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STRUCTURE OF ATMOSPHERIC AEROSOL IN UPPER SILESIA (POLAND) – CONTRIBUTION OF PM2.5 TO PM10 IN ZABRZE, KATOWICE AND CZĘSTOCHOWA IN 2005–2007

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Keyword: PM10, PM2.5, dust fraction, suspended dust, dust concentrations, particles, winter season, summer season.

Abstract: The PM2.5/PM10 ratio expresses the anthropogenic share in atmospheric dust. Very high values of this ratio, i.e. high contribution of PM2.5 to PM10, have occurred recently in atmospheric air within European industrialized areas. The paper compiles results of three year pair wise measuring of concentrations of PM2.5 and PM2.5–10 and compares shares of PM2.5 in PM10 at three urban background sites in Upper Silesia Poland (towns of Zabrze, Katowice and Częstochowa). At all the three locations, the PM2.5/PM10 ratio of daily concentrations of dust only occasionally differed considerably from the PM2.5/PM10 ratios for the seasonal and yearly concentrations that, in turn, did not differ from the PM2.5/PM10 ratios at urban sites in Europe.

INTRODUCTION

The size of ambient particles depends on their origin. Almost all their properties, their impact on the environment or health – on their size. The smaller they are the farther from their source they float [8] and more deeply penetrate lungs.

Therefore, most often the ambient dust is classified by size of its particles. The ambient air contains particles of aerodynamic diameters from 0.002 to 100 μm [21], but in most cases, due to their influence on the chemistry of atmosphere, their physical properties and significance to human health, it is necessary and sufficient to consider the two main fractions:

- fine dust, PM2.5 – particles of aerodynamic diameter not exceeding 2.5 μm, most often related to combustion, may be of primary (from a source) or secondary (from chemical reactions in the atmosphere) origin [4, 6];
- coarse dust, PM2.5–10 – particles of aerodynamic diameter between 2.5 and 10 μm, mainly from mechanic processes, includes also pollens and spores;
- and their sum, PM10, i.e. particles of aerodynamic diameter not exceeding 10 μm.

According to the data published by the European Commission [4], the concentration of PM2.5 plays the key role in assessment of the health hazard from air pollutants. For some last few years, PM2.5 in Europe has been investigated quite thoroughly [2, 18, 22]. Many studies yield close or identical PM10 and PM2.5 concentrations [1, 7] i.e. negligible PM2.5–10 mass. Therefore, replacement of the PM10 limit values with standards for PM2.5 and intensified researches on PM2.5–10 to recognize relations between both fractions seem to be necessary. They may help to limit emission of the dominating fraction in areas threatened by violation of the PM standards.

In the presented work, results from three years of simultaneous measurements of PM2.5 and PM2.5–10 are exploited to compare shares of PM2.5 in PM10 at three different urban background sites (Zabrze, Katowice, Częstochowa). The specific conditions, different from conditions in other parts of Europe or Poland, affecting emission of PM were the reason for choosing the investigation areas. While emission of PM (both primary and secondary) in most European countries comes from traffic [3, 9, 24, 25], in Poland, especially in urban areas, municipal and industrial emission dominates [5, 16, 17, 19, 20].

**SAMPLING SITES**

The measurements were carried out during 2005–2007 period in three towns:

1. **Zabrze** – the western part of the Upper Silesian agglomeration – the measuring point was located in the premises belonging to the Institute of Environmental Engineering, M. Skłodowskiej-Curie 34, in the town centre. About 500 m north there is a four-lane, quite busy, national 88 road. About 500 m east, behind not very trafficked six-lane Korfanty Lane; high blocks of flats and houses are situated. Towards the south and south-east stretches the diversified housing and industry of the Zabrze downtown. In the west, the Institute borders with high blocks of the M. Skłodowska-Curie housing estate. The surrounding buildings are heated by the central network or by combusting hard coal.

2. **Częstochowa** – the northern part of the Silesian region – the measuring point was located within premises belonging to the Regional Inspectorate of Environmental Protection, Rząsawska Street 24–28, in Wyczerpy, the north-eastern part of Częstochowa. About 100 m away, there is Rząsawska Street – a local road with moderate traffic. The sampler was located on a grassy yard in front of the building of the Regional Inspectorate of Environmental Protection. The site is neither affected by traffic nor by industry. In the adjacent areas there are large storehouses.

3. **Katowice** – the central part of the Upper Silesian agglomeration – the measuring point was located within premises belonging to the Institute for Ecology of Industrial Areas, Kossutha Street, the Witos residential quarter, the western part of Katowice.
Blocks of flats, railway line, the DTŚ highway and the Tysiąclecia housing estate in the north, market areas in the east, the Witos quarter in the south and in the west living quarters and industrial terrains abandoned by the hard coal mine “Kleofas” surround the site.

All the sites represent urban background conditions. They are surrounded by housing estates and blocks of flats. Each site lies about 500 m away from a busy road which might be also a source of suspended dust. All the three points are described in [10–15].

Concentrations of PM2.5 and PM2.5–10 in Zabrze were measured from April to December 2006 and during every second month, starting from January, in 2007. In Katowice, the concentrations were measured every second month of 2007 starting from February. In Częstochowa – during the whole year 2005 except for maintenance break.

Arrangement of the measuring points within Silesia is presented in Figure 1.

![Fig. 1. Location of the measuring sites](image)

**METHOD**

Application of a sequential two-channel Rupprecht and Patashnick’s Dichotomus Partisol® Plus 2025 sampler allowed to pair wise measuring of concentrations of coarse (PM2.5–10) and fine (PM2.5) particles. PM2.5–10 was collected on glass, PM2.5 on Teflon filters. The stream of dust was split into two fractions by a virtual impactor. The sampler recorded the meteorological parameters and volume of sucked air. PM2.5/PM10 ratio, concentrations of PM10 and statistical parameters of series of results were computed. Concentrations were determined gravimetrically (Mettler Toledo micro scales, electric charge neutralizer) according to the method described in [19–25].

Air humidity and temperature in the weighing room were controlled and kept equal to about 50% and 20°C, respectively. Before weighing, filters were conditioned for 48 hours in the weighing room.
RESULTS

Częstochowa
Table 1 presents basic statistical parameters of the series of PM2.5, PM2.5–10, PM10 concentrations and PM2.5/PM10 ratios for Częstochowa in 2005.

Table 1. Statistical parameters of the series of daily dust concentrations in Częstochowa, 2005

<table>
<thead>
<tr>
<th>Period</th>
<th>Statistical parameter</th>
<th>Concentration [µg/m³]</th>
<th>PM2.5</th>
<th>PM2.5–10</th>
<th>PM10</th>
<th>PM2.5/PM10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>I quarter</td>
<td>average</td>
<td>46.4</td>
<td>6.7</td>
<td>53.0</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>17.6</td>
<td>0.2</td>
<td>23.0</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>106.4</td>
<td>17.1</td>
<td>123.5</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II quarter</td>
<td>average</td>
<td>33.8</td>
<td>14.1</td>
<td>48.0</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
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<td>0.0</td>
<td>10.1</td>
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<td>maximum</td>
<td>139.6</td>
<td>72.0</td>
<td>140.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III quarter</td>
<td>average</td>
<td>22.3</td>
<td>17.3</td>
<td>39.6</td>
<td>0.6</td>
<td></td>
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<tr>
<td></td>
<td>minimum</td>
<td>2.7</td>
<td>1.4</td>
<td>6.4</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>69.3</td>
<td>139.8</td>
<td>153.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV quarter</td>
<td>average</td>
<td>42.4</td>
<td>9.2</td>
<td>51.6</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>9.7</td>
<td>0.0</td>
<td>12.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>98.6</td>
<td>28.7</td>
<td>113.5</td>
<td>1.0</td>
<td></td>
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<tr>
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<td>number of measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>average</td>
<td>43.1</td>
<td>8.8</td>
<td>51.9</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>(I and IV quarter)</td>
<td>minimum</td>
<td>9.7</td>
<td>0.0</td>
<td>12.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>106.4</td>
<td>28.7</td>
<td>123.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>average value</td>
<td>27.6</td>
<td>15.9</td>
<td>43.4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>(II and III quarter 2005)</td>
<td>minimum</td>
<td>0.1</td>
<td>0.0</td>
<td>6.4</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>139.6</td>
<td>139.8</td>
<td>153.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2005</td>
<td>average value</td>
<td>32.3</td>
<td>13.7</td>
<td>46.0</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>0.1</td>
<td>0.0</td>
<td>6.4</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>139.6</td>
<td>139.8</td>
<td>153.5</td>
<td>1.0</td>
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<td>number of measurements</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zabrze – 2006
Table 2 presents basic statistical parameters of the series of PM2.5, PM2.5–10, PM10 concentrations and PM2.5/PM10 ratios for Zabrze in 2006.
Table 2. Statistical parameters of the series of daily dust concentrations in Zabrze, 2006

<table>
<thead>
<tr>
<th>Period</th>
<th>Statistical parameter</th>
<th>Concentration [µg/m³]</th>
<th>PM2.5</th>
<th>PM2.5–10</th>
<th>PM10</th>
<th>PM2.5/PM10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>average value</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>minimum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>maximum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I quarter</td>
<td>average value</td>
<td>23.0</td>
<td>11.6</td>
<td>34.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>5.0</td>
<td>1.4</td>
<td>9.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>76.9</td>
<td>69.2</td>
<td>99.8</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II quarter</td>
<td>average value</td>
<td>18.8</td>
<td>12.3</td>
<td>31.1</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>3.6</td>
<td>2.2</td>
<td>9.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>54.5</td>
<td>29.6</td>
<td>82.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III quarter</td>
<td>average value</td>
<td>49.9</td>
<td>12.2</td>
<td>62.1</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>5.4</td>
<td>2.5</td>
<td>8.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>171.1</td>
<td>29.9</td>
<td>196.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>92</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV quarter</td>
<td>average value</td>
<td>49.9</td>
<td>12.2</td>
<td>62.1</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>5.4</td>
<td>2.5</td>
<td>8.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>171.1</td>
<td>29.9</td>
<td>196.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winter (IV quarter)</td>
<td>average value</td>
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<td>12.0</td>
<td>32.8</td>
<td>0.6</td>
<td></td>
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<tr>
<td></td>
<td>minimum</td>
<td>3.6</td>
<td>1.4</td>
<td>9.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>76.9</td>
<td>69.2</td>
<td>99.8</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
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<td>number of measurements</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Summer (II and III quarter)</td>
<td>average value</td>
<td>30.6</td>
<td>12.0</td>
<td>42.7</td>
<td>0.7</td>
<td></td>
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<tr>
<td></td>
<td>minimum</td>
<td>3.6</td>
<td>1.4</td>
<td>8.2</td>
<td>0.2</td>
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</tr>
<tr>
<td></td>
<td>maximum</td>
<td>171.1</td>
<td>69.2</td>
<td>196.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>267</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Zabrze – 2007**

Table 3 presents basic statistical parameters of the series of PM2.5, PM2.5–10, PM10 concentrations and PM2.5/PM10 ratios for Zabrze in 2007.

In 2007, the sampler worked alternately in Zabrze and Katowice, its location was changed monthly. The numbers of measurements at both sites were close and numbers of summer and winter measuring days comparable. In Zabrze, measurements were carried out in January, March, May, July, September and November. The quarterly averages in Table 3 refer to particular months as follows:
- quarter I – January, March,
- quarter II – May,
- quarter III – July, September,
- quarter IV – November.
Table 3. Statistical parameters of the series of daily dust concentrations in Zabrze, 2007

<table>
<thead>
<tr>
<th>Period</th>
<th>Statistical parameter</th>
<th>Concentration [µg/m³]</th>
<th>PM2.5/PM10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PM2.5</td>
<td>PM2.5–10</td>
</tr>
<tr>
<td>I quarter</td>
<td>average</td>
<td>43.3</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>4.9</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>215.6</td>
<td>123.7</td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>II quarter</td>
<td>average</td>
<td>15.2</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>6.0</td>
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<tr>
<td></td>
<td>maximum</td>
<td>39.5</td>
<td>19.1</td>
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<td>number of measurements</td>
<td>27</td>
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<tr>
<td>III quarter</td>
<td>average</td>
<td>19.3</td>
<td>11.1</td>
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<td>minimum</td>
<td>4.2</td>
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<td>maximum</td>
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<td>number of measurements</td>
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<tr>
<td>IV quarter</td>
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<tr>
<td>Winter</td>
<td>average value</td>
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<td>11.6</td>
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<td>(I and IV quarter)</td>
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<td>4.9</td>
<td>1.3</td>
</tr>
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<td></td>
<td>maximum</td>
<td>215.6</td>
<td>123.7</td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Summer</td>
<td>average</td>
<td>18.1</td>
<td>8.6</td>
</tr>
<tr>
<td>(II and III quarter)</td>
<td>minimum</td>
<td>4.2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>68.6</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
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<td></td>
</tr>
<tr>
<td>2007</td>
<td>average</td>
<td>33.0</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>4.2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>215.6</td>
<td>123.7</td>
</tr>
<tr>
<td></td>
<td>number of measurements</td>
<td>182</td>
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</tr>
</tbody>
</table>

**Katowice – 2007**

Table 4 presents basic statistical parameters of the series of PM2.5, PM2.5–10, PM10 concentrations and PM2.5/PM10 ratios for Katowice in 2007.

Measurements were carried out in Katowice in February, April, June, August, October and December. The quarterly averages in Table 3 refer to particular months as follows:
- quarter I – February,
- quarter II – April, June,
- quarter III – August,
- quarter IV – October, December.
### Table 4. Statistical parameters of the series of daily dust concentrations in Katowice, 2007

<table>
<thead>
<tr>
<th>Period</th>
<th>Statistical parameter</th>
<th>PM2.5 [µg/m³]</th>
<th>PM2.5–10 [µg/m³]</th>
<th>PM10 [µg/m³]</th>
<th>PM2.5/PM10</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I quarter</td>
<td>II quarter</td>
<td>III quarter</td>
<td>IV quarter</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>43.3</td>
<td>19.1</td>
<td>17.4</td>
<td>43.0</td>
</tr>
<tr>
<td></td>
<td>minimum</td>
<td>9.3</td>
<td>6.9</td>
<td>9.7</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>maximum</td>
<td>85.0</td>
<td>75.1</td>
<td>28.1</td>
<td>125.4</td>
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<tr>
<td></td>
<td>number of measurements</td>
<td>27</td>
<td>46</td>
<td>26</td>
<td>61</td>
</tr>
</tbody>
</table>

**DISCUSSION**

Each of Figures 2, 3 and 4 compares PM2.5/PM10 at the examined sites in appropriate measuring periods.
Fig. 2. The box plots for PM2.5/PM10 in winter seasons

Fig. 3. The box plots for PM2.5/PM10 in summer seasons
The winter PM2.5/PM10 ranges are quite similar for all sites. All lower quartiles are about 0.75, upper – 0.88. Medians for all sites and periods are almost equal (about 0.8). The PM2.5/PM10 ratio is high – a probable effect of residential heating. The winter PM2.5/PM10 ratio is statistically specific of kind of the three places – urban background. Parameters of winter PM2.5/PM10 distributions for Zabrze in 2006 and 2007 are close, for Katowice and Zabrze in 2007 nearly the same.

The situation changes a little in summer (Fig. 3). The summer PM2.5/PM10 ratios are lower for each place and year. The highest ratio, about 0.79, is for Zabrze 2007. The ratio ranges are wider than in winter at each site and year. The lower quartiles differ noticeably, upper ones – significantly. The medians also differ for each place and year. Statistically, Częstochowa 2005, Zabrze 2006, Zabrze 2007 and Katowice 2007 differ in summer more than in winter in terms of the PM2.5/PM10 ratio. In summer, the number of higher PM2.5/PM10 values is greater in Zabrze 2007 than in Zabrze 2006. The Katowice 2007 summer PM2.5/PM10 ratios are lower than in Zabrze 2007 and less diversified.

Comparison of the winter PM2.5/PM10 ratios for Częstochowa 2005, Zabrze 2006, Zabrze 2007 and Katowice 2007 to the summer ones (Figs 2 and 3) suggests a large effect of municipal emission. In winter its impact dominates and traffic jams emission, equalizes the ratios. In summer, when there is no municipal emission, diversified influence of traffic occurs.

The yearly PM2.5/PM10 ratio series (Fig. 4) have high upper quartiles, exceeding 0.8, differing only a little for Częstochowa 2005, Zabrze 2007 and Katowice 2007. The upper quartiles for Zabrze 2006 is lower than 0.8. Medians for Częstochowa 2005, Zabrze 2007 and Katowice 2007 do not differ much. Medians for Zabrze 2006 and Zabrze 2007 differ more.
CONCLUSIONS

1. In winter, PM2.5 highly contributes to PM10 – it is a direct significant effect of the municipal emission.
2. Lowering of the share of PM2.5 in PM10 in summer suggests increased contribution of mineral fraction to immission.
3. The results of measurements in Częstochowa, Zabrze and Katowice are specific of urban background.
4. In the period under investigations, singular values of the PM2.5/PM10 ratio significantly differed from averages, but generally, the averages were close to averages in other European agglomerations.

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REFERENCES

STRUCTURE OF ATMOSPHERIC AEROSOL IN THE UPPER SILESIAN AGGLOMERATION ...


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Stosunek PM2,5/PM10 jest wskaźnikiem udziału pyłu pochodzenia antropogenicznego w zanieczyszczonym pyłem powietrza na danym obszarze. Przeprowadzone w ostatnich latach badania w terenach silnie zurbanizowanych pokazują bardzo wysoki udział PM2,5 w PM10. Celem pracy jest zestawienie otrzymanych na przestrzeni trzech lat wyników jednoczesnych pomiarów PM2,5 i PM2,5–10 i porównanie udziałów PM2,5 w PM10 w trzech różnych punktach charakterystycznych dla tła miejskiego na Górnym Śląsku (Zabrze, Katowice, Częstochowa). Wyniki pomiarów prowadzonych w Częstochowie, Zabrzu i Katowicach są reprezentatywne dla obszarów tła miejskiego aglomeracji. W okresie badań stosunek PM2,5/PM10 w badanych miejscach niekiedy przyjmował pojedyncze wartości znacznie odbiegające od średnich, generalnie jednak wartości średnie nie odbiegają od średniego notowanego stosunku tych frakcji w aglomeracjach miejskich Europy.
ADVANCED OXIDATION OF DICLOFENAC IN VARIOUS AQUATIC ENVIRONMENTS

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Keywords: Diclofenac, Fenton’s reaction, photolysis, UV/H₂O₂, aquatic solution.

