	Bukowina Tatrzańska	0.0016	0.0021	0.0061	6.5	10.5	12.5	2	2	3
3	Białka	Bukowina Tatrzańska	0.0025	0.0015	0.0072	5.5	10.5	11.5	2	2	3
4		Białka Tatrzańska	0.0029	0.0032	0.0063	6.5	11	11.3	2	2	3
5		Dębno – at the mouth to the Czorsztyn Reservoir	0.0046	0.0039	0.0071	7.6	10.5	12.8	2	2	3
6	Dunajec	Waksmud	0.0059	0.0069	0.0059	6.2	11.3	12.3	2	3	3
7		Łopuszna	0.0058	0.0051	0.0058	6	11.2	12.2	2	2	3
8		Harklowa	0.0049	0.0032	0.0052	6.2	11.5	12.5	2	2	3
9		Dębno – at the mouth to the Czorsztyn Reservoir	0.0052	0.0062	0.0052	6.8	11	12.5	2	3	3
10	Czorsztyn Reservoir	150 m behind the dam	0.0021	0.0032	0.0055	6.8	11.6	12.5	2	2	3
11	Sromowce Reservoir	Sromowce Reservoir	0.0012	0.0032	0.0049	6.5	11	13	2	2	2
12	Dunajec	Niedzica	0.0045	0.0038	0.0062	6.2	11.5	13.5	2	2	3
13		Sromowce	0.0052	0.0049	0.0055	5.2	11.8	12.2	3	2	3
14		Szczawnica Niżna	0.0054	0.0072	0.0054	5	11	13.2	2	3	3
15		Krościenko	0.0059	0.0049	0.0059	5.1	11.7	12.5	3	2	3
16		Tylmanowa	0.0042	0.0032	0.0051	5.1	11.8	12.8	2	2	3
17	Ochotnica	Ochotnica Dolna	0.0021	0.0015	0.0062	5	12	12.5	2	2	3