Abstract: Many of the drugs used are not completely metabolized in the human body and with urine and faces are introduced into the sewage system. Finally, due to their incomplete removal during the conventional wastewater treatment process (CWTP), they can be released into the receiving water. One of the medications frequently detected in surface water is diclofenac. The present study addresses the problem of diclofenac removal in various aquatic samples using advanced oxidation processes (AOPs). The experiments were performed in distilled water and in biologically treated wastewater. The following AOPs were applied: Fenton’s reagent, UV- and UV/H₂O₂-processes. The concentration of diclofenac in distilled water corresponded to the concentration of this drug in human urine (ca. 20 mg·dm⁻³). The real wastewater samples contained diclofenac concentrations ranging from 630 to 790 ng·dm⁻³. The photodegradation of diclofenac was carried out in the photoreactor with a medium pressure Hg-vapor lamp (400 W). In the Fenton’s reaction different molar ratios of H₂O₂/Fe²⁺ were used. The diclofenac mineralization (TOC removal) strictly depended on the amount of H₂O₂ applied in the Fenton’s reaction. Diclofenac was rapidly degraded by direct photolysis (UV) and in UV/H₂O₂ process both in distilled water and in wastewater samples. The results proved that the advanced oxidation processes are effective in diclofenac removal from aquatic samples. The pseudo first order rate constants for diclofenac photodegradation were determined.

INTRODUCTION

Pharmaceuticals present in the environment are at a very low concentration (ng- or µg per dm³) [7], which is generally a non-toxic level [2] and frequently undergo rapid transformation or decay. Nevertheless their ubiquitous, continuous discharge into the environment and uncertainty regarding chronic impact of residual pharmaceutical on human health makes them intrinsically key pollutants.

After administration, many drugs are extracted non-metabolized by patients and enter with urine and faces the sewage system [10]. Finally, due to incomplete removal of pharmaceuticals and their metabolites during the conventional wastewater treatment process (CWTP), they are released into the receiving water. This is the most significant entry route for pharmaceuticals into the aquatic environment [20]. Diclofenac (2-[[2’,6’-(dichlorophenyl)amino]phenylacetic acid) belongs to the group of analgesic agents and is classified as a non-steroidal anti-inflammatory drug. It is often used to treat inflammatory and painful diseases of rheumatic and non-rheumatic origin. The basic data
concerning diclofenac is listed in Table 1. Approximately, 3.7 Mg of the prescription drug – diclofenac is annually sold in Poland. In comparison to other analgesic substance such as ibuprofen, which is degraded in more than 90%, diclofenac removal in CWTP is rather low ranging from 20 to 40% [4–8]. Non significant improvement of diclofenac removal (to about 50%) can be obtained using the membrane bioreactor (MBR) [11]. It can be explained by a very low sorption to activated sludge flocks (sorption coefficient $K_d$ amounted to 1.6 dm$^3$·kg$^{-1}$), and low degradation in the biological system, i.e. the value of degradation constant $k_{biol}$ is below 0.1 (dm$^3$·g$^{-1}$·d$^{-1}$). According to the classification scheme proposed by Joss et al. [9], no substantial removal (generally below 20%) by degradation can be expected for diclofenac. Diclofenac is one of the medicaments most frequently detected in aquatic environment such as surface waters and its traces were found in drinking water [7]. Its concentration in raw municipal wastewater exceeded the level of few µg·dm$^{-3}$ [1, 20].

Table 1. Basic data concerning diclofenac

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Diclofenac</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C16H11Cl2NO2</td>
</tr>
<tr>
<td>Molar mass</td>
<td>296.16 g·mol$^{-1}$</td>
</tr>
<tr>
<td>CAS number</td>
<td>15307-86-5</td>
</tr>
<tr>
<td>Structural formula</td>
<td>(sodium salt of diclofenac)</td>
</tr>
</tbody>
</table>

Photochemical reaction is likely to be the most important abiotic process affecting the fate of non-biodegradable and non-sorbing pharmaceuticals in the environment. Diclofenac can be photodegraded in the surface waters by sunlight [1, 14]. For instance, even in winter conditions the half life for direct photolysis of diclofenac (µg level) in bi-distilled water was estimated as 5 days [1]. Recently, the degradation performance of high concentrated solutions of diclofenac (50 mg·dm$^{-3}$) was proved in the pilot plant scale using compound parabolic collector [15]. The authors observed significant solar photolytic degradation reaching 85% for diclofenac solution within 62 h of operation.

The UV-based advanced oxidation processes (AOPs) have high potential for elimination of diclofenac. Some previous studies reported the use of Fenton photo-assisted treatment [15, 18], $H_2O_2$/UV [6, 22], $O_3$/UV [6] or $TiO_2$/UV [3, 12]. In order to prevent accumulation and unfavorable transformation of pharmaceutics into the environment, an effective treatment technology for the removal of such compounds is indispensable. The aim of the study was to investigate the removal efficiency of diclofenac using such oxidation processes as: ultraviolet irradiation (UV), Fenton’s reaction and UV/$H_2O_2$-process. Two approaches were tested: i) elimination of diclofenac from the treated wastewater (end-of-pipe treatment), ii) diclofenac elimination from its relatively high concentrated
solutions, which corresponded to its concentration in human urine (ca. 20 mg.dm\(^{-3}\)). This latter is reflected in treatment processes applied for a source separated waste.

**MATERIALS AND METHODS**

The experiments were performed in distilled water and biologically treated wastewater. The concentration of diclofenac in distilled water corresponded to the concentration of this drug in human urine (20 mg.dm\(^{-3}\)). In the treated wastewater the experiments at real concentrations of diclofenac (630–790 ng.dm\(^{-3}\)) were performed. The collected wastewater samples were taken after biological treatment from urban sewage treatment plant (STP) of Kloten (Switzerland). The detailed description of STP is presented in the references (e.g. [8]).

**Analytical methods**

The detection of diclofenac in the biologically treated wastewater was performed by gas chromatography/mass spectrometry (GC/MS) after solid phase extraction (SPE) and derivatisation by a diazomethane/diethylether – solution. After the reaction time, the diazomethane was destroyed by adding the acidic acid/acetone solution (1:10, v/v). Prior to SPE the wastewater samples were filtered, acidified with sulphuric acid to pH 2 and a surrogate standard (Br-diclofenac) was added. PCB nr 30 as an internal standard was used. The analytical standards were purchased from Sigma-Aldrich. The GC/MS measurements were performed on a gas chromatograph HP 5890 (equipped with autosampler HP 7673), coupled with the mass spectrometer HP 5971. The Restek XTI – 5 (30 m x 0.25 mm x 0.25 µm) as GC – column was used. The limit of detection (LOD) of diclofenac in the treated wastewater samples was at the level of 0.02 µg.dm\(^{-3}\). All GC/MS analyses were performed in a single-ion monitoring (SIM) mode, according to the methods concerning acidic drugs determination proposed by Ternes [19] and Ternes et al. [21]. The diclofenac concentrations in the distilled water were confirmed by high performance liquid chromatography (HPLC) (HPLC-UVD 340u, Gynkotek). The LichroCard 250-4 (Lichrospher 100, Merck) as the HPLC – column was used. The acetonitrile and phosphate buffer (5 mmol K\(_2\)HPO\(_4\), adjusted with H\(_3\)PO\(_4\) to pH 3) in a ratio of 60:40 (v/v) was applied as a mobile phase. The acetonitrile used for the experiments was of the highest commercially available, grade and it was purchased from POCH – Gliwice (Poland). A flow rate of mobile phase was 1 cm\(^3\).min\(^{-1}\) and the detection wavelength was set at 220 nm. Under the conditions described, the retention time (RT) of diclofenac was equal 6.8 ± 0.1 min. An external standard method was used for diclofenac determination in distilled water. The limit of quantification (LOQ) was set at first at the lowest point of linear calibration while the ratio signal/noise (S/N) exceeded the value 10 (S/N > 10). The concentration of total organic carbon (TOC) during all experiments was controlled using total carbon analyzer TOC-V\(_{\text{CSH}}\) (Shimadzu).

**Experiments set up**

The following advanced oxidation processes (AOPs) were used: Fenton’s reaction, photolysis (UV) and photolysis accelerated with hydrogen peroxide (UV/H\(_2\)O\(_2\)) in oxidation of diclofenac. The Fenton’s reagent was applied only for oxidation of the diclofenac solution. The solution was prepared by dissolving 20 mg.dm\(^{-3}\) of diclofenac in distilled
water (HPLC grade). The oxidation by means of Fenton’s reagent was performed in the glass reactor (volume of 1 dm³). The solution in the reactor was slowly stirred during the experiment and sampled after definite times (1, 2, 5, 10, 15, 20, 30, 45 and 60 min). In the Fenton’s reagent different molar ratios of \( \text{H}_2\text{O}_2 / \text{Fe}^{2+} \) (0.3/1; 0.6/1 and 1.2/1) were used. The pH of solution was adjusted with sulphuric acid to pH 3. The amount of \( \text{H}_2\text{O}_2 \) was estimated basing on the COD of diclofenac solution, according to the equation (1).

\[
1 \text{ g COD} = 1 \text{ g O}_2 = 0.03125 \text{ mol O}_2 = 0.0625 \text{ mol H}_2\text{O}_2 = 2.125 \text{ g H}_2\text{O}_2
\]  

The photochemical investigations were carried out in the reactor UviLab P400 (ViTaTec, Germany). The biologically treated wastewater and distilled water spiked with diclofenac standard as experimental matrices were used. In the photochemical processes the system was operated as a plug-flow reactor (Fig. 1a) or as a circulation loop (Fig. 1b). A medium-pressure mercury lamp (\( P = 400 \text{ W} \)) in quartz casing was immersed in the glass reactor (\( V = 0.350 \text{ dm}^3 \)). All experiments were performed using half of the maximal lamp power (\( P = 200 \text{ W} \)). The average path length of light through the solution was equal 10 mm. In the UV/\( \text{H}_2\text{O}_2 \) experiments the overdosed concentrations of \( \text{H}_2\text{O}_2 \) were applied – 1 g \( \text{H}_2\text{O}_2 \cdot \text{dm}^{-3} \) in the case of distilled water spiked with diclofenac standard and 1 mg \( \cdot \text{dm}^{-3} \) in the case of the treated wastewater. The pH of the experimental matrices was adjusted to 7. The photochemical investigation was performed at the ambient temperature (ranging from 23 to 25°C). Reported values were the average of 3 replicates.

RESULTS AND DISCUSSION

**Fenton’s reagent**

For the diclofenac solution (20.0 mg \( \cdot \text{dm}^{-3} \)), the average concentration of TOC amounted to 11.4 mg C-\( \text{dm}^{-3} \) and COD was equal 35.0 mg \( \text{O}_2 \cdot \text{dm}^{-3} \). After the pH correction with sulphuric acid to the value of 3, a considerable elimination of diclofenac concentration was observed. It ranged from 35.0 to 47.0% of the initial diclofenac concentration. The decrease of diclofenac concentration in the solution at pH = 3 could have been caused by the partial diclofenac precipitation. Diclofenac is weak acid (\( \text{pK}_a = 4.15 \)), soluble in its
deprotonised form, but practically insoluble when it is protonised. As reported by Perez-Estrada et al. [15] the similar diclofenac behavior at acidic pH was observed. Prior to HPLC-analysis all samples were filtered and partially precipitated diclofenac (including the chemical sludge originated from Fenton’s process) remained on the glass fiber filter. The elimination of TOC from diclofenac solution as a consequence of pH decreasing varied from 18 to 32%.

Consequently, the removal of diclofenac with Fenton’s reagent at pH around 3, should be summarized as oxidation, the precipitation and re-dissolution processes occurred simultaneously in the reaction mixture [15]. Irrespective of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) ratio used in the Fenton’s reagent, above 90% of diclofenac disappearance within 1 min was observed (Fig. 2). In the result of the oxidation with Fenton’s reagent the concentrations of TOC in the diclofenac solution were reduced. The dependency between the concentration of \( \text{H}_2\text{O}_2 \) in the Fenton’s reagent and the efficiency of the TOC-removal was noticed (Fig. 3). The maximal TOC removal (ca. 75%) was achieved when a molar ratio of \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) used in a Fenton’s reagent amounted to 0.6/1.0. When the ratio \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) was 0.3/1.0, the TOC removal did not exceed the value of 35%. It should be noted that significant changes of diclofenac concentrations can be noticed already within the few first minutes of the process.

Fig. 2. Diclofenac removal during the Fenton’s reaction (performed in water)
Diclofenac photodegradation in water (UV- and UV/H$_2$O$_2$-processes)

Diclofenac has the maximum absorbance at 273 nm, but also can absorb irradiation from a broad UV-range and partly in the solar region (Fig. 4). The initial concentration of diclofenac in the distilled water amounted to 20.0 mg·dm$^{-3}$ (TOC = 11.4 mg·dm$^{-3}$). The Figure 5 depicts the removal percentages of diclofenac in water recorded in the experiments with the UV-radiation and in the UV/H$_2$O$_2$-process. The 45% of diclofenac removal with reference to its initial concentration after 1 min of the UV-process was observed. After 5 min of UV-process, the initially colorless diclofenac solution changed into red-brown color. A new peak with RT of 1.86 min appeared on the chromatogram (data not shown). The peak was not successfully identified. On the chromatogram the peak with RT = 1.86 min was still present to the end of the irradiation time (30 min). The diclofenac concentration after 15 min of irradiation reached level below of LOQ. The coloration of diclofenac solution during the UV-process can be caused by the formation of the diclofenac photoproducts. Petrovic and Barceló [16] identified by means of LC-TOF-MS the diclofenac photoproduct with quinone-imine structures. Other possibility is a formation of the principal products, carbazole derivatives, generated due to the diclofenac dechlorination and formation of an inter-ring carbon bond [13, 17]. The carbazole structure is an active chromophore absorbing visible light. The appearance of specific red-brown color under solar irradiation of diclofenac was reported by Perez-Estrada et al. [15].

In the case of UV/H$_2$O$_2$-process, the addition of H$_2$O$_2$ (1.0 g·dm$^{-3}$) brought about the diclofenac decomposition by 9%. After 1 min of operation, the diclofenac removal exceeded 60%. The specific red-brown color of diclofenac solution appeared after 5 min of UV/H$_2$O$_2$-process. In the same time the peak with RT = 1.86 min was observed on the chromatogram. The diclofenac removal exceeded 97% and after another 5 min of the process (irradiation time = 10 min) its concentration was below LOQ. The decoloration of experimental solution after approximately 15 min of the UV/H$_2$O$_2$-process was observed.
In the same time, on the chromatogram, the peak at RT = 1.86 min was not present. It suggests that in the UV/H\textsubscript{2}O\textsubscript{2}-process not only the diclofenac molecules, but also the molecules of the diclofenac by-product were decomposed. The addition of H\textsubscript{2}O\textsubscript{2} in the UV-process probably caused the cleavage of carbon ring in the diclofenac derivatives and leads to the carboxylic acid formation \textit{via} the classic degradation pathways [22]. For diclofenac oxidation by means of UV-radiation and in the UV/H\textsubscript{2}O\textsubscript{2}-process the pseudo
first order rate constants \((k)\) were calculated (Tab. 2). The addition of \(H_2O_2\) by diclofenac irradiation with UV caused 1.6-times acceleration of its decay with comparison to the decay in the absence of \(H_2O_2\). After 5 min of diclofenac photolysis, the TOC-removal exceeded 13% and after next 5 min of the process the TOC-removal reached 23%. TOC removal after 30 min of irradiation was at the level of 30%. The TOC removal after 5 min of UV/\(H_2O_2\)-process was at the level of 17%. After 30 min of this process, near by 40% TOC removal was noticed (Fig. 6).

![Fig. 6. TOC removal during diclofenac oxidation using the UV- and UV/H_2O_2-processes in water](image)

Table 2. Pseudo first order kinetic constants \((k)\) of diclofenac photodegradation in water

<table>
<thead>
<tr>
<th>Process</th>
<th>(k) [min(^{-1})]</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>0.449</td>
<td>0.984</td>
</tr>
<tr>
<td>UV/(H_2O_2)</td>
<td>0.716</td>
<td>0.986</td>
</tr>
</tbody>
</table>

**Diclofenac photodegradation in wastewater (UV- and UV/\(H_2O_2\)-processes)**

The diclofenac concentration in the biologically treated wastewater varied from 630–790 ng·dm\(^{-3}\), while the average COD of wastewater during the whole experimental period was equal to 29.0 mg·dm\(^{-3}\). Considering the low diclofenac concentrations in the treated wastewater, the degradation of this compound by means of UV-radiation and in the UV/\(H_2O_2\) proceeded very rapidly in the both cases.

After 1 min of diclofenac photolysis and in the UV/\(H_2O_2\)-process the diclofenac removals were at the level of 79% and 83%, respectively. Complete diclofenac decay (the concentration below of LOD) was obtained within 2 min of UV/\(H_2O_2\)-process and within 3 min of UV-irradiation (Fig. 7). Due to the specific color of wastewater matrix and a very low concentration of diclofenac, no apparent color variation (resulting from a generation of diclofenac by-products) could be distinguished. The pseudo first order rate constants \((k)\) are presented in Table 3. The calculated kinetic constant for diclofenac decay in the
UV/H$_2$O$_2$-process was equal to 1.78 min$^{-1}$ and this value was only 1.05-folds higher than kinetic constant determined for UV-process (without H$_2$O$_2$ addition).

Fig. 7. Diclofenac removal by means of UV- and UV/H$_2$O$_2$-processes in wastewater

<table>
<thead>
<tr>
<th>Process</th>
<th>$k$ [min$^{-1}$]</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>1.694</td>
<td>0.995</td>
</tr>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>1.780</td>
<td>0.910</td>
</tr>
</tbody>
</table>

Table 3. Pseudo first order kinetic constants ($k$) of diclofenac photodegradation in wastewater

In the wastewater the H$_2$O$_2$ addition accelerated the diclofenac decomposition rate, but the positive effect was not so obvious in comparison with the results of experiments performed in the distilled water (at higher concentration of diclofenac). This result can partly be explained by a composition of wastewater samples (solution matrix), which could strongly influence the performance of photochemical processes. It is widely accepted that carbonate/bicarbonate anions act as the effective OH° radical scavengers. Consequently, the ions present in the wastewater, such as HCO$_3^-$/CO$_3^{2-}$, could deactivate the reactive intermediates of oxygen generated during the H$_2$O$_2$ photolysis. This phenomenon merits a closer examination using the diclofenac solution. On the other hand, matrix of wastewater did not affect direct photolysis of diclofenac molecules.

CONCLUSION

In the case of diclofenac oxidation with Fenton’s reagent irrespective of H$_2$O$_2$/Fe$^{2+}$ ratio, above 90% of diclofenac disappearance within 1 min of the process was observed. The maximal TOC removal (75%) was achieved when a molar ratio of H$_2$O$_2$/Fe$^{2+}$ used in a Fenton’s reagent was equal to 0.6/1.0. The decrease of diclofenac concentration (from
35.0 to 47.0% of the initial concentration) after pH adjustment to 3 can be attributed to the partial precipitation of this compound. The removal of diclofenac by means of Fenton’s reagent (at pH = 3) should be perceived not only as advanced oxidation process but also as simultaneously occurred processes including oxidation, precipitation and re-dissolution diclofenac in the reaction mixture.

The kinetic calculated on the basis of the results of photochemical experiments’ constants indicated that the addition of hydrogen peroxide accelerated the rate of diclofenac disappearance. In the case of the investigation performed in water, the addition of hydrogen peroxide accelerated the diclofenac decay rate from the value $k = 0.440 \text{ min}^{-1}$ (without $H_2O_2$) to the value $k = 0.716 \text{ min}^{-1}$ (in the presence of $H_2O_2$).

The obtained results proved that advanced oxidation processes (AOPs) are effective in diclofenac removal from the aquatic samples and the UV/H$_2$O$_2$-process can play a significant role in diclofenac removal from the aquatic environment, for instance as tertiary treatment (polishing stage) after the biological wastewater treatment.

Acknowledgements
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REFERENCES


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ADVANCED OXIDATION OF DICLOFENAC IN VARIOUS AQUATIC ENVIRONMENTS

ZAAWANSOWANY ROZKŁAD DIKLOFENAKU W ŚRODOWISKU WODNYM

Większość farmaceutyków stosowanych w medycynie nie ulega całkowitemu zmetabolizowaniu w ciele pacjenta i wraz z moczem i kałem trafia do systemu kanalizacyjnego. Ze względu na swe właściwości, nie są one całkowicie usuwane ze ścieków w konwencjonalnych procesach oczyszczania ścieków i wraz ze ściekami oczyszczenymi mogą przedostawać się do odbiorników. Diklofenak jest lekiem często identyfikowanym w wodach powierzchniowych. Prezentowane w niniejszej publikacji badania dotyczą problemu usuwania diklofenaku ze środowiska wodnego za pomocą zaawansowanych procesów utleniania (ang. advanced oxidation processes, AOPs). Badania prowadzono w roztworach wodnych diklofenaku (przygotowanego z wykorzystaniem wody destylowanej) oraz w ściekach po biologicznym procesie oczyszczania. W badaniach zastosowano następujące techniki AOPs: utlenianie odczynnikiem Fentona, utlenianie za pomocą promieniowania UV oraz proces UV/H2O2. Mineralizacja diklofenaku (określana jako usunięcie OWO) bezpośrednio zależała od ilości H2O2 w odczynniku Fentona stosowanego podczas badań. Diklofenak ulegał szybkiemu rozkładowi za pomocą promieniowania UV oraz procesu UV/H2O2. W ramach niniejszych badań obliczone zostały pseudo pierwszorzędowe stałe szybkości rozkładu diklofenaku przy zastosowaniu metod fotochemicznych.
INFLUENCE OF FISHERY MANAGEMENT AND ENVIRONMENTAL FACTORS ON OCCURRENCE OF HETEROTROPHIC, HEMOLYTIC AND MESOPHILIC BACTERIA AND AEROMONAS HYDROPHILA IN WATERS OF THE DRwęCA RIVER, POLAND

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Keywords: Aeromonas hydrophila, hemolytic bacteria, psychrophilic, psychrotolerant and mesophilic heterotrophic bacteria, water.

Abstract: The research covered the determination: of the numbers of heterotrophic bacteria: psychrophilic, psychrotolerant, mesophilic and percentage participation of hemolytic bacteria and Aeromonas hydrophila (with aerolysine and hemolysine genes) in the waters of the Drwęca River depending on environmental factors and fishery management. The mean quantities of heterotrophic bacteria (HPC) at 4, 14 and 28°C ranged: 0.78–7.57·10³, 1.40–6.65·10³ and 1.93–16.23·10³ cfu·cm⁻³, respectively. The percentage participation of hemolytic heterotrophic bacteria (HemPC) and A. hydrophila among psychrophilic, psychrotolerant, mesophilic microorganisms determined at 4, 14, 28°C, ranged: 7.9–10.4, 6.8–12.2, 8.6–22.0 and 1.1–6.4%, respectively. Statistically significant correlation between examined bacteria and temperature values, flows and O₂ saturations confirm that the occurrence of those microorganisms depends on the degree of microbiological contamination of that ecosystem, resulting from the fishery management and environmental factors.

INTRODUCTION

A river is a system comprising both the main reach and the tributaries, carrying on one-way flow a significant load of matter in dissolved and particulate phases from both natural and anthropogenic sources [2]. Those water ecosystems are characterized by a variety of heterotrophic microflora. Its quantitative and qualitative composition changes depending on climatic, morphometric and environmental conditions (temperature, pH, oxygen saturation) as well as anthropogenic factors (sewage inflow, recreation, fishery management) [16, 19, 26, 27, 40]. Climatic zones, the seasons of the year and inflow of various contaminants have an impact on periodic dominance of different types and species of bacteria belonging to psychrophilic, psychrotolerant or mesophilic microorganisms [7,
Due to their enzymatic properties, they perform the most important role, as by decomposing autochtonic and allochtonic organic matter [11, 16, 27], they take part in natural processes of self-purification of flowing waters [38]. However, an increase in the number of bacteria, especially mesophilic ones, in surface waters may pose a direct or indirect sanitary and epidemiological threats to aquatic organisms, people and animals [6, 30, 44]. This applies particularly to bacteria species with an ability to produce hemolysin which is considered one of the most important pathogenic factors [12, 34, 44]. It is especially adverse in the case of protected waters, one of which being the upper reach of the Drwęca River – since 1961 an aquatic and ichthyologic nature reserve. Previous research over the waters of the Drwęca River, conducted in the years 2001–2004, showed a quantitative and qualitative variety of heterotrophic microflora related to physicochemical parameters of the water and human activity [18, 19] and dominance of mesophilic *Aeromonas hydrophila* [26] potentially pathogenic to people and fish [4, 25, 34]. Therefore, this study was aimed at establishing the changes in: quantitative occurrence of heterotrophic bacteria (psychrophilic, psychrotolerant and mesophilic ones), the number and percentage participation of hemolytic microorganisms and mesophilic strains of *Aeromonas hydrophila* (with aerolysine and hemolysine genes) in the waters of the Drwęca River depending on environmental and anthropogenic factors.

**MATERIAL AND METHODS**

**Study area**
The Drwęca River, which is a right tributary of the Vistula River, flows through a lake district. The river is 207.2 km long and drains a catchment basin of 534 350 ha in surface area. The section of the river flowing within the boundaries of the Province of Warmia and Mazury is about 95 km long. In its upper reach the river flows through a small lake known as Ostrowin and a typical ribbon lake called Drwęckie [39] (Fig. 1). In 1961 the whole length of the Drwęca River was turned into a nature reserve. This aquatic nature reserve covers 1888.4 ha from the river sources to its outflow to the Vistula. The reserve, called the “River Drwęca Nature Reserve”, was established to protect the river’s water habitats as well as the fish living in the Drwęca such as trout, salmon, brown trout and vimba. The Drwęca River Nature Reserve is the longest ichthyological reserve in Poland, comprising 444.38 ha of protected area. Owing to large differences in elevation between the Drwęca and its tributaries, at several sections the river appears submontane in character. This favors the occurrence of rare fish and lamprey species, the species which prefer waters high in oxygen saturation [35–37].

In its upper reach, the valley of the Drwęca River forms a gorge 20–30 m deep and 8 km long. Known as Czarci Jar (Devil’s Gorge), the gorge comprises a Polish Angling Association fish hatchery. The major sources of point pollution reaching the Drwęca include household and industrial sewage and wastewater as well as post-production water from three fish farms (in the villages of Czarci Jar and Rychnowska Wola) [39].

**Sampling sites**
The microbiological assays covered a 15-km long section of the upper reach of the Drwęca. Water samples were collected at 8 sampling sites designated in certain characteristic places along the river from its sources to the inflow into Lake Ostrowin (Fig. 1):
- site I – 2 km away from the river sources, as the control site (the least of all the sampling sites exposed to contamination);
- site II – the outflow from the ‘trout section’ of the fish farm no. 1 (which produced 6.5 Mg of trout fry in 2005 and 5 Mg in 2006) located in the village of Czarci Jar;
- site III – the outflow from the ground fish farming ponds at the fish farm no. 1 in Czarci Jar;
Sampling
Water samples were collected from the Drwęca River at 0.3–0.5 m depth every 4–6 weeks from January 2005 to December 2006. Water was collected directly into sterile bottles according to the Standard Methods [20]. The time which elapsed between each sampling event and assays never exceeded 6 hours. In 2005–2006, 30 water samples were collected and analyzed per each site. Generally, the microbiological and physicochemical tests were performed on 240 water samples from the Drwęca River.

Microbiological studies
Microbiological analyses of all water samples from the river were determined by spread plate procedure on tryptone soy agar (TSA) (Oxoid) containing 5% (v/v) of sheep blood [10]. The studies included:
- the numbers of the psychrophilic heterotrophic bacteria as HPC 4°C and percentage estimation of psychrophilic hemolytic heterotrophic bacteria as HemPC 4°C after 10 day incubation at 4°C [13] among HPC 4°C,
- the numbers of psychrotolerant heterotrophic bacteria as HPC 14°C and percentage estimation of the psychrotolerant hemolytic heterotrophic bacteria as HemPC 14°C after 7 day incubation at 14°C [45] among HPC 14°C,
- the numbers of mesophilic heterotrophic bacteria as HPC 28°C and percentage estimation of the mesophilic hemolytic heterotrophic bacteria as HemPC 28°C and mesophilic *A. hydrophila* after 72 hour incubation at 28°C [38] among HPC 28°C.

The microbiological analyses were run in three parallel repetitions following general microbiological standards. The mean and range were calculated.

The results obtained for HPC 4°C, HPC 14°C and HPC 28°C were assumed and recalculated in colony forming units (cfu) per 1 cm$^3$ of water according to the methodology described by Standard Methods [20]. To investigate HemPC 4°C, HemPC 14°C and HemPC 28°C the strains, producing the transparent circular zones around the colonies, on TSA containing 5% of sheep blood, were assumed and recalculated in colony forming units (cfu) per 1 cm$^3$ of water. Next, percentage estimation of those hemolytic bacteria were calculated among HPC 4°C, HPC 14°C and HPC 28°C, respectively. For determination of quantitative occurrence of the mesophilic strains of *A. hydrophila*, the total colonies HemPC 28°C were preliminarly screened using the following tests: gram stain, oxidase, susceptibility to O/129 vibriostatic disk (10 and 150 μg), motility, glucose and trehalose fermentation and nitrate reduction. Only the strains found to be gram negative, oxidase positive, negative for O/129 vibriostatic, motile, glucose and trehalose fermenting and nitrate reducing were identified with API 20 NE strips (bioMérieux).
Molecular analysis
From the 152 strains preliminarily identified, with API 20 NE strips (bioMérieux), as belonging to *A. hydrophila*, nucleic acids were isolated by CTAB method [15] with own modifications (personal communications, Korzekwa, 2008). Quality and quantity of isolated DNA were determined photometrically at 260 nm (OD$_{260}$) and adjusted to a final template PCR concentration of about 20 μg·cm$^{-3}$ in TE buffer. Multiplex PCR was realized for 16S rDNA, hemolysin and aerolysin sequences present in *A. hydrophila* tested genomes. Primers A16S based on the *A. hydrophila* ATCC 7966 16S rRNA sequence (GenBank accession no. X74677) were applied to confirm presence of the 16S rRNA specific gene as an internal control [43]. The AHH1 primer set was designed to amplify a 130-bp fragment of *A. hydrophila* extracellular hemolysin gene *ahh1* [24]. The AH-aerA primer set amplified a 309-bp fragment of the *A. hydrophila* aerolysin gene *aerA* (GenBank accession no. M16495) [43]. DNA samples (10 ng per reaction mixture) were amplified in a 20·10$^{-6}$ dm$^3$ reaction mixture consisting of 1.25 mM magnesium chloride; 200 μM (dNTP), 2.0 μM AHH1 primers; 1.5 μM AH-aerA, 0.05 μM A16S primers (Integrated DNA Technologies, Coralville, USA), and 1.25 U of Tfl DNA polymerase (Epicentre Biotechnologies, Madison, USA). DNA templates were amplified by thermocycler model 2400 (Mastercycler gradient, Eppendorf, Germany) with thermal profile according to Wang et al. [43]. Amplification parameters for all primer sets included an initial denaturation at 95°C for 5 min, followed by 50 cycles of denaturation at 95°C for 0.5 min, annealing of the primers at 59°C for 0.5 min, and primer extension at 72°C for 0.5 min. A final extension at 72°C for 7 min was used. Amplicons were electrophoretically separated in 1.5% ethidium bromide stained agarose at 5 V·cm$^{-1}$, and then visualized with UV (Kucharczyk, TE, Poland). The obtained patterns (Fig. 2) were compared with superladder-MID1 mass molecular marker (GenSura Laboratories). Among the 152 studied strains 83 were finally confirmed as *A. hydrophila* with aerolysine and hemolysine genes. Next, percentage estimation of *A. hydrophila* were calculated among HPC 28°C.

![Fig. 2. Example of patterns obtained after multiplex-PCR of *Aeromonas hydrophila* realized for presence confirmation of: species-specific 16S rDNA (~ 356 bp; bottom band), aerolysine gene (~ 306 bp, middle band) and hemolysine gene (~ 150 bp; upper band); MM – molecular marker, 1 – *A. hydrophila* LMG 7864, 3 – blind sample (PCR mixture plus DNA template without primers)](image)

Physicochemical tests
In the experimental period, the river water was additionally subjected to physicochemical determinations of the following parameters: temperature (°C), flow (dm$^3$·s$^{-1}$), pH and
oxygen saturation (mg O$_2$·dm$^{-3}$). All microbiological and physicochemical determinations were carried out on the same (common) water samples. The physicochemical determinations: temperature, flow, pH, oxygen saturation, were conducted by multimeasurement apparatus Hydrolab Multi 12 (Schott, Germany) with the precision of measurements: ± 0.1°C, ± 1.0 dm$^3$·s$^{-1}$, ± 0.01 pH, ± 0.01 mg O$_2$·dm$^{-3}$ respectively.

**Statistical evaluation**

The results of microbiological and physicochemical examinations were subjected to statistical evaluation by determining the correlation (estimation by Spearman’s correlation) between a given set of parameters with simple correlation coefficients [42]. The Spearman’s correlation coefficient was calculated with the use of the STATISTICA PL 7.0 computer software.

**RESULTS**

**Microbiological studies**

The numbers (means and ranges) of the HPC 4°C, HPC 14°C and HPC 28°C and percentage participation of occurrence of the studied HemPC 4°C, HemPC 14°C, HemPC 28°C and *A. hydrophila* among HPC 4°C, HPC 14°C and HPC 28°C occurring in the waters of the Drwęca River over the years 2005–2006 are presented in Table 1. Their quantitative occurrence fluctuated within the range of a few orders of magnitude depending on the bacteria group assayed (psychrophilic, psychrotolerant, mesophilic) as well as the sampling site and period of study. Regardless of temperature requirements, the smallest mean quantities of HPC 4°C, HPC 14°C and HPC 28°C (respectively: 0.78·10$^3$, 1.40·10$^3$ and 1.93·10$^3$ cfu·cm$^{-3}$) were found at site I (2 km away from the source of the river), while the largest quantities (respectively: 7.57·10$^3$, 6.65·10$^3$ and 16.23·10$^3$ cfu·cm$^{-3}$) – at site VI (the outflow from fish farm no. 2 located in Rychnowska Wola). Similar regularities were also recorded for the minimum and maximum numbers thereof. Throughout the study period, the smallest quantitative occurrence of HPC 4°C and the highest numbers of HPC 14°C and HPC 28°C found in summer months, corresponded to the maximum values of water temperature (19.9–20.8°C) and the minimum concentrations of oxygen dissolved in the water (6.40–6.88 mg O$_2$·dm$^{-3}$). Regardless of the temperature preferences, the smallest mean percentage participation of HemPC 4°C, HemPC 14°C and HemPC 28°C was found at sites I and VIII. It amounted to, respectively: 7.9, 6.8 and 8.6% for the former, and 7.0, 8.9 and 10.1% for the latter, among HPC 4°C, HPC 14°C and HPC 28°C. The highest contamination with HemPC 4°C, HemPC 14°C and HemPC 28°C was characteristic of site VI, where on average the percentage participation of hemolytic bacteria among HPC 4°C, HPC 14°C and HPC 28°C was recorded at: 10.4, 12.2 and 22.0%. Taking into account temperature requirements, the mean percentage participation of HemPC 4°C and HemPC 14°C fluctuated slightly in the water samples at most of the same sampling sites. It ranged from 6.8 to 12.2% depending on the place of sampling. In turn, the highest percentage participation of hemolytic bacteria at all the sampling sites was found for HemPC 28°C. It ranged from 8.6% at site I to 22.0% at site VI. The mesophilic hemolytic bacteria *A. hydrophila* (with aerolysine gene) constituted from 0 to 25.6% among HPC 28°C depending on the sampling site, the period of study and certain physicochemical parameters assayed (temperature, flows, pH and dissolved O$_2$ satura-