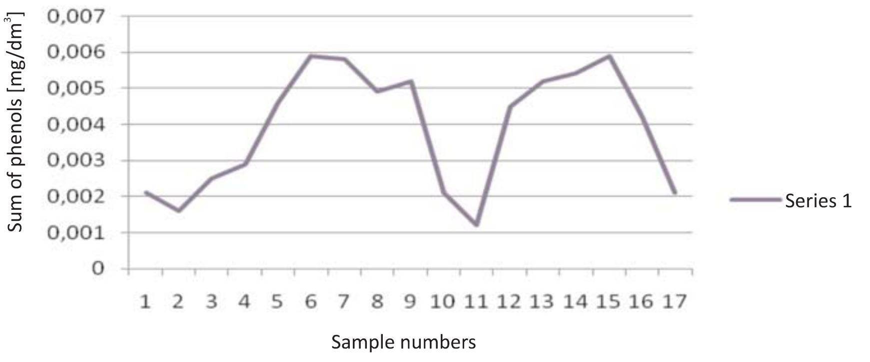

Fig. 5. The content of phenol compounds in the samples analysed on 17.04.2009

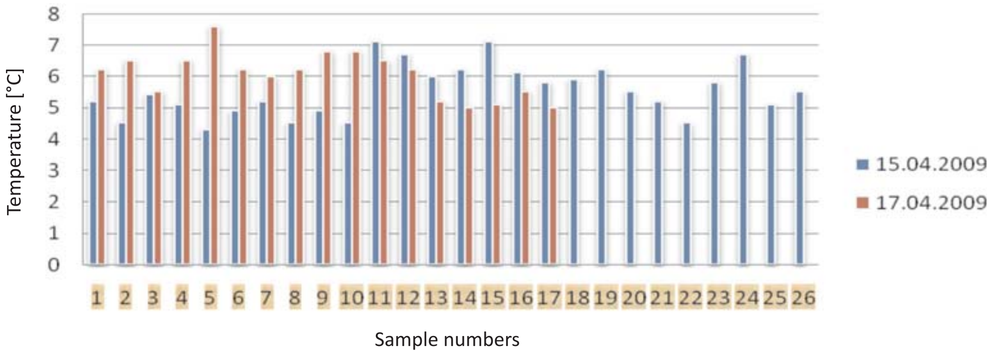

Fig. 6. Water temperature on 15.04.2009 and 17.04.2009

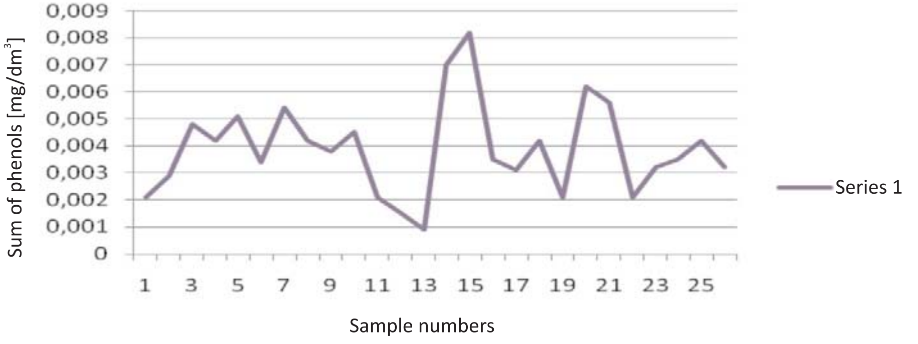

Fig. 7. The content of phenol compounds in the samples analysed on 12.09.2009

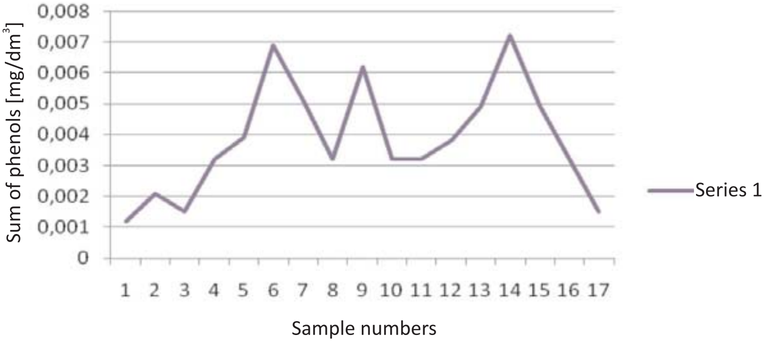

Fig. 8. The content of phenol compounds in the samples analysed on 15.09.2009

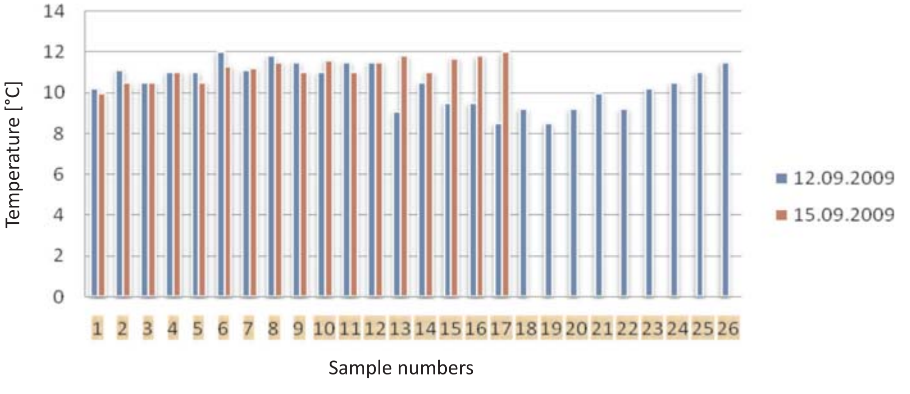

Fig. 9. Water temperature in samples taken on 12.09.2009 and 15.09.2009

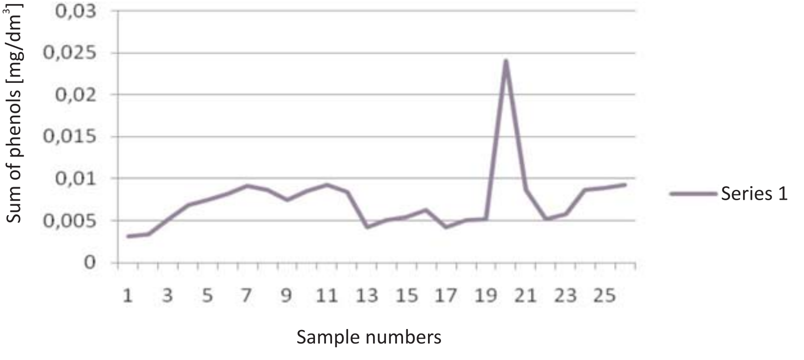

Fig. 10. The content of phenol compounds in the samples analysed on 15.06.2010

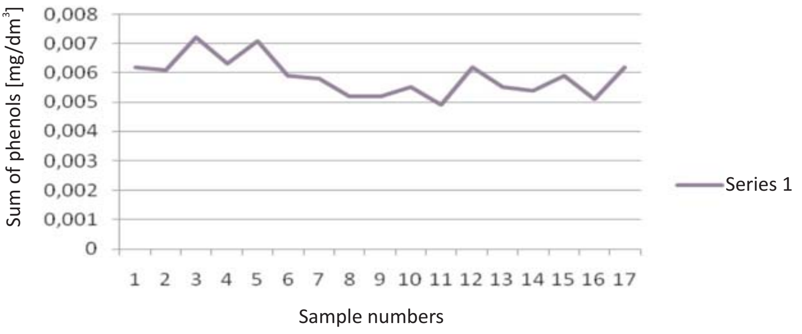

Fig. 11. The content of phenol compounds in the samples analysed on 17.06.2010

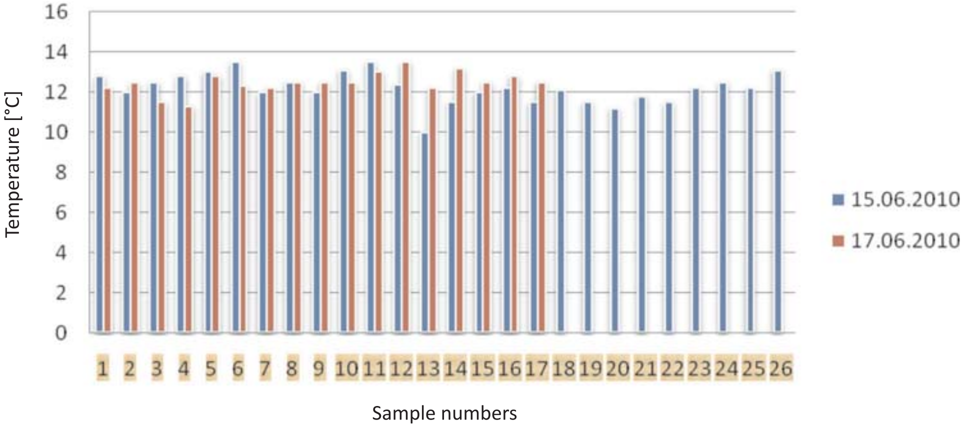

Fig. 12. Water temperature in the samples analysed on 15.09.2010 and 17.06.2010

5.2. The Statistic Analysis of Results

The Statistic analysis of results is presented in tables 5 and 6.

Table 5. Selected statistic parameters for all the samplings in 2009

Statistic parameter	Value [mg/dm^3]
Mean	0.003248
Value (max)	0.0072
Value (min)	0.0007
Median	0.0029
Standard deviation	0.001743

Table 6. Selected statistic parameters for all the samplings in 2010

Statistic parameter	Value [mg/dm^3]
Mean	0.0067674
Value (max)	0.0241
Value (min)	0.0031
Median	0.0061
Standard deviation	0.0031472

6. Conclusions

The studies took 14 months, when the analyses were carried out on 242 water samples. Exact definition of the emission sources of these compounds to waters was relatively difficult, because in the area of the Upper Dunajec catchment no large emitters of these pollutants were identified. The main source of these pollutants is releasing municipal and household wastewaters as well as area pollution of different kind. The area pollution mainly comes from the outflow of the agricultural areas, containing certain amounts of phenol compounds from artificial fertilizers and