<table>
<thead>
<tr>
<th>Group of bacteria</th>
<th>Sampling sites</th>
<th>I (30)</th>
<th>II (30)</th>
<th>III (30)</th>
<th>IV (30)</th>
<th>V (30)</th>
<th>VI (30)</th>
<th>VII (30)</th>
<th>VIII (30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPC 4°C</td>
<td></td>
<td>0.78 (1)</td>
<td>1.91</td>
<td>5.04</td>
<td>3.92</td>
<td>3.63</td>
<td>7.57</td>
<td>3.59</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>(0.1–1.9^2)</td>
<td>0.2–11.1</td>
<td>0.1–36.5</td>
<td>0.1–28.4</td>
<td>0.1–24.4</td>
<td>0.1–45.3</td>
<td>0.1–8.2</td>
<td>0.2–4.7</td>
<td></td>
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<tr>
<td>HPC 14°C</td>
<td></td>
<td>1.40</td>
<td>1.66</td>
<td>2.33</td>
<td>3.18</td>
<td>1.99</td>
<td>6.65</td>
<td>4.94</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>(0.3–3.3)</td>
<td>0.1–6.0</td>
<td>0.1–7.8</td>
<td>0.1–11.3</td>
<td>0.2–6.0</td>
<td>0.2–33.1</td>
<td>0.2–13.3</td>
<td>0.2–8.9</td>
<td></td>
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<tr>
<td>HPC 28°C</td>
<td></td>
<td>1.93</td>
<td>3.84</td>
<td>3.7</td>
<td>3.4</td>
<td>3.3</td>
<td>16.23</td>
<td>4.03</td>
<td>3.84</td>
</tr>
<tr>
<td></td>
<td>(0.4–5.9)</td>
<td>0.1–12.7</td>
<td>0.4–11.6</td>
<td>0.5–10.7</td>
<td>0.1–15.7</td>
<td>0.8–63.6</td>
<td>0.6–18.8</td>
<td>0.1–20.0</td>
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<tr>
<td>HemPC 4°C</td>
<td></td>
<td>7.9</td>
<td>7.6</td>
<td>8.0</td>
<td>9.7</td>
<td>7.8</td>
<td>10.4</td>
<td>9.8</td>
<td>7.0</td>
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<tr>
<td></td>
<td>(2.8–18.7)</td>
<td>1.3–17.9</td>
<td>1.7–14.3</td>
<td>1.6–23.1</td>
<td>0.0–22.2</td>
<td>3.3–16.4</td>
<td>2.7–15.8</td>
<td>1.0–25.6</td>
<td></td>
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<td>HemPC 14°C</td>
<td></td>
<td>6.8</td>
<td>9.3</td>
<td>10.2</td>
<td>10.5</td>
<td>8.5</td>
<td>12.2</td>
<td>10.7</td>
<td>8.9</td>
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<tr>
<td></td>
<td>(0.9–11.5)</td>
<td>3.6–33.3</td>
<td>1.1–27.3</td>
<td>0.5–29.8</td>
<td>2.1–16.7</td>
<td>1.4–31.3</td>
<td>1.0–38.1</td>
<td>0.0–25.1</td>
<td></td>
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<tr>
<td>HemPC 28°C</td>
<td></td>
<td>8.6</td>
<td>15.5</td>
<td>15.0</td>
<td>15.3</td>
<td>13.2</td>
<td>22.0</td>
<td>18.1</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>(1.3–18.2)</td>
<td>5.3–36.8</td>
<td>0.9–38.1</td>
<td>1.6–29.4</td>
<td>0.7–36.4</td>
<td>4.8–95.0</td>
<td>6.8–31.1</td>
<td>3.7–18.3</td>
<td></td>
</tr>
<tr>
<td><em>A. hydrophila</em></td>
<td></td>
<td>1.1</td>
<td>1.6</td>
<td>2.1</td>
<td>1.6</td>
<td>2.4</td>
<td>5.8</td>
<td>6.4</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>(0.0–4.8)</td>
<td>0.0–6.5</td>
<td>0.0–9.8</td>
<td>0.0–8.0</td>
<td>0.5–11.0</td>
<td>1.3–18.9</td>
<td>2.5–25.6</td>
<td>1.1–16.8</td>
<td></td>
</tr>
</tbody>
</table>

\( ^1 \) mean, \( ^2 \) range, ( ) – number of samples
On average, they were found to be the fewest at site I (1.1% among HPC 28°C), and the most numerous at sites VI and VII (5.8 and 6.4% respectively). Throughout the period of study, this species was not found to occur at sites I, II, III, and IV and only in winter months when the water temperature ranged from 0.2 to 1.0°C. In turn, the highest percentage participation of *A. hydrophila* (18.9 and 25.6% HPC 28°C) was recorded in July 2005 at sites VI and VII respectively, when the water temperature fluctuated within the range of 18.9 to 19.9°C.

**Physicochemical studies**

The ranges of the physicochemical parameters (temperature, flow, pH and oxygen) measured in the waters of the Drwęca River in 2005–2006 are presented in Table 2. Their values changed within a few orders of magnitude, depending on the sampling site, period of study and kind of parameter. In the study period, the temperature of the water varied from 0.2°C (in January 2005) to 20.8°C (in July 2006). The smallest mean value of this parameter (6.4°C) was noticed at site I, whereas the highest one (9.8°C) occurred at site III. The values of flows Drwęca River ranged from 82.0 to 832.0 dm³·s⁻¹. The smallest mean flow of the river water (99.0 dm³·s⁻¹) was detected at site I, and the highest one (688.0 dm³·s⁻¹) observed at site VIII. The value of water reaction (pH) measured for the water samples collected from the Drwęca River varied from 7.16 to 8.32. The smallest mean value of this parameter (7.47) was noticed at site VIII, whereas the highest one (7.96) occurred at site III. The concentrations of oxygen dissolved in water of the Drwęca River ranged from 6.40 to 12.96 mg O₂·dm⁻³. The smallest mean concentration of this index was observed at site II (8.46 mg O₂·dm⁻³), the highest ones were noticed at sites VI and VII (11.48 and 11.14 mg O₂·dm⁻³, respectively).

**Statistical evaluation**

The results of the statistical analysis of the correlation between the numbers of the studied bacteria (HPC 4°C, HPC 14°C, HPC 28°C, HemPC 4°C, HemPC 14°C, HemPC 28°C, *A. hydrophila*) recovered from the water of Drwęca River during the whole time of the study and the values of some physicochemical compounds (temperature, flow, pH, O₂) in the analyzed water samples are shown in Table 3. The Spearman’s test proved that there were both positive and negative statistically significant (p < 0.05) correlations:

- the counts of all the assayed groups of microorganisms versus values of temperature and oxygen saturation of the water samples collected from the Drwęca River;
- the quantitative occurrence of HemPC 28°C and mesophilic strains *A. hydrophila* versus water flow values;
- the quantitative occurrence of HPC 4°C with HemPC 4°C, HPC 14°C and HPC 28°C;
- HemPC 4°C with HemPC 14°C, HemPC 28°C and mesophilic *A. hydrophila*;
- HPC 28°C with HemPC 28°C and mesophilic *A. hydrophila*;
- HemPC 28°C with the quantitative occurrence of mesophilic *A. hydrophila*. 

IWONA GOŁAŚ I WSP.
Table 2. The values of some physicochemical parameters of the waters of the Drwęca River in 2005–2006

<table>
<thead>
<tr>
<th>Sampling sites</th>
<th>Number of samples</th>
<th>Physicochemical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature [°C]</td>
</tr>
<tr>
<td>I</td>
<td>30</td>
<td>6.4 $^1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2–11.4 $^2$</td>
</tr>
<tr>
<td>II</td>
<td>30</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5–18.3</td>
</tr>
<tr>
<td>III</td>
<td>30</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8–20.8</td>
</tr>
<tr>
<td>IV</td>
<td>30</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0–15.2</td>
</tr>
<tr>
<td>V</td>
<td>30</td>
<td>8.0</td>
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<tr>
<td></td>
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<td>1.0–14.9</td>
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<tr>
<td>VI</td>
<td>30</td>
<td>8.0</td>
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<tr>
<td></td>
<td></td>
<td>1.0–18.9</td>
</tr>
<tr>
<td>VII</td>
<td>30</td>
<td>8.1</td>
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<tr>
<td></td>
<td></td>
<td>1.0–19.9</td>
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<tr>
<td>VIII</td>
<td>30</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
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<td>0.4–16.1</td>
</tr>
</tbody>
</table>

$^1$ – mean, $^2$ – range
Table 3. Statistic estimation by Spearman’s correlation (p < 0.05, N = 240) between the numbers [cfu·cm⁻³] of studied groups of microorganisms recovered from the water of the Drwęca River during whole time of study and some physicochemical parameters in water; BD eliminated in couple

<table>
<thead>
<tr>
<th></th>
<th>HPC 4°C</th>
<th>HemPC 4°C</th>
<th>HPC 14°C</th>
<th>HemPC 14°C</th>
<th>HPC 28°C</th>
<th>HemPC 28°C</th>
<th>A. hydrophila</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
<td>-0.06*</td>
<td>-0.26*</td>
<td>0.22*</td>
<td>0.30*</td>
<td>0.27*</td>
<td>0.17*</td>
<td>0.44*</td>
</tr>
<tr>
<td>Flow [dm³·s⁻¹]</td>
<td>0.08</td>
<td>0.12</td>
<td>-0.08</td>
<td>-0.041</td>
<td>-0.037</td>
<td>-0.16*</td>
<td>-0.17*</td>
</tr>
<tr>
<td>Reaction [pH]</td>
<td>-0.033</td>
<td>0.056</td>
<td>0.01</td>
<td>-0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>Oxygen [mg O₂·dm⁻³]</td>
<td>0.36*</td>
<td>0.27*</td>
<td>-0.39*</td>
<td>-0.11*</td>
<td>-0.23*</td>
<td>-0.13*</td>
<td>-0.34*</td>
</tr>
<tr>
<td>HPC 4°C</td>
<td>1.00</td>
<td>0.87*</td>
<td>-0.57*</td>
<td>-0.14</td>
<td>-0.27*</td>
<td>-0.05</td>
<td>-0.11</td>
</tr>
<tr>
<td>HemPC 4°C</td>
<td>0.87*</td>
<td>1.00</td>
<td>0.17</td>
<td>-0.59*</td>
<td>0.07</td>
<td>-0.26*</td>
<td>-0.18*</td>
</tr>
<tr>
<td>HPC 14°C</td>
<td>-0.57*</td>
<td>0.17</td>
<td>1.00</td>
<td>0.17</td>
<td>0.21</td>
<td>0.01</td>
<td>-0.01</td>
</tr>
<tr>
<td>HemPC 14°C</td>
<td>-0.14</td>
<td>-0.59*</td>
<td>0.17</td>
<td>1.00</td>
<td>0.06</td>
<td>0.15</td>
<td>-0.05</td>
</tr>
<tr>
<td>HPC 28°C</td>
<td>-0.27*</td>
<td>0.07</td>
<td>0.21</td>
<td>0.06</td>
<td>1.00</td>
<td>0.47*</td>
<td>0.23*</td>
</tr>
<tr>
<td>HemPC 28°C</td>
<td>-0.05</td>
<td>-0.26*</td>
<td>0.01</td>
<td>0.15</td>
<td>0.47*</td>
<td>1.00</td>
<td>0.29*</td>
</tr>
<tr>
<td>A. hydrophila</td>
<td>-0.11</td>
<td>-0.18*</td>
<td>-0.01</td>
<td>-0.05</td>
<td>0.23*</td>
<td>0.29*</td>
<td>1.00</td>
</tr>
</tbody>
</table>

HPC – heterotrophic plate count, HemPC – hemolytic plate count, * – statistically important differences (p < 0.05)
DISCUSSION

The research results obtained, concerning the number of heterotrophic bacteria, the numbers and percentage participation of the potentially pathogenic hemolytic and mesophilic bacteria *A. hydrophila* in the Drwęca water, demonstrated differences in their occurrence ranging from one to a few orders of magnitude, depending on the group of microorganisms assayed (HPC or HemPC), their temperature requirements, the sampling site and the time of sampling. Directly proportional relations between the water temperature and HPC 14 and 28°C as well as the minimum and maximum HPC 4°C corresponding to the highest and lowest values of that parameter in the samples of the water from the Drwęca River indicated dominance of the studied psychrotolerant bacteria (HPC 14°C) and/or the mesophilic ones (HPC 28°C) over the summer months, as well as the psychrophilic bacteria (HPC 4°C) in the winter periods. It was confirmed by statistical analysis, which demonstrated statistically significant (positive or negative) relations between the water temperature and oxygen saturation, respectively: HPC 14°C, HPC 28°C and HPC 4°C. In the waters of the Drwęca River, significant negative correlations between HPC 4°C on the one side and HPC 14°C and HPC 28°C on the other indicate a seasonal nature of the occurrence of particular groups of bacteria under examination, whose numbers are also conditioned by the content of oxygen dissolved in water, which changes depending on the water temperature [1]. It is confirmed by the maximum numbers of HPC 4°C recorded in the winter months at 10.40–12.96 mg O₂⋅dm⁻³ as well as HPC 14 and 28°C in the summer months at 6.40–6.88 mg O₂⋅dm⁻³. Similar trends and relations between the water temperature and the content of oxygen dissolved in it on the one side and the numbers of heterotrophic bacteria on the other were found in the waters of two Canadian rivers: the Meduxnekeang and the Dunbar by Bell *et al.* [7] as well as in the samples of water from the Portrero de los Funes River in Argentina Almeida *et al.* [3]. The smallest and the largest mean ranges of the occurrence of all the HPC groups assayed, regardless of their temperature requirements, observed respectively at site I (control site) and sites VI and VII (constituting outflows from fish farms no. 2 and 3) indicate a local and/or periodic influence of intensive fishery management on the microbiological quality of the Drwęca River waters. It results from the fact that organic substances supplied to the water in the form of unused fish feed and fish excrement create favorable conditions for the growth and development of heterotrophic microorganisms [9, 17, 31]. This is also confirmed by similar trends in the minimum and maximum numbers of heterotrophic bacteria (proteolytic, ammonifying and denitrifying ones) at appropriate sites recorded in previous research over the Drwęca River waters [18, 19]. In aquatic environments, the presences of hemolytic bacteria may pose an epidemiological threat to people and organisms inhabiting them [5, 12]. In the Drwęca River waters, the changing numbers of HemPC 4°C, 14°C and 28°C depending on the period of study, temperature and O₂ saturation were confirmed by statistical analysis. Their lowest percentage participation found at sites I and VIII confirms the fact that those microorganisms, represented by numerous bacteria species, belonging, among others, to the genera: *Escherichia* spp., *Yersinia* spp., *Vibrio* spp. or *Aeromonas* spp., commonly occur in aquatic environments where they often get from the catchment area [14, 33, 41]. In turn, the highest contamination with all the hemolytic microorganisms under examination recorded in the summer months at site VI suggests an adverse local and/or periodic impact of the fishery management. In the circumstances of intensive
fattening, fish excrete large numbers of bacteria belonging to various genera [8, 21, 22, 46, 47], which, despite their potential pathogenicity, constitute saprophytic microflora of the fish [10, 23]. In the studied samples of the Drwęca River waters, the determined percentage diversity of the identified mesophilic bacteria *A. hydrophila* among HPC 28°C and the statistically significant differences in their numbers depending on the time and place of sampling confirm the thesis that the occurrence of those strains changes under the influence of various environmental factors and depending on the level of contamination of water reservoirs [4, 26, 28, 30]. It is also proved by the statistically significant correlations (p < 0.05) between the numbers of the bacteria of that species on the one side and HPC 28°C and HemPC 28°C on the other, as well as the values of physicochemical parameters (temperature, flow and O₂).

**CONCLUSION**

In the waters of the Drwęca River, the quantitative diversification of the bacteria under examination, particularly between the periods of study, indicates a significant impact of environmental and/or fishery management. It was confirmed by the statistical analysis which demonstrated correlation between their quantitative occurrence and the temperature values and O₂ concentration in the water. The highest contamination with HPC 4°C, HPC 14°C and HPC 28°C as well as the highest percentage participation of all the studied HemPC and identified mesophilic strains of *A. hydrophila* (with aerolysine and hemolysine genes) found in water samples from sites VI and/or VII (constituting outflows from fish farms no. 2 and 3) in the summer months suggest a local and/or periodic adverse impact of fishery management. Statistically significant correlations (p < 0.05) between the quantitative occurrence of mesophilic bacteria *A. hydrophila* on the one side and HPC 28°C and HemPC 28°C on the other, as well as the values of physicochemical parameters (temperature, flow and O₂) confirm the thesis that the occurrence of those microorganisms in the waters of the Drwęca River depends on the degree of microbiological contamination and environmental factors. Along with the changes in physicochemical parameters of the Drwęca River waters, related to the seasons of the year and/or intensification of the fishery management, there occur a lot of reciprocal processes between particular physiological groups, genera or species of microorganisms, manifesting themselves in dominance of different groups of microorganisms [7], including also potentially pathogenic strains or pathogens [34].

**Acknowledgements**

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**REFERENCES**


Badania obejmowały oznaczenia liczebności bakterii heterotroficznych: psychrofilnych, psychrotolerancyjnych i mezofilnych oraz procentowego udziału bakterii hemolizujących i Aeromonas hydrophila w wodach rzeki Drwęcy w zależności od czynników środowiskowych i gospodarki rybackiej. Średnie liczebności bakterii heterotroficznych: psychrofilnych, psychrotolerancyjnych i mezofilnych oraz procentowego udziału bakterii hemolizujących i Aeromonas hydrophila w wodach rzeki Drwęcy, Polska

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CHARACTERISTIC OF GRANULATED ACTIVATED SLUDGE FED WITH GLYCERIN FRACTION FROM BIODIESEL PRODUCTION

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Keywords: Glycerin fraction from biodiesel production, granulated activated sludge, free settling test, waste treatment.

Abstract: In the presented research glycerin fraction from biodiesel industry was used for granulated aerobic activated sludge production in a typical sequencing batch reactor (h/d equal 2.1). After 7 weeks of operation, granulated activated sludge with SVI at the level of 40–50 cm³·g⁻¹ was obtained. At organic compounds load of 1.43 ± 0.1 mg COD·mg VSS⁻¹·d⁻¹, the efficiency of carbon removal was 94.14 ± 2.7% and most of the introduced COD was removed during the first 2–3 hours of aeration. The sieve analysis revealed that 60% (w/w) of biomass consisted of particles with a diameter in the range of 4–8 mm. A free settling test procedure proved that granules with a diameter between 2–4 mm were numerically most abundant in biomass (32.3%) and that the settling volume, mass and Reynolds number values significantly (p < 0.05) increased parallel with increasing granule diameter. Adverse tendency was observed for the mean effective, buoyant density of a granule in a liquid.

INTRODUCTION

Systems with immobilized biomass are widely used for treating wastewater because of a resistance to environmental factors and high concentration of pollutants. In recent years, attention was focused on a new form of immobilization that is biogranulation. This process involves cell-to-cell interactions resulting in formation of dense microbial consortia – granules. The main advantages of granulated activated sludge are very good settling ability, long biomass retention time and biomass concentration as well as ability to withstand high organic loading rate [15]. From engineering perspective employing technologies based on granulated activated sludge results in smaller dimensions of clarifiers, shorter standstill for settling and more time for biological removal of pollutants.

Most of the research on biogranulation is carried out in reactors with h/d ratio of 10 or more [5, 27, 28]. The literature data indicate that in order to obtain aerobic granules different organic substrates, like glucose, acetate [18], phenol [11], dairy effluents [22] or wastewater, were used as the carbon source [3, 9]. It seems especially advantageous to use organic wastes form different branches of economy for granulated activated sludge production.
Present trends in fuel market encourage the production of biodiesel. Biodiesel is the name of a clean burning alternative fuel, produced from domestic, renewable resources [8]. Its production can be carried out in both large factories and small installations for a farmer own use. It is made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. Unfortunately, the process leaves behind other byproducts than methyl esters (the chemical name for biodiesel) that is so called glycerin fraction. Glycerin fraction consists of glycerin (about 30–75%), methanol (5–20%), mono- and diglycerides, free fatty acids, phospholipids, water, soaps etc. – their percentage participation depends on the substrate and parameters of transesterification process [17].

In large factories a glycerin fraction is purified and can be further processed, in the case of production for farmers own use, however, chemical purification of contaminated glycerin is unprofitable and there is a risk that the glycerin fraction will be treated as waste. Because of a high load of organic compounds, contaminated glycerin may cause environmental pollution or disturb wastewater treatment plant functioning. To partially resolve this problem the glycerin fraction can be used as a carbon source for granulated activated sludge production. Granulated activated sludge is a promising technology for decentralized wastewater treatment [14] and can be used, for example, in household sewage treatment plants.

The aim of the presented research was to investigate possibilities of forming of aerobic granulated activated sludge in the reactor with h/d of 2.1 fed with glycerin fraction from biodiesel production. This research, according to our knowledge, is the first time when granulated activated sludge was obtained on the base of this substrate. In order to characterize the obtained biomass, free settling tests and wet sieving analysis were employed. Employment of a typical SBR reactor and easily available organic substrate enhances a utilitarian potential of presented technology of granulated activated sludge production.

MATERIALS AND METHODS

SBR operation

The experiment was carried out for 130 days. In the experiment a 8.0 dm$^3$ sequencing batch reactor with a height of 36 cm and 17 cm diameter was employed (h/d = 2.1). Seed sludge was collected from a conventional municipal wastewater treatment plant in Olsztyn (Poland). The glycerin fraction (423 g COD·dm$^{-3}$, oil and grease 77 g·dm$^{-3}$, total nitrogen 0.98 g N·dm$^{-3}$) were obtained from a farmer biodiesel installation in Lubomino (Poland). The temperature in the experiment room was ambient (varying from 18 to 21°C) and pH in reactor was kept between 7 and 8. The reactor was supplied with a constant air velocity of 8 dm$^3$·min$^{-1}$, and wastewater exchange ratio of 75% was employed. The SBR operated in 12-hour cycle, with the following operating strategy: aeration (705 min), settling (5 min) decantation (5 min) and filling (5 min). During the filling period 4 dm$^3$ of artificial wastewater and 2 dm$^3$ of mixture of glycerin fraction and tap water were added to the reactor to make the final working volume of 8 dm$^3$. The artificial wastewater was composed of NH$_4$Cl (76.1 mg·dm$^{-3}$), Na$_2$HPO$_4$·12H$_2$O (46.0 mg·dm$^{-3}$), NaCl (10.1 mg·dm$^{-3}$), KCl (4.7 mg·dm$^{-3}$), CaCl$_2$ (3.5 mg·dm$^{-3}$), MgSO$_4$·7H$_2$O (16.7 mg·dm$^{-3}$), NaHCO$_3$ (243.2 mg·dm$^{-3}$), Na$_2$CO$_3$ (162.2 mg·dm$^{-3}$), FeCl$_3$·6H$_2$O, MnSO$_4$·H$_2$O, ZnSO$_4$,
The glycerin fraction was added in amount that led to mean COD concentration in the reactor at the beginning of aeration phase of 0.522 ± 0.11 g COD·dm$^{-3}$.

**Analytical measurements**

Sampling was made at the influent and effluent of the reactor. All samples were filtered using 0.2 µm micro-pore filter before being assayed. Oil and grease in glycerin fraction were measured using Soxhlet extractor and total nitrogen was measured by distillation method. Chemical oxygen demand, total suspended solids, volatile suspended solids and sludge volume index were measured according to Standard Methods [2]. On the 114 and 120 day of the experiment, samples were taken every hour during SBR cycle to describe COD and TSS concentration changes in the reactor.

**Activated sludge characteristic**

Respirometric measurements were performed in duplicate using OxiTop® System (WTW, Germany). Samples of granulated activated sludge were taken after 120 days of reactor operation at the end of SBR cycle. The biomass was washed in duplicate with phosphate buffer then with distilled water, and the TSS was measured. The procedure was conducted as previously described [4].

The particle size selection of granulated activated sludge was done according to commonly used particle size analysis of soil [21]. A wet sieving technique using Retsch AS 200 Sieve Machine was employed with the following sieve size classes: 0.25, 0.5, 1, 2, 4, and 8 mm. For sieving, 750 cm$^3$ of granulated activated sludge was taken. The sieving process was supported by tap water (temperature 12°C) from the spray nozzle which was located above the uppermost sieve. The water left the sieve stack together with the last fraction through the outlet in the collector. Rinsing was carried out until the liquid leaving the sieve stack outlet was no longer turbid with solid particles. In this experiment sieving lasted for 5 minutes and an amplitude of vibration was 1.5 mm.

In order to examine physical properties of granulated activated sludge and separated granule classes the free settling test procedure described by [23] was used. Granulated activated sludge sample of 2 cm$^3$ was taken from the reactor and placed in a column filled with tap water (temperature 12°C). A floc settling was photographed in the dark room. The settling flocs were illuminated with photo-flash-lamp controlled by an electronic system ensuring flashes every 3 seconds. The digital camera (Canon G5, resolution 5 Mpic.) shutter was kept open for 5 flashes for every photo. Four photos were taken during 15 to 20 min of settling, before the next sludge sample was introduced. In the experimental run 24 photos were taken. During the experiment 573 granules were examined. The equivalent diameter, granule radius and settling velocity of granules were measured using the software UTHSCSA Image Tool version 3.0. According to the Stoke’s law the following physical parameters were determined: density of granules, effective, buoyant density of aggregate in liquid, granule volume, granule mass, Reynolds number, and fractal dimension of granule. For calculations it was provided that the granules were impermeable and spherical. Water density and viscosity values were presumed for 12°C and made 0.9995 g·cm$^{-3}$ and 1.230·10$^{-3}$ kg·m$^{-1}$·s$^{-1}$ respectively.

According to Stoke’s law the granules density may be expressed as:
\[ \rho_f = \rho_w + \frac{9V_\eta}{2r^2 g} \]  

(1)

This is the real density of a granule containing aggregated microorganisms and water. The effective, buoyant density of an aggregate in liquid (excluding water) may be expressed as:

\[ \rho_e = \rho_f - \rho_w \]  

(2)

The granule volume was calculated on the basis of the equation for the volume of the sphere. The granule mass was calculated as:

\[ m = V_f \cdot \rho_e \]  

(3)

The Reynolds number of granules settling was determined on the basis of the following equation:

\[ \text{Re} = \frac{2 \cdot V \cdot r \cdot \rho_w}{\eta} \]  

(4)

An important parameter that characterizes a fractal object is the fractal dimension, which corresponds to the space-filling capacity of an object. The mass of a fractal object with fractal dimension ranging \(1 \leq D \leq 3\) can be considered to be proportional to its size [29]. With known granule density, granule mass, and with known dependence for fractal objects:

\[ m \propto r^D \]  

(5)

provided that the granule is spherical, \((m)\) may be expressed as:

\[ m = \frac{4 \cdot \pi \cdot r^3}{3} \cdot \rho_e \]  

(6)

so

\[ r^D = \frac{4 \cdot \pi \cdot r^3}{3} \cdot \rho_e \]  

(7)

hence

\[ \rho_e \propto r^{D-3} \]  

(8)

and

\[ \log \rho_e \propto (D-3) \cdot \log r \]  

(9)

\((D-3)\) means the slope of the log-log line; therefore the fractal dimension may be obtained as:

\[ D = 3 + \frac{\Delta \log \rho_e}{\Delta \log r} \]  

(10)

Statistical analyses

The analysis of variance between mean values of estimated parameters of granules was carried out with the use of ANOVA test at the significance level of \(p < 0.05\).

The normality of the distribution was confirmed by Szapiro-Wilk’s test, whereas the hypothesis of the homogeneity of variances across the groups was verified on the basis of Levene’s test. In the text after symbol ± standard deviation was given.

RESULTS

In the presented experiment SVI value of the seed sludge was 103 cm\(^3\)-g\(^{-1}\). After a startup of the experiment this value gradually decreased parallel with the growth of granules.
and after about 80 cycles (40 days) of reactor operation it stabilized at the level of 40–50 cm$^3$·g$^{-1}$ (Fig. 1A). Small granules with a diameter of about 2 mm were observed for the first time after 70 cycles, after 80 cycles of reactor operation a well shaped granulated activated sludge was obtained in the reactor (Fig. 1B).

Chemical analyses were started from cycle 50. During investigation period the mean cellular residence time (sludge age) averaged 2.2 ± 0.4 day. At mean organic compounds load of 1.43 ± 0.1 mg COD·mg VSS$^{-1}$·d$^{-1}$, the removal of COD during the experiment averaged 94.14 ± 2.7% (Fig. 2A) and chemical oxygen demand in the effluent did not exceed 124 mg COD·dm$^{-3}$. COD concentration changes during the SBR cycle (mean values from cycles 114 and 120) are presented in Figure 2B. After wastewater addition, COD concentration in the reactor was 450 ± 19 mg O$_2$·dm$^{-3}$, during the first 3 hours it rapidly decreased to about 40 mg COD·dm$^{-3}$ and remained at this level to the end of SBR cycle. Biomass increased according to 0-order reaction (data not shown) and the mean growth
yield of microorganisms was 0.41 ± 0.23 mg TSS·mg⁻¹ COD. Respirometric measurements showed that oxygen uptake for endogenous respiration was at the level of 11.4 ± 5.8 mg O₂·g VSS⁻¹·h⁻¹ and no oxygen depletion for nitrification was observed. The oxygen depletion for substrates oxidation was, however, high and averaged 69.5 ± 6.5 mg O₂·g VSS⁻¹·h⁻¹.

In order to characterize the obtained biomass, the sieve analysis and free settling tests were employed. The sieve analysis showed that more than 60% (w/w) of biomass consisted of particles with the diameter in the range of 4–8 mm. Granules with diameters 2–4 mm and > 8 mm had also significant contribution in total biomass – 10.7 and 18.4% (w/w), respectively (Fig. 3). On the basis of the cumulative curve of granules size distribution it was calculated that 80% (w/w) of all granules had diameter in the range from 2.1 to 9.8 mm.

The analysis of granulated activated sludge digital photos allowed for detailed characterization of granulated activated sludge as a whole and granules in particular size classes (Tab. 1). The granulated activated sludge was characterized by a mean settling velocity of 3.26 ± 2.19 mm·s⁻¹, effective, buoyant density of 3.86 ± 5.64 mg·cm⁻³ and granule equivalent diameter of 2.71 ± 2.14 mm. In general, the settling of granulated activated sludge had laminar character because Reynolds number value was below 2300. The ratio of settling velocity to granule diameter (V/R) equaled 1.79 and confirmed the good settling properties of granulated activated sludge. The mean real density of granules containing aggregated microorganisms and water was on the level of 1.0034 ± 0.0056 g·cm⁻³, and was higher than the density of water in the same temperature (12°C). The fractal dimension calculated for granulated activated sludge was 1.459, with r² of log(ρₑ) - log(r) equal 0.768 (Tab. 1.).
Wet sieving procedure categorized granules in 6 size classes. Statistical analysis proved significant (p < 0.05) differences of all measured parameters between the classes. Granules with the diameter between 2–4 mm were numerically most abundant in biomass and consisted in 32.3% of all granules (Tab. 1). It was observed that V, V_f, m and Re values significantly (p < 0.05) increased parallel with increasing granules diameter. The granules with diameter below 2 mm, weighted less than 0.058 ± 0.037 mg while larger granules with diameter exceeding 2 mm had mass in the range from 0.078 ± 0.047 to 0.508 ± 0.183 mg. Adverse tendency was observed for the mean effective, buoyant density of an aggregate in a liquid (ρ_e) (Tab. 1). For small granules (0.25 < R < 2 mm) it was in range between 5.01 ± 3.23 and 13.66 ± 10.63 mg·cm⁻³, but larger granules with R higher than 2 mm had relatively small ρ_e ranging from 0.13 ± 0.1 to 0.88 ± 0.08 mg·cm⁻³.

An additional experiment proved that a twofold increase in glycerin fraction load resulted in disintegration of the granules in the reactor in given technological conditions. The obtained biomass was also stored for 4 weeks at 4°C in the effluent wastewater without oxygen and substrate supply. After 4 weeks most of the granules preserved their structural integrity.

DISCUSSION

The major selection pressures responsible for aerobic granulation are settling time and wastewater exchange ratio. On the basis of literature data in the presented experiment settling time of 5 minutes and wastewater exchange ratio of 75% were employed [16, 20]. The transition from flocculated sludge to sludge with low SVI (40–50 cm³·g⁻¹) typical
for granulated activated sludge [27, 28] proved that the chosen strategy was successful. Moreover, only granules with diameter between 0.25–0.5 mm had Re below 1, characteristic for activated sludge flocs [12]. Remaining granules classes had Re value higher than 1 and this fact additionally confirmed granulation of activated sludge.

In the presented research wet sieving technique and free settling tests were employed for granules characteristics. Because of their simplicity and low testing cost, the free-settling tests are the most widely described method in literature for measuring the flocs basic physical properties [6]. From practical point of view, free settling tests may be useful for technological description of granulated activated sludge properties. Providing that highly compacted flocs (granules) are impermeable, this method allows for determining settling velocity, mass, volume and fractal dimension of granules.

Reynolds number values pointed out that the sludge settling in the reactor had laminar character and SVI changes in time showed that settle ability improved as the granulation progressed. Presuming that granules are characterized by Re > 1 [12], 2.5% (w/w) of biomass in the reactor (a sum of masses of particles with diameter below 0.5) were flocs. Free settling tests results indicate that granules with Re > 1 had equivalent diameter higher than 0.5 mm and minimal settling velocity of about 2 mm·s$^{-1}$. On the basis of these results it can be concluded that in order to separate the small fraction of flocs from granules in employed reactor, sedimentation period should be shortened to about 1–1.5 minute, so that only particles with settling velocity equal or higher than 2 mm·s$^{-1}$ would be separated.

Settling velocity of microbiological aggregates depends on the geometric parameters of these particles as well as their density and porosity. Fractal dimension of an object is a quantitative measure of how the primary particles occupy the floc interior space. Li and Ganczarczyk [13] proved that aggregates generated in water and wastewater treatment processes exhibit a fractal dimension between 1.4 and 2.8. The values close to 1.4 are representative for flocs with smooth surface, while 2.8 is typical for very wrinkled and porous flocs [12]. The low value of fractal dimension indicates that granules obtained in the experiment were compact and relatively smooth in comparison with typical flocs. Our experimental data also point to a very important consequence of the fractal, self-similar nature of the aggregates, i.e., their density noticeable decrease with an increasing size.

A wet sieving technique can be used for activated sludge characteristic of both aerobic [26] and anaerobic granulated activated sludge [19]. Presuming that the smallest floc is made of two microcolonies (125 µm) [25], we decided to use the smallest sieve with the holes of 250 µm diameter. Usually microbial flocs formed in a conventional wastewater biological treatment are loose aggregates with undefined shape and a size from 0.05 to 0.2 mm [10]. The average diameter of aerobic granules varies in the range from 0.2 to 5 mm and is mainly due to a balance between growth and abrasive detachment due to strong hydrodynamic shear force in aerobic reactors [15]. In our experiment wet sieving proved that granules with diameter in the range 2–4 mm were numerically most abundant while 60% (w/w) of granulated activated sludge mass posed particles with a diameter in the range of 4–8 mm. Similar results were obtained by Wang et al. [28]. In research conducted in SBR fed with glucose as a carbon source at organic loading rate of 4.8 kg COD·m$^{-3}$·d$^{-1}$ granules were dominant sludge forms with most of diameters about 6–9 mm. Authors explain that for a given organic loading rate and shearing force, the dynamic growth-decay equilibrium was maintained in the reactor. As a result, the granules existing in the reactor were matured ones with a larger size.
Despite the high organic compounds load the efficiency of carbon removal in the presented technology was high (94.14 ± 2.7%) and most of the introduced COD was rapidly removed during the first 2–3 hours of aeration. It can be assumed that the length of the cycle could have been shortened without decrease in carbon removal efficiency. The respirometric measurements indicated that the rate of substrate oxidation by investigated granulated activated sludge was relatively high. For example, in research conducted by [1] in a plant treating mainly domestic wastewater, oxygen uptake rate varied between 26.3–38.9 mg O₂·g VSS⁻¹·h⁻¹ and was about two times lower in comparison with values obtained in the presented research. The observed high activity of microorganisms confirms a very good potential of granulated activated sludge in organic pollutants removal. The mean growth yield of microorganisms of 0.41 ± 0.23 mg TSS·mg⁻¹ COD was similar to values obtained by [26]. Authors reported that growth yield of microorganism in reactors differing in superficial air velocity changed from 0.48 to 0.33 MLSS·mg⁻¹ COD for an air velocity of 0.5 to 4 dm³·min⁻¹, respectively.

Literature data reveal that nearly 100% of aerobic and anaerobic granules are produced in column-type air or liquid up flow reactors, since a high ratio of reactor height to diameter seems to favor the formation of granular sludge [15]. It improves selection of granules by the difference in settling velocity [5] and ensures a longer circular flow trajectory which provides a more effective hydraulic attrition to microbial aggregates. The high shearing force can induce microorganisms to secrete more exopolysaccharides, which mediate cohesion and adhesion of cells and play a crucial role in maintaining the structural integrity of aerobic granules [26]. In the presented experiment granulated activated sludge was obtained in a traditional, not a column-type, SBR with h/d ratio of 2.1. This fact confirms that SBRs presently used in wastewater treatment plants can be adapted to granulated activated sludge technology. It is, however, necessary to stress that the drawback of this solution is a larger supply of air to the reactor (8 dm³·min⁻¹) in comparison with column reactors in which air supply at the level of 2.4–6 dm³·min⁻¹ is employed [11, 25, 26].

The fact that granules maintained their structural integrity despite the long storage implies that the obtained granulated activated sludge can be used when substrate availability changes with time, as it happens during biodiesel production. The fact that a 2-fold increase in glycerin fraction load resulted in disintegration of the granules can be explained by results obtained by Moy et al. [18]. Authors proved that after reaching organic loading rate of 9 g COD·dm⁻³·d⁻¹ (acetate addition) granules in the reactor disintegrated, and they concluded that for a given organic substrate granules formation can be successful only in a defined range of concentrations. It can be also assumed that collapsing of the granulation process after 2-fold increase in organic carbon load could have been caused by the fact that glycerin fraction has toxic influence on microorganisms caused by methanol and soaps presence.