pesticides. These sources are difficult to control [27]. Identifying the inflow of area pollutants from the catchment as a result of atmospheric pollution and agricultural land use, including farming, is difficult to carry out. As a result of the analyses and based on the Enactment of Minister of Environment of 11th February 2004 on the classification of presenting the state of surface and underground waters, the monitoring and the way of interpretation and presentation the state of these waters (Dz. U. No. 32/2004, position 284), it can be stated that water in the Upper Dunajec catchment in most cases can be put into class II of purity, because mean measurements from all the samplings of 2009 was 0.003248 mg/dm^3. This is the value close to the border value of class II. The values of results for the measurements of 2010 are distinctly higher from the remaining values. The mean value of these measurements was 0.0067674 mg/dm^3 which puts this water into class III of purity. Analysing the whole situation, I believe that the reason for such a high difference in the results, compared to 2009 is the occurrence of two flood waves, which affected the area in May and June 2010. Analysing graphs, one can clearly see what the content of phenol compounds is in the respective areas. It can be seen very well that in some sampling places this value is significantly higher, which is mainly connected with the lack of sewer system in these areas and high amount of agricultural areas. In surface waters phenols decompose within 3–4 days, and this process is much easier and faster, when water contains other organic pollutants, making this way a good medium for biological organisms. This gets slower at the temperature 10°C, and stops completely in temperature 4°C, which makes a logical explanation of the elevated content of phenols in lower water temperature. In the presented temperature graphs it can be seen that the best conditions for the process of self-purification were in June.

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