CONCLUSIONS

It is possible to obtain aerobic granulated activated sludge feeding the traditional SBR reactor (h/d equal 2.1) with glycerin fraction from biodiesel production as a sole organic carbon source. The obtained granulated activated sludge was characterized by low SVI (40–50 cm³·g⁻¹), 60% (w/w) of granulated activated sludge constituted spherical aggre-
gates with diameter in the range of 4–8 mm. The effectiveness of COD removal averaged 94.14 ± 2.7% and most of the introduced COD was rapidly removed during the first 2–3 hours of aeration. On the basis of free settling test results it can be concluded that, for given technological parameters and reactor configuration in order to remove flocs from the granulated biomass, the time of settling should be adjusted so that only granules with settling velocity of 2 mm·s\(^{-1}\) or higher are separated.

**LIST OF ABBREVIATIONS**

COD – chemical oxygen demand [mg COD·dm\(^{-3}\)],
D – fractal dimension,
d – reactor diameter [cm],
g – the standard gravity [m·s\(^{-2}\)],
h – reactor height [cm],
m – mass of granule [mg],
N – number of analyzed granules,
% N – share of each granule fractions in total number of analyzed granules [%],
p – significance level,
R – equivalent diameter of granule [mm],
r\(^2\) – determination coefficient,
R\(_e\) – Reynolds number,
SBR – sequencing batch reactor,
SVI – sludge volume index [cm\(^3\)·g\(^{-1}\)],
TSS – total suspended solids [mg·dm\(^{-3}\)],
V – settling velocity [mm·s\(^{-1}\)],
V\(_f\) – granule volume [cm\(^3\)],
VSS – volatile suspended solids [mg·dm\(^{-3}\)],
η – liquid viscosity [kg·m\(^{-1}\)·s\(^{-1}\)],
ρ\(_e\) – effective, buoyant density of an aggregate in liquid [mg·cm\(^{-3}\)],
ρ\(_f\) – density of granule [g·cm\(^{-3}\)],
ρ\(_w\) – density of the liquid [g·cm\(^{-3}\)].

**REFERENCES**

CHARAKTERYSTYKA OSADU CZYNNEGO GRANULOWANEGO HODOWANEGO NA FRAKCJI GLICYRNOWEJ Z PRODUKCJI BIODIESLA

Osad czynny granulowany hodowano z wykorzystaniem frakcji glicerynowej powstałej przy produkcji biodiesla. Po 7 tygodniach hodowli w warunkach tlenowych w reaktorze SBR (h/d = 2,1) uzyskano granulowany osad czynny charakteryzujący się indeksem osadu na poziomie 40–50 cm 3·g⁻¹. W warunkach hodowli przy obciążeniu osadu ładunkiem zanieczyszczeń na poziomie 1,43 ± 0,1 g ChZT·g sm⁻¹·d⁻¹, efektywność usuwania związków węglowych wyniosła 94,14 ± 2,7%. Analiza sitowa wykazała, że około 60% masy osadu czynnego stanowiły granule o średnicy 4–8 mm. Równolegle na podstawie testu swobodnego opadania wyznaczono ilościowy udział granul o różnych średnicach w osadzie czynnym granulowanym. Stwierdzono, że

CHARACTERISTIC OF GRANULATED ACTIVATED SLUDGE FED WITH ...
granule o średnicy 2–5 mm stanowiły najliczniejszą frakcję tj. około 32% wszystkich granul osadu czynnego. Prędkości opadania, masy oraz wartości liczby Reynoldsa dla granul znacząco wzrastały (p < 0.05) wraz ze wzrostem ich średnicy. Obserwowano, że wraz ze spadkiem średnicy granul następował wzrost ich średniej gęstości w cieczy.
FORMATION OF THE ACTIVATED SLUDGE BIOCENOSIS
DURING LANDFILL LEACHATE PRE-TREATMENT IN SBR

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Keywords: Landfill leachates, SBR, activated sludge, biocenosis, Zoogloea ramigera, filamentous bacteria, Opercularia sp.

Abstract: It has been proved that at the established SBR technological regime, 74–71% effectiveness of the removal of impurities expressed as COD (in the influent 955–1059 mg O₂·dm⁻³, respectively) can be obtained at Bx 0.40–0.45 mg COD·mg⁻¹·d⁻¹. Ammonium nitrogen, in the concentration of up to 292 mg NH₄-N·dm⁻³ was removed in 93% at Bx 0.40–0.96 mg COD·mg⁻¹·d⁻¹. The simultaneous denitrification described by 93% effectiveness of total nitrogen removal occurred, too. Activated sludge had the attributes of an engaged sludge in leachates pretreatment at Bx between 0.40–0.45 mg COD·mg⁻¹·d⁻¹. Its biocenosis consisted of zoogleal and filamentous bacteria, protozoa Mastigota nd., Diffugia nd., Aspidisca sp., Lionotus sp., Oxytricha sp., Opercularia sp., Tokophrya sp. and rotifera. At the critical values of Bx (0.96–1.64 mg COD·mg⁻¹·d⁻¹), when leachates pretreatment effectiveness sharply dropped, biocenosis of activated sludge consisted only of zoogleal and filamentous bacteria, hyphae fungi, Mastigota nd. and Opercularia sp.

INTRODUCTION

Landfilling is an important waste management technology aimed at protecting the biosphere from harmful influences. A total of 566 municipal landfill sites with organized leachate management are in operation in Poland [21]. Both a high content of toxic substances and the presence of numerous chemical and microbiological impurities make them a considerable threat to the environment as well as health and epidemiological hazard. Studies conducted at the Institute of Environmental Engineering Systems, Warsaw University of Technology, since 2003 showed that psychrophilic heterotrophic bacteria dominate quantitatively in leachates while spore forming bacteria and potentially pathogenic species of microscopic fungi occur in smaller numbers. The total number of mesophilic bacteria and thermotolerant coli form bacteria, the bacteria Clostridium perfringens and Listeria monocytogenes, are indicators of sanitary contamination of leachates [5]. As demonstrated by the U.S. Environmental Protection Agency, faecal coliform bacteria and Streptococcus faecalis occur in leachates from municipal landfills [21]. Thus, reliable methods of preventing the air and the ground-water environment in the vicinity of landfills from chemical and microbiological impurities must be developed to protect the environment. To achieve this, the degree of chemical and microbiological leachate contamination must be assessed and the efficiency of contaminant removal at individual unit treatment proc-
ess must be evaluated. Treatment methods of the landfill leachates may be divided into physicochemical and biological or a combination of both. Main physicochemical methods used in landfill leachate treatment include adsorption on active carbon, coagulation/floculation, membrane processes and advanced oxidation (O₃, O₃/H₂O₂, Fenton’s reaction, O₃/UV, O₃/H₂O₂/UV, UV/TiO₂). The molecular weight of complex organic compounds decreases in these processes, which enhances their susceptibility to biodegradation; however, full mineralization of organic substances occurring in leachates is not obtained. A greater efficiency is achieved with combined biological and physicochemical methods such as nitrification/denitrification/O₃/UV, nitrification/denitrification/precipitation/O₃, precipitation/membrane reactor/reversed osmosis, biological pre-treatment/TiO₂/UV/biological oxidation, activated sludge/electron-beam radiation [3, 18, 20, 21, 24].

The efficiency of biological methods is dependent mostly on the chemical composition of leachates, including the content of organic compounds and their susceptibility to degradation defined by the COD/BOD₅ ratio, the content of nitrogen, phosphorus and heavy metals. This is in turn influenced by the landfill age. Therefore, biological methods are mostly suitable for treatment of leachates from young landfills in which organic compounds occur as easily biodegradable compounds. As conventional technologies of the activated sludge and biological filters do not guarantee a full elimination of chemical and biological contaminants even in the case of leachates from young landfills, much attention has lately been paid to the use of the activated sludge method in SBRs. This technology is based on a long-term supply of leachate to reactor under alternating aerobic and anoxic conditions in the fill phase. It provides a high efficiency of the removal of carbon, nitrogen and phosphorus compounds while sludge bulking is eliminated. The advantages of this method are the small size of SBRs which can be then located near landfills and the possibility of the installation of a cover protecting the soil and the air from contamination by pathogenic microorganisms occurring in leachates. Studies on the practical application of this technology to treat leachates were conducted by, for instance, Dimadopoulus et al. [4], Surnacz-Górska et al. [19], Loukidou and Zouboulis [13], Klimiuk and Koc-Jurczyk [7], Klimiuk and Kuligowska [8, 9], Neczaj et al. [15], Kuligowska et al. [11, 12], and Zhou et al. [27].

The aim of this study was to determine the influence of an SBR load of chemical contaminants defined by COD on the formation of the activated sludge biocenosis. The results will be used to assess the SBR technology for the sustainable development of the activated sludge biocenosis that guarantees a high efficiency of the removal of leachate contaminants.

**SCOPE OF THE STUDY**

The technological parameters optimized in preliminary studies conducted within M. Szyłak-Szydłowski’s PhD project [22] were used in leachate pre-treatment. The following were determined during the process control:
- sludge concentration (d.m.) in the reactor during the mixing and aeration phases,
- sludge volume index,
- in the leachates entering to and flowing out from the reactor: pH, CODₚ, ammonia nitrogen (NH₄-N), nitrite nitrogen (NO₂-N), nitrate nitrogen (NO₃-N), total Kjeldahl nitrogen and total phosphate phosphorus,
- number of microorganism groups constituting the biocenosis of the activated sludge.
MATERIALS AND METHODS

**Sampling**

Leachates delivered to the collection well located near the landfill site designed for waste other than inert and hazardous waste, so-called municipal waste, in the south-eastern part of the town of Otwock via a drainage system were examined. The site has been in use since 1998, and its operation will be discontinued in 2012. Municipal wastes containing a high amount of biodegradable organic matter exceeding 20 Mg·d$^{-1}$ are deposited in the site. The estimated site capacity is 12·10$^5$ Mg; only 2.7·10$^5$ Mg has been used so far. The landfill is lined with a 2 mm PEHD geomembrane. Wastes are stored in districts on plots, whose thickness is 1.5–2 m, and the lining thickness is 0.15 m. Leachate waters and landfill gas quantities in the landfill as well as surface and underground waters near the landfill are monitored. The leachates were characterized by COD 3080 mg O$_2$·dm$^{-3}$, total organic carbon 1.254 mg C·dm$^{-3}$, BOD$_5$/COD – 0.181, SO$_4^{2-}$ – 160 mg SO$_4^{2-}$·dm$^{-3}$, SO$_4^{2-}$·Cl$^-$ – 0.074, 0.163 mg Cu·dm$^{-3}$, 2.065 mg Zn·dm$^{-3}$, 0.207 mg Pb·dm$^{-3}$, 0.017 mg Cd·dm$^{-3}$, 0.216 mg Cr·dm$^{-3}$, 0.003 mg Hg·dm$^{-3}$, electrolytic conductivity 19.5 mS·cm$^{-1}$ and pH 7.5 [5].

Leachate pre-treatment was conducted in an SBR with the working volume 6.9 dm$^3$, equipped with a mixer and the fine bubble aeration system that supplies oxygen concentration of 2 mg O$_2$·dm$^{-3}$. The activated sludge from the municipal waste treatment plant in Piaseczno near Warsaw was used as the seed of the reactor. The sludge concentration in the reactor remained in the range of 3–4 g·dm$^{-3}$, and the sludge age ($\theta_x$) at 12.5 d. The hydraulic retention time (HRT) was 16 hours, and the sludge load ($B_x$) ranged from 0.40 to 1.64 mg COD·mg$^{-1}$·d$^{-1}$, obtained by an increase in the percentage participation of leachates (5, 10, 15, 20 and 30%) in the mixture with synthetic wastewaters prepared according to the recipe given by Klimiuk and Wojnowska-Baryła [10].

The system worked in three 8-hour cycles per day. Each cycle consisted of a 45-minute fill phase, 30-minute mixing phase, 2.10 hour aeration phase, 45 minute mixing phase, 1.50 hour aeration phase, 1.30 hour settling phase and 30 minute decanting phase (including 25 minutes of decanting and 5 minute idling).

These parameters were “optimized” in so-called monitoring examinations (first stage of experiments), where the efficiency of impurities removal from the mixture of leachates and sewage at different duration time of each cycle phases was determined. These experiments are wider described in Szyłak-Szydlowski doctoral thesis.

Control examinations of the process in the ranges given above were conducted after two-weeks when $B_x$ changed.

**Chemical determinations**

Chemical oxygen demand (COD) was determined with the dichromate method as given in the standard PN-74/C-04578.03. Mineral nitrogen forms were determined with spectrophotometric methods, ammonia nitrogen (NH$_4^-$-N) (direct nesslerisation) as given in PN-C-04576-4:1994, nitrite nitrogen (NO$_2^-$-N) as given in PN-EN 26777:1999, and nitrate nitrogen (NO$_3^-$-N) as given in PN-82/C-04576.08. Total Kjeldahl nitrogen was determined with the titration method as given in PN-73/C-04576.12. Phosphate phosphorus was determined with the spectrophotometric method (molybdenum method) as given in PN-91/C-04537/09. The sludge dry mass was determined with the weight method as given in PN-EN827.
**Biological determinations**

Microscopic observations of the activated sludge biocenosis were conducted with an Op- ton contrast-phase microscope. The determinations are given as the frequency of individual group of microorganism per cm$^3$ of the sludge.

**RESULTS AND DISCUSSION**

Examinations were conducted in two stages. The first stage, recognized as preliminary, so-called monitoring, was purposed of determination of duration time and arrangement of particular cycle phases in SBR, providing effectiveness of contaminations removal, with set sludge load value, expressed by COD (see materials and methods). The second stage, whose results are presented below, constituted so-called proper examinations, heading for defining influence of sludge load ($B_x$) on effectiveness of impurities removal, with arrangement and duration of particular stages of cycle in SBR, set in the first stage of examinations.

The studies showed that COD equal 955 mg O$_2$·dm$^{-3}$ on average in the influent was removed in 74%, and ammonia nitrogen characterized by the initial concentration 61 mg NH$_4$-N·dm$^{-3}$ in 99% at $B_x$ 0.40 mg COD·mg$^{-1}$·d$^{-1}$ obtained at the 5% leachate content in the mixture containing synthetic wastewaters. Rapid nitrification with the production of nitrates also occurred as the concentration of these compounds in the effluent wastewaters increased to 26.7 mg NO$_3$-N·dm$^{-3}$. A significant reduction in the total nitrogen concentration from 106 to 33 mg N$_{tot}$·dm$^{-3}$ indicated the occurrence of simultaneous denitrification. A low efficiency of phosphorus removal (only 26%, at the initial P-PO$_4$ concentration of 14.3 mg P-PO$_4$·dm$^{-3}$) observed at this sludge load should be noticed (Tab. 1).

A $B_x$ increase to 0.45 mg COD·mg$^{-1}$·d$^{-1}$ obtained by a 10% addition of leachates to synthetic wastewaters resulted in a COD increase in the influent to 1059 mg O$_2$·dm$^{-3}$, ammonia nitrogen to 104 mg NH$_4$-N·dm$^{-3}$ and nitrite nitrogen to 0.590 mg NO$_2$-N·dm$^{-3}$. Consequently, total nitrogen in the influent reached 145 mg N$_{tot}$·dm$^{-3}$. Concentrations of the other contaminants in wastewaters did not change significantly. Under these conditions, the removal efficiency of contamination defined by COD and ammonia nitrogen was still high (71 and 97%, respectively), and nitrification (NO$_3$-N was 15.8 mg NO$_3$-N·dm$^{-3}$ in the effluent) and simultaneous denitrification (a decrease in total nitrogen concentration from 145 to 23 mg N$_{tot}$·dm$^{-3}$) also occurred. The efficiency of phosphorus removal fell down was 27%.

A significant decrease in the removal efficiency of contamination defined by COD to only 45% was observed when $B_x$ increased to 0.69 mg COD·mg$^{-1}$·d$^{-1}$ at the 15% addition of leachates to the mixture containing synthetic wastewaters. Influent COD was 1613 mg O$_2$·dm$^{-3}$, and the concentrations of individual nitrogen forms were: 202 mg NH$_4$-N·dm$^{-3}$, 0.270 mg NO$_2$-N·dm$^{-3}$ and 0.20 mg NO$_3$-N·dm$^{-3}$. The efficiency of ammonia nitrogen removal was still high (95%) due to nitrification. Simultaneous denitrification of nitrates also occurred as indicated by the 82% removal of total nitrogen; a drop in the phosphorus content was slight (16%) (Tab. 1).

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An increase in $B_x$ to 0.96 mg COD·mg$^{-1}$·d$^{-1}$ following an increase in the percentage participation of leachates (20%) in the mixture containing synthetic wastewaters resulted in an increase in the influent COD to 2069 mg O$_2$·dm$^{-3}$ and nitrogen forms to 292 mg NH$_4$-N·dm$^{-3}$, 1.07 mg NO$_3$-N·dm$^{-3}$. Nitrite nitrogen concentration was 0.100 mg NO$_2$-N·dm$^{-3}$.
Table 1. Effectiveness of the landfill leachates pretreatment in SBR depending on impurities sludge loading (mean values)

<table>
<thead>
<tr>
<th>Participation of leachates in the mixture with synthetic wastewaters [%]</th>
<th>Sludge loading, [mg COD·mg⁻¹·d⁻¹]</th>
<th>Sample Parameter</th>
<th>COD [mg O₂·dm⁻³]</th>
<th>N-NH₄ [mg·dm⁻³]</th>
<th>N-NO₂ [mg·dm⁻³]</th>
<th>N-NO₃ [mg·dm⁻³]</th>
<th>N-org [mg·dm⁻³]</th>
<th>N_Kjeldahl [mg·dm⁻³]</th>
<th>N_N [mg·dm⁻³]</th>
<th>P-PO₄ [mg·dm⁻³]</th>
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<tbody>
<tr>
<td>5</td>
<td>0.40</td>
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<td>955</td>
<td>61</td>
<td>0.030</td>
<td>0.69</td>
<td>44</td>
<td>106</td>
<td>106</td>
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<td>0.030</td>
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<td></td>
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<td>% removal</td>
<td>74</td>
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<td>–</td>
<td>81</td>
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<tr>
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<td>1059</td>
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<td>% removal</td>
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<td>–</td>
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<td>–</td>
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</table>
The removal efficiency of contamination expressed in COD was low (40%) at the high efficiency of ammonia nitrogen removal (97%). A significantly smaller increase in the amount of nitrates (to 7.80 mg NO₃-N·dm⁻³) indicated an occurrence of nitrification and denitrification processes, proceeded with high intensity. A high decrease of total nitrogen (93%) indicated an intensive process of simultaneous denitrification. Phosphorus removal was still not very efficient (17%).

A sudden drop in the efficiency of pre-treatment of leachates constituting 30% in the mixture with synthetic wastewaters (influent COD 3406 mg O₂·dm⁻³, 351 mg NH₄-N·dm⁻³, 1.040 mg NO₂-N·dm⁻³ and 4.67 mg NO₃-N·dm⁻³) occurred at Bx of 1.64 mg COD·mg⁻¹·d⁻¹. Under these conditions, the efficiency of COD removal was 15% and the process of nitrification was inhibited, as indicated by high concentration of NH₄-N in the effluent. However, an 85% removal of ammonia nitrogen took place and the process of simultaneous denitrification occurred (total nitrogen elimination in 82%). A significant phosphorus removal from the wastewaters delivered to the reactor no longer occurred (26%).

In conclusion, the technological examinations showed that leachate pre-treatment may be conducted with a highly efficient removal of carbon compounds expressed as COD only at Bx of 0.40 to 0.45 mg COD·mg⁻¹·d⁻¹ obtained by adding 5–10% leachates to synthetic wastewaters imitating municipal wastewaters. For this range of Bx, the influent COD was between 955 and 1059 mg O₂·dm⁻³, and the elimination of the contamination described by it was 74–71%, respectively. Thus it significantly exceeded the efficiency obtained by Kuligowska et al. [11] equal 87.7; 79.3 and 70.9% for the influent COD equal 570, 580 and 612 mg O₂·dm⁻³, respectively. A similar removal efficiency of contamination expressed as COD (85.5–79.3%), at the concentration in the influent equal 1090 mg O₂·dm⁻³) was also obtained by Diamadopoulos et al. [4] in the process conducted for the aeration phase of 20–14 hours, respectively, and also by Kuligowska et al. [12] (83–77% – concentration in the influent 1380 mg O₂·dm⁻³) at the sludge age 33–11 d, HRT 12–2 hours and an 18 hour aeration phase, respectively. According to Zhou et al. [27], the high sludge age (25 d) and the long aeration phase in the cycle (18 hours) encourage a high efficiency of the treatment process. Under these conditions, these authors obtained a 94% elimination of COD with the concentration of 5077 mg O₂·dm⁻³ and a 99% elimination of ammonia nitrogen with the concentration of 728 mg NH₄-N·dm⁻³.

In the present examinations, a significant degree of ammonia nitrogen removal from the wastewaters was observed up to 20% leachate content in the mixture with synthetic wastewaters (mean concentration in the influent 292 mg NH₄-N·dm⁻³, mean removal efficiency 97%). Therefore, a greater removal efficiency of this form of mineral nitrogen was obtained than in the wastewater treatment process conducted by Diamadopoulos et al. [4] and Kuligowska et al. [11]. The former obtained a 49–35% efficiency of NH₄-N removal (concentration in the influent 107 mg NH₄-N·dm⁻³) for the aeration stage 20–14 hours, respectively, and the latter a 99.8–99.9% elimination of NH₄-N whose concentration equaled 60–130 mg NH₄-N·dm⁻³.

The present studies show that the process of simultaneous denitrification indicated by a simultaneous considerable drop in the concentration of total nitrogen in the effluent (mean 93%) also occurred in the SBR up to 292 mg N-NH₄-N·dm⁻³ in the delivered wastewaters. The nitrification process of phase I and II occurred with significant intensity in the aeration phase up to $Bx = 0.69$ mg COD·mg⁻¹·d⁻¹, at which the influent COD was 1613 mg O₂·dm⁻³. This is consistent with previous studies by Surmacz-Gór ska et al. [20], who
observed that nitrification occurred without significant disturbances for COD values in the influent ranging between 1000 and 2000 mg O\textsubscript{2}·dm\textsuperscript{-3} in the SBR. When COD concentration increases, its hardly biodegradable part inhibits nitrification, and the authors recommend a longer wastewater aeration time to encourage its degradation. A significant removal of phosphorus was not observed during the pre-treatment process. Its amount in effluent wastewaters was 9.7–14.8 mg P-PO\textsubscript{4}·dm\textsuperscript{-3} for the load range examined in the study. Therefore, further treatment of effluent wastewaters with chemical methods must be conducted to reduce the phosphorus concentration to the level that does not cause eutrophication of water reservoirs receiving treated wastewaters.

Significant changes in the abundance and generic composition of microorganisms constituting the sludge biocenosis also occurred during leachate pre-treatment conducted at various values of $Bx$ (Fig. 1). The activated sludge used to inoculation of SBR showed the properties of well worked out sludge in treating the municipal wastewaters as it was characterized by well formed brownish flocs in the number 208·10\textsuperscript{3}·cm\textsuperscript{-3}, with visible numerous aggregations of zoogloeal bacteria (2.4·10\textsuperscript{3}·cm\textsuperscript{-3}) and typical colonies of Zoogloea ramigera (12.6·10\textsuperscript{3}·cm\textsuperscript{-3}) or filamentous bacteria (11.4·10\textsuperscript{3}·cm\textsuperscript{-3}). The microfauna consisted of 6 taxa belonging to the flagellate group of protozoa (8.4·10\textsuperscript{3}·cm\textsuperscript{-3}), free-swimming protozoa of the genus Aspidisca (4.2·10\textsuperscript{3}·cm\textsuperscript{-3}), Lionotus sp. (4.8·10\textsuperscript{3}·cm\textsuperscript{-3}) and Oxytricha (0.6·10\textsuperscript{3}·cm\textsuperscript{-3}), attached protozoa of the genus Vorticella and rotifers (7.2·10\textsuperscript{3}·cm\textsuperscript{-3}).

After the 7-day period of leachates dosage in the 5% quantitative ratio to municipal wastewaters (mean influent COD 955 mg O\textsubscript{2}·dm\textsuperscript{-3}) in the amount ensuring $Bx$ at 0.40 COD·mg\textsuperscript{-1}·d\textsuperscript{-1}, sludge flocs became light brown, big, merged, settling well (sludge index 102 cm\textsuperscript{3}·g\textsuperscript{-1}), with numerous aggregations of zoogloeal bacteria (95.4·10\textsuperscript{3}·cm\textsuperscript{-3}) and typical colonies of Zoogloea ramigera (12.6·10\textsuperscript{3}·cm\textsuperscript{-3}) and filamentous bacteria (18·10\textsuperscript{3}·cm\textsuperscript{-3}). The microfauna consisted of 5 taxa belonging to the flagellate group of protozoa (Mastigota nd., Aspidisca sp., Oxytricha sp., Opercularia sp., shelled amoebae) and rotifers (3.0·10\textsuperscript{3}·cm\textsuperscript{-3}). The genera Aspidisca (4.8·10\textsuperscript{3}·cm\textsuperscript{-3}) and Opercularia (13.8·10\textsuperscript{3}·cm\textsuperscript{-3}) dominated in the group of protozoa. The continuation of the pre-treatment process at the above reactor load caused a decrease in the number of zoogloeal aggregations of bacteria (to 12.2·10\textsuperscript{3}·cm\textsuperscript{-3}), protozoa of the flagellate group and belonging to the genus Aspidisca (up to 0.6·10\textsuperscript{3}·cm\textsuperscript{-3}) and a significant increase in the number of Opercularia sp. (up to 33·10\textsuperscript{3}·cm\textsuperscript{-3}) in the sludge. Free-swimming protozoa of the genus Lionotus (0.6·10\textsuperscript{3}·cm\textsuperscript{-3}) and shelled amoebae (1.2·10\textsuperscript{3}·cm\textsuperscript{-3}) also occurred (Tab. 2). The total number of protozoa in the activated sludge was thus similar to that recognized as the maximum number typical for well working activated sludge ranging from 10\textsuperscript{3} to 5·10\textsuperscript{4}·cm\textsuperscript{-3} [1, 14].

An increase in the sludge load to 0.45 COD·mg\textsuperscript{-1}·d\textsuperscript{-1} by adding 10% leachates to synthetic wastewaters caused flocs dispersion and a drop in their size but it did not deteriorate sludge settling properties (sludge index was 96 cm\textsuperscript{3}·g\textsuperscript{-1}). The number of zoogloeal bacterial aggregations was similar to that recorded for the load of 0.40 mg COD·mg\textsuperscript{-1}·d\textsuperscript{-1} (23.4·10\textsuperscript{3} – 72·10\textsuperscript{3}·cm\textsuperscript{-3}); Zoogloea ramigera, however, disappeared and the number of Opercularia sp. decreased to 2.8·10\textsuperscript{3} – 4.2·10\textsuperscript{3}·cm\textsuperscript{-3}. The adverse influence of the sludge on the microfauna in the wastewaters dosaged to the reactor was indicated by an increase in the number of Mastigota nd. (2.1·10\textsuperscript{3}·cm\textsuperscript{-3}), the disappearance of shelled amoebae, protozoa of the genera Lionotus and Oxytricha, at the end of the study period – as well as Aspidisca sp. and rotifers and the appearance of telotrochs deattached from the stalks of attached ciliates. Attached ciliates of the genus Tokophrya sp. (0.6·10\textsuperscript{3}·cm\textsuperscript{-3}) occurred
Fig. 1. Results of biological examinations of activated sludge in Sequencing Batch Reactor at sludge loading values of $B_x = 0.40$–1.64 mg ChZT·mg$^{-1}$·d$^{-1}$.
Table 2. Results of biological examinations of activated sludge in Sequencing Batch Reactor

<table>
<thead>
<tr>
<th>Participation of leachates in the mixture with synthetic wastewaters [%]</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge loading [mg COD·mg⁻¹·d⁻¹]</td>
<td>0.40</td>
<td>0.45</td>
<td>0.96</td>
<td>1.64</td>
</tr>
<tr>
<td>Sludge index [cm³·g⁻¹]</td>
<td>102</td>
<td>96</td>
<td>80</td>
<td>72</td>
</tr>
<tr>
<td>Date of examination</td>
<td>12.05.05</td>
<td>24.05.05</td>
<td>20.06.05</td>
<td>12.07.05</td>
</tr>
</tbody>
</table>

General characteristic of the sludge

| Sludge flocs                                                                 | –       | –       | –       | –       | –       | –       |
| aggregations of zoogloal bacteria                                        | 95.4·10³ | 12.2·10³ | 23.4·10³ | 72·10³  | 3·10³  | 1.2·10³ |
| Zoogloea ramigera (Itzigsohn, 1868)                                      | 4.2·10³  | –       | –       | –       | –       | –       |
| filamentous bacteria                                                     | 18·10³  | 16.8·10³ | 32.4·10³ | 14·10³  | 52.2·10³ | 43.8·10³ |
| Mastigota nd.                                                            | 1.8·10³  | 0.6·10³  | –       | 2.1·10³ | –       | 3.6·10³  |
| Aspidisca sp.                                                            | 4.8·10³  | 0.6·10³  | 0.6·10³  | –       | –       | –       |
| Glaucoma sp.                                                             | –       | –       | –       | –       | –       | 1.2·10³  |
| Lioonous sp.                                                             | –       | 0.6·10³  | –       | –       | –       | –       |
| Oxytricha sp.                                                            | 0.6·10³  | –       | –       | –       | –       | –       |
| Opercularia sp.                                                          | 13.8·10³ | 33·10³  | 4·10³   | 2.8·10³ | 22.2·10³ | 3.5·10³  |
| Tokophrya sp.                                                            | –       | –       | 0.6·10³ | –       | –       | –       |
| shelled amoebae (Difflugia nd.)                                          | –       | 1·2·10³  | –       | –       | –       | –       |
| telotroch                                                                | –       | –       | 1·4·10³  | –       | –       | –       |
| Rotatoria nd.                                                            | 3.0·10³  | 1·8·10³  | 1·8·10³  | –       | 0.6·10³  (dead) | –       |
periodically in the sludge. Four taxa of microorganisms constituted the microfauna at the above sludge load.

A sudden deterioration of the quality of the activated sludge caused an increase in its load to 0.96 mg COD·mg⁻¹·d⁻¹ by dosage 20% leachates in the mixture with synthetic wastewaters. Further flocs fragmentation and encystation, accompanied by a drastic decrease in the number of bacteria forming zoogloenal aggregations (down to 3·10³·cm⁻³) in them, a reduction in the number of the microfauna to two taxa (Glaucoma sp. – 1.2·10³·cm⁻³ and Opercularia sp. – 22.2·10³·cm⁻³) and the death of rotifers, occurred. At the same time, the number of filamentous bacteria increased significantly in the sludge (to 52.2·10³·cm⁻³), which may indicate a high resistance of these bacteria to toxic compounds occurring in leachates.

The sludge load of 1.64 mg COD·mg⁻¹·d⁻¹ at the 30% addition of leachates to synthetic wastewaters enhanced the phenomena described above. The number of aggregations of zoogloenal bacteria fell down to 1.2·10³·cm⁻³, while that of filamentous bacteria was still very high (43.8·10³·cm⁻³). Moulds (3000·cm⁻³) occurred in the sludge. These organisms did not influence adversely sludge settling properties and the volume index was still low and equaled 72 cm³·g⁻¹. Flagellates (3.6·10³·cm⁻³) and Opercularia sp. (3.5·10³·cm⁻³) were the only animal organisms in the sludge.

In conclusion, the studies showed that the activated sludge in the SBR had properties of a well working sludge when 5–10% of leachates were dosaged in the mixture with synthetic wastewaters at which the influent COD was 955–1059 mg O₂·dm⁻³, 61–104 mg N-NH₄·dm⁻³, 0.030–0.590 mg NO₂-N·dm⁻³, 0.57–0.69 mg NO₃-N·dm⁻³ and 13.3–14.3 mg P-PO₄·dm⁻³, and Bx 0.40–0.45 mg COD·mg⁻¹·d⁻¹. Besides zoogloenal and filamentous bacteria forming the flocs body, the microfauna of the sludge was composed of 5 and 4 taxa, respectively. Similar abundance of taxa in the activated sludge was recorded by Kuligowska et al. [11] during the treatment of wastewaters characterized by COD of 612 mg O₂·dm⁻³. Flagellates and attached protozoa of the genera Opercularia and Vorticella were the most important representatives of the microfauna. Filamentous bacteria were not recorded. These authors showed an even greater diversity of the microfauna (15–22 taxa) in the activated sludge adapted for the treatment of wastewaters characterized by COD ranging from 570 to 580 mg O₂·dm⁻³. Shelled amoebae of the genus Centropyxis sp., attached ciliates Acineta uncinata, Epistilis plicatilis, Opercularia coarctata and free-swimming ciliates Aspidisca cicada dominated in the microfauna then.

An increase in the leachate participation in the wastewaters dosaged to the reactor to 20 and 30% and by this Bx values to 0.96 and 1.64 mg COD·mg⁻¹·d⁻¹ caused a considerable decrease in the abundance of zoogloenal bacteria in the sludge, a sudden disappearance of the majority of protozoa and rotifers. At the same time, this encouraged the growth of filamentous bacteria. Apart from zoogloenal bacteria and attached protozoa of the genus Opercularia, this group of bacteria may be considered to be a characteristic component of the activated sludge biocenosis adapted for the pre-treatment of the study leachates (Fig. 2).

The disappearance of the microfauna in the activated sludge at Bx of 0.96 to 1.64 mg COD·mg⁻¹·d⁻¹ should be attributed to the presence of carbon compounds that are difficult to biodegrade or toxic in the study leachates. This is indicated by the high COD value in the treated wastewaters of 1246 and 2879 mg O₂·dm⁻³, respectively. The influence of the concentrations of mineral nitrogen forms was smaller as they did not exceed
the values characteristic of toxic activity or inhibiting microfauna growth in the activated sludge (Tab. 3). The content of heavy metals in the pre-treated wastewaters did not inhibit the growth of protozoa and rotifers in the sludge, too. According to Abraham et al. [1], protozoa belonging to Aspidisca cicada, Chilodonella uncinata, Vorticella convallaria and Vorticella microstoma species tolerate concentrations of Fe > 2 mg·dm$^{-3}$, Zn > 0.5 mg·dm$^{-3}$, Cu > 0.06 mg·dm$^{-3}$ and Cr = 0.10 mg·dm$^{-3}$, that is significantly exceeding the concentrations of these metals in the pre-treated wastewaters.

The present studies are sufficient to suggest that the efficiency of leachate pre-treatment may be enhanced by increasing the number of microorganisms adapted to degrading the contaminations occurring in them. These are zoogloeal and filamentous bacteria as well as protozoa of the genus Opercularia in the case of the study leachates. The studies by Żubrowska-Sudół [28] and Podedworna and Żubrowska-Sudół [16] showed that moving-bed sequencing batch biofilm type reactors (MBSBBR) in which the growth of microorganisms occurs as activated sludge and biofilm on the surface of movable plastic carriers with a large specific surface create conditions conducive to an intensive multiplication of microorganisms. This technology allows a large load of contaminations to be taken in without changing the reactor volume, guarantees nitrification regardless of the wastewater retention time and activated sludge age, as well as makes the process of integrated denitrification and biological phosphorus removal possible under conditions of
Table 3. Comparison of the concentrations of different forms of mineral nitrogen in pretreated wastes at the critical sludge load values with toxic concentrations for activated sludge microfauna

<table>
<thead>
<tr>
<th>Concentration of different forms of mineral nitrogen at the critical sludge load values (Bx)</th>
<th>Inhibition or toxic treatment (activity) on activated sludge microfauna</th>
<th>Author, year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N-NH₄⁺</td>
<td>N-NO₂⁻</td>
</tr>
<tr>
<td>influent</td>
<td>0.96 mg COD·mg⁻¹·d⁻¹</td>
<td>0.100</td>
</tr>
<tr>
<td>effluent</td>
<td>292</td>
<td>0.100</td>
</tr>
<tr>
<td>influent</td>
<td>1.64 mg COD·mg⁻¹·d⁻¹</td>
<td>0.050</td>
</tr>
<tr>
<td>effluent</td>
<td>351</td>
<td>1.040</td>
</tr>
<tr>
<td></td>
<td>52.1</td>
<td>0.070</td>
</tr>
</tbody>
</table>

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REFERENCES


FORMATION OF THE ACTIVATED SLUDGE BIOCENOSIS DURING LANDFILL ...


W pracy wykazano, że przy przyjętym reżimie technologicznym pracy SBR uzyskać można 74–71% efektywności usuwania zanieczyszczeń wyrażonych w ChZT (stężenie w dopływie 955–1059 mg O₂·dm⁻³) przy Bx w zakresie 0,40–0,45 mg ChZT·mg⁻¹·d⁻¹. Azot amonowy w stężeniu do 292 mg NH₄-N·dm⁻³ usuwany był w 97% przy Bx w zakresie 0,40–0,96 mg ChZT·mg⁻¹·d⁻¹. Jednocześnie zachodził proces symultanicznej denitryfikacji obrazowany 93% efektywnością usuwania Nₚₕ. Osad czynny wykazywał cechy osadu wpracowanego do podczyszczania odcieków przy Bx w zakresie 0,40–0,45 mg ChZT·mg⁻¹·d⁻¹. Jego biocenozę stanowiły bakterie zoogéralne i nitkowane, pierwotniaki Mastigota nd., Difflugia nd., Aspidisca sp., Lionotus sp., Tokophrya sp. i wrotki. Przy wartościach krytycznych Bx (0,96–1,64 mg ChZT·mg⁻¹·d⁻¹), przy których gwałtownie spadła efektywność podczyszczania odcieków, biocenozę osadu stanowiły jedynie bakterie zoogéralne i nitkowane, grzyby strzępkowe oraz Mastigota nd. i Opercularia sp.
PHOSPHORUS RELEASE FROM LAKE BOTTOM SEDIMENTS AFFECTED BY ABIOTIC FACTORS

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Keywords: Lake, bottom sediments, abiotic factors, phosphorus release, sequential extraction.

Abstract: The likelihood of phosphorus release from lake bottom sediments into bulk water as a result of changes in the physicochemical conditions in the lake has been analyzed by the method of sequential extraction proposed by Tessier et al. The procedure developed for estimation of the threat to water ecosystems posed by heavy metals accumulated in the bottom sediments, can be successfully applied in estimation of the release of other substances, including biogenic ones, as the subsequent states of extraction simulate the abiotic conditions and processes that can naturally take place in the near-bottom water layer and in the bottom sediment.

INTRODUCTION

In lake water phosphorus occurs in relatively low amounts, however, the effect of its presence can be profound. In natural conditions this element is usually a factor limiting primary production [16, 17]. In the bulk phosphorus occurs in the form of suspension as an abioseston (mineral trypton), bioseston (plankton) and organic trypton and in the dissolved form – mainly as orthophosphates. The above phosphorus species occur in water at a dynamic equilibrium. The phosphates are absorbed by phytoplankton and in the periods of its abundant development the concentration of phosphates in bulk water practically decreases to zero. The possible excess of phosphates is bound by the ions of iron, aluminium and calcium or is adsorbed on the surface of the suspension [2]. The phytoplankton and organic trypton are consumed by the zooplankton and as products of metabolism phosphates are released back to bulk water. Phosphorus can be also released from organic matter by biochemical reactions with phosphatases. However, the greatest amounts of phosphorus are accumulated in the bottom sediments fed with sedimenting suspensions. It is the main process eliminating phosphorus from bulk water, especially in deep lakes in which its migration back to epilimnion is difficult [6, 8, 18]. The reverse process, i.e. the release of phosphorus from the bottom sediments is often the main source of phosphates in lake water and it is referred to as the “inner source” of phosphorus in lakes [4, 17]. From the surface layers of the bottom sediment phosphorus is released into the bulk by the biotic path (enzymes, bacteria and benthonic organisms) and as a result of abiotic physical and chemical factors such as pH, redox potential, temperature, etc.
[1, 4, 7, 9, 16, 17]. There are many methods of phosphorus fractionation in bottom sediments addressed to different forms of its binding to the matrix [1, 4, 7]. This study was undertaken to estimate the likelihood of phosphorus release from the bottom sediments as a result of changes in the abiotic conditions that can happen in near-bottom water layer in the lake.

**MATERIALS AND METHODS**

The analyses were made of 16 samples of lake bottom sediments collected from Lake Góreckie in the area of the Wielkopolski National Park. It is a typical dimictic channel lake surrounded mainly by forests. The lake area is 104.1 ha, its maximum depth is 17.2 m and its mean depth is 8.9 m. Analysis of the lake trophy showed an increase in its fertility up to hypertrophy [14].

The concentration of total phosphorus in the samples studied varied from 0.004% to 0.117% of dry mass of the sediment. Depending on the sample collection site and on the depth of sample collection the sediment contained (for dry mass) 2.6% to 23.4% of organic matter, 0.19% to 1.50% of iron, 0.008% to 0.069% of manganese and 3.4% to 15.6% of calcium. The samples collected in deeper sites of the lakes contained greater amounts of organic matter, iron, manganese, calcium and phosphorus. The samples collected at shallow sites were characterized by a greater amount of silica. These results indicate that the main mechanisms of sediment formation are precipitation and sedimentation.

Estimation of the likelihood of phosphorus release from the bottom sediments as a result of changes in abiotic factors was performed by the way of sequential extraction, simulating at particular stages different conditions that can happen in a near-bottom layer of the lake. The well-known scheme of metal extraction proposed by Tessier et al. [15, 19] was used. The method is based on distinction of the five main fractions:

1. the exchangeable fraction – the most mobile one;
2. the fraction released under acidification of the environment up to pH 5.0, bound to carbonates;
3. the fraction released in the reducing conditions, bound to hydrated iron and manganese oxides;
4. the fraction released on mineralization, bound to organic matter;
5. the residual fraction permanently immobilized in the natural conditions.

The same division can be applied not only to the release of metals but also other components of bottom sediments, including phosphates. In particular fractions the phosphates were determined by the spectrophotometric method based on the use of molybdenum and ascorbic acid as a reducing agent [5]. Absorbancy was measured at the wavelength of 700 nm on a UV-1601 spectrophotometer made by Shimadzu.

**RESULTS AND DISCUSSION**

Distribution of phosphorus among the particular fractions is presented in Figure 1. At pH 7, at the liquid-solid state equilibrium only a small part (3.5% on average) of the phosphorus accumulated in the sediment was released to the bulk water. Acidification of the water to pH 5, usually characterizing the near-bottom layer, resulted in the release of further 11.4% of phosphorus, on average. The strongest release of phosphorus from the
bottom sediments was observed in strongly reducing conditions, when about 30% of the total content of phosphorus (on average) was released to the bulk. This high release is related to reduction of iron(III) and formation of soluble iron(II) phosphate [2, 6, 13, 17]. Relatively small percentage of phosphorus was released as a result of mineralization of organic matter. In the conditions applied only 9.2% (on average) of its total content was released into the water. The fractionation of phosphorus in sediments according to the Psenner scheme [7] showed a considerable contribution of the fraction bound to organic matter and aluminium. The potential threat with the phosphorus released from this fraction is not much and can be well approximated by fraction 4 in the sequential extraction according to Tessier. By far the greatest amount of phosphorus (~ 46% on average) is bound permanently in the sediment, most probably in the form of apatite [6], and its liberation to the bulk water would require treatment with concentrated acids at elevated temperatures. Therefore, this fraction can be treated as permanently immobilized in the bottom sediments in the natural conditions.

Fig. 1. Distribution of phosphate from Lake Góreckie bottom sediments in particular fractions

Because of a considerable contribution of fraction 3, bound to hydrated iron and manganese oxides, a possible correlation between the content of iron, manganese and phosphorus in the bottom sediments was tested.

The plot illustrating a correlation between the content of phosphorus and that of iron in the lake bottom sediments is shown in Figure 2. The correlation is rather strong as follows from the correlation coefficient value $r = 0.6502$ [12] and indicates an important role of iron in binding of phosphorus in bottom sediment.
The correlation between the content of phosphorus and that of manganese in the Lake Góreckie bottom sediment is shown in Figure 3. The correlation is characterized by the much lower coefficient than that obtained for the correlation between the content of phosphorus and iron, of 0.3775, indicating weak correlation [12]. Also the correlation between the content of phosphorus and that of calcium characterized by the coefficient \( r = 0.2555 \) was very weak [12]. The relatively low correlation coefficients describing the correlations between the content of phosphorus and that of iron, manganese and calcium are a consequence of a diversity of the mechanisms of phosphorus binding with these elements. Phosphorus can make with them the insoluble phosphates and can be adsorbed on the precipitating hydrated oxides. The poorest correlation with the content of calcium additionally follows from the fact that in the sediment samples studied calcium occurred in considerable amounts many times greater than the stoichiometric equivalents of the bound phosphorus.

Fractionation of phosphorus in the bottom sediments by the sequential extraction proposed by Tessier [15, 19] does not allow for a differentiation of the phosphorus fraction bound to aluminium. The acidification at stage 3 of the extraction leads to its partial release and incorrect classification as the phosphorus bound to iron and manganese. The main pool of phosphorus bound to aluminium is released in the last (the fifth) stage of extraction and adds to the residual fraction assumed as biologically unavailable. This distribution of the phosphorus bound to aluminium among the fractions distinguished is indicated by the results of aluminium fractionation in the lake bottom sediment samples.
performed according to the Tessier scheme [10]. The above problem does not have a significant effect on the evaluation of the threat to the lake ecosystem related to the phosphorus bound with aluminium as this fraction is relatively low mobile. However, in shallow polymeric lakes in which the epilimnion is in direct contact with bottom sediments, the significance of this fraction can increase. A strong alkalization of the lake water caused by intense photosynthesis can result in pH increase even up to 10, which may induce a significant release of orthophosphates bound to aluminium [11].

CONCLUSION

The release of phosphate from the lake bottom sediments to the bulk water significantly depends on the red-ox conditions in the near bottom layer and in the sediment. This dependence is a consequence of the profound role of iron in the bonding of phosphates. In the reducing conditions the insoluble iron(III) salts convert into well-soluble iron(II) salts, which is accompanied by the release of orthophosphates whose presence exerts negative effect on the lake ecosystem. Unfortunately, such conditions occur usually in the strongly eutrophic water and additionally decrease their quality.

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BADANIA NAD UWALNIANIEM FOSFORU Z JEZIORYCH OSADÓW DENNYCH POD WpływEM CZYNNIKÓW ABIOTYCZNYCH

W pracy przedstawiono wyniki badań nad potencjalną możliwość uwalniania fosforu z osadów dennych do wody w wyniku zmian warunków fizyko-chemicznych panujących w jeziorze. W badaniach posłużono się ekstrakcją sekwencyjną, zaproponowaną przez Tessiera i współpracowników. Procedura ta, opracowana do
oceny zagrożenia ekosystemu wodnego ze strony skumulowanych w osadach dennych metali ciężkich, może być zastosowana również do oceny podatności na uwalnianie innych składników osadów, w tym i substancji biogennych. Poszczególne etapy ekstrakcji symulują bowiem warunki abiotyczne, jakie mogą zaistnieć w strefie naddennej i w samym osadzie w warunkach naturalnych.
EFFECTS OF GNEISS MINING ON WATER QUALITY

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Keywords: Sedimentation sump, benefication plant, effluent, gneiss, sediment, pollution.

Abstract: 70 Mg/day of fine grained waste gneiss in slurry condition, together with 700 m³/day of water from the wet benefication plant flow from the Mikleuška gneiss quarry (Croatia) into the Kamenjača stream. The stream flows between two gneiss quarries, originating in the northern catchment area of which approximately 15 km² is predominantly covered by forest. The quality of water in the Kamenjača permanent stream should be protected from any contamination due to the activities in the Mikleuška quarry. The paper describes the aspects of sustainable technical, environmental and economical protection of the water quality in Kamenjača regarding gneiss mining.

INTRODUCTION

The gneiss quarry (gneiss being a structural engineering stone) is on the south slopes of Moslavačka gora at the village of Mikleuška, 19 km north of Kutina along the Popovača – Podgarič road and following the Kamenjača mountain stream. The owners of the quarry have built a 2 m high concrete dam across the stream at the 155 m level, near the plateau of the Mikleuška quarry, to secure water supply for the quarry. Since 1998, the quarry has produced and sold about 100 000 m³ of gneiss per annum.

Gneiss is classified into the following fractions by means of screens and a wet separation classifier: less than 4 mm, 4–8 mm, 8–30 mm and 30–60 mm. The three larger fractions are transported by an open conveyor belt to the disposal sites in the open. It is estimated that some 700 m³ of suspended gneiss particles daily passes from the sedimentation sump into Kamenjača waters. The quantity of water required for wet suspension of 20 dm³/s is secured by a pump installed at the water retention of the stream (Fig. 1).

Sericitized and condensed rough useful suspension can be classified by wet and not dry separation only. The process lets out about 130 g/dm³ of murky waste water with concentrated suspended matter. The matter so drawn from the wet separation, and floating on top, enters the stream every 8 to 10 hours each working day.

Gneiss excavation does not endanger seriously the quality of the stream water for gneiss mineral particles do not dissolve in water. Dissolved contaminants have not been found in the Kamenjača stream (the drainage basin of which is made of gneiss mainly),
nor downstream from the location of the murky waste water drain used in the wet separation.

The paper shows the results of testing the properties of waste water in the stream and the procedure for dimensioning the rectangular horizontal sedimentation sumps, used as the cheapest procedure for elimination of suspended matter from waste water. In order to improve present conditions and to secure better exploitation of quarry resources, a study showing the effects of the Mikleuška quarry on its environment has been done [8]. It recommends excavation of useful substances at the levels of 162 to 155 m and from the 175 to 160 m in the Mikleuška I and the Mikleuška II quarries, respectively. Excavation of the area below the present working plateau in the Mikleuška I quarry may free up space for the sedimentation sump, and a lagoon must be arranged for additional sedimentation of finer particles at the lowest levels in the quarry (151.2 to 153.5 m). Following extraction, the sedimentation sumps will be reshaped into sports or recreation pools. The lagoon may be used for fish breeding.

GEOLOGICAL CONDITIONS

The sedimentation basin is similar to a lake and lies upon a transgressively folded base of crystalline foundation. The end of the Helvetic period marked the beginning of the influence of marine sedimentation. The Helvetic sediments contain transgressively torton conglomerates, infirmly bound coarse grained sandstones and locally developed limestone inside them. The Pliocene rhomboidea sediments consist mainly of sands and marls, less frequently of sandstone and clay. Quaternary sediments of heterogeneous grain size distribution often occur on the hillsides of Moslavačka gora, especially in the stream valleys [10].

The exploitable part of the Mikleuška I and II quarry beds is found in the crystalline massif at the south-eastern border of Moslavačka gora. Magmatic, biotitic and double-micaceous gneissic rocks are predominant in the area.
Large portion of gneiss in the open bed is sericitized. Therefore, the site contains sodium-calcium clay-stones with large quantities of lamellar sericite (H$_2$, KAl$_3$, SiO$_3$, O$_3$). The claystones like those are prone to intensive crumbling during excavation and transportation. For this reason, the rock must be washed in wet separation [3]. The cover of the useful suspension is made of humus, yellow-brown sandy clays and crumbling, condensed gneiss.

The intrusion of the Moslavina granite into the older metamorphic complex caused its metasomatic alteration with partial or complete re-melting. This formed a waist of heterogeneous and homogeneous magmatic rock of hectometers to kilometers sizes. Gneiss has a similar chemical composition to that of granite, consisting of about 45% flint, 40 to 45% claystone, 10 to 15% mica and some other silicates in smaller amounts. Gneiss components are mainly water non-soluble and do not endanger the quality of water.

**POTENTIAL POLLUTION OF THE WATER FLOW IN THE QUARRY**

The quarry in the process of wet separation of rock now uses 20 dm$^3$/s of the water from the Kamenjača stream during each 8–10 hour per workday. Approximately, the same quantity of 700 m$^3$/day of water flows back to the stream carrying suspended gneiss particles. The quarry owner estimates that some 10 000 m$^3$/year of market-valued stone fractions is lost in this way.

Potential risks which may have a bad effect on the water quality in the Kamenjača stream [11] are: stationary gas oil tank, small stock of machine oil, in situ septic pit for quarry personnel, occasional washing of equipment, constant washing of stone, various waste materials from the office, and equipment maintenance shop. Intensive mine erosion due to the effects of precipitation has not been observed. Also, there is no increase of suspended particles in the Kamenjača stream caused by removal and excavation of gneiss in relation to the drain of precipitation water from forest paths and ploughland.

No dissolved detrimental matter has been found in precipitation water samples falling, draining and/or being collected in the open pits of the Mikleuška gneiss quarries and in useful suspension and waste accumulation sites. Silicate, insignificantly soluble rock-gneiss, showing no significant effect on the quality of the stream, with the exception of solid particles in water at the wet separation draining location have been found and excavated [3].

The Kamenjača stream is properly protected against small supplies of fuel and lubricants, excrements in solid waste and other pollutants in the water system. However, the consequences of gneiss beneficiation in wet separation are not acceptable for the quality of the stream water. Larger quantities of suspended stone particles are present in the water used for occasional washing of equipment and regular washing of fine stone fractions in wet separation. It comprises a washing cylinder, 3 screens with the openings of 30 mm, 8 mm and 4 mm, continuous conveyors and a spiral classifier. Some 40 m$^3$/hour of 0–60 mm stone in approximately 8 dm$^3$/s water is washed in the cylinder. The same quantity of stone is washed on three screens, using approximately 12 dm$^3$/s water.

**WATER ANALYSIS AND REMOVAL OF SOLID PARTICLES**

The water quality at the separation drains and downstream the quarry was not investigated in the past. On this occasion, samples of water were taken for quality tests in the...
laboratory of the Faculty of Geotechnical Engineering in Varaždin, the Faculty of Mining, Geological and Petroleum Engineering in Zagreb, and “Petrokemija” d.d. in Kutina.

Figure 2 shows the grain size distribution of the matter suspended in the water samples taken at the waste water drain site (following wet separation), and 50 m downstream the drain. Its data are determined by aerometric tests and by sieving the sediment separated from the water sample. Curve 1 refers to the waste water drain in the stream in December 1998. Curve 2 refers to the drain of the water from the wet separation during January 1999. Values of 33.26% of sand, 55.80 silt and 10.94% of sediment clay are noted on the sample 1 curve (Fig. 2). The total amount of dry matter in suspension measured is 133 g/dm$^3$.

![Grain size distribution curves](image)

Fig. 2. Grain size distribution curves of particle sedimentation from the sample of waste and saturated waters 1 – sample from the drain, December 1998; 2 – sample from the drain, January 1999; 3 – sample 50 m downstream the drain, January 1999

Investigations carried out in the laboratory of Petrokemija, d.d. in Kutina [2, 5] determined the necessity of purification of waste water used in the process of wet separation due to a high drift content. These investigations have shown that the quality of water in the sample taken 50 m downstream the waste water drain does not meet standard water quality values due to increased content of SiO$_2$ and pollution/murkiness values too high for maximum permissible concentrations.

Table 1 shows the values determined in the laboratory of the Faculty of Geotechnical Engineering in Varaždin [6]. The possibilities of relatively fast sedimentation of gneiss particles suspended during the quiescence of the water sample or the laminar flow
of water should be pointed out. The fastest clearing of water was observed in the quicker-
transported water sample taken in January 1999 at the wet separation drain site, then in
the fresh water sample taken 50 m downstream the drain site, while the longest time of
sample clearing belongs to the longer-transported water sample taken in December 1998
at the waste water drain site. The differences found are probably the results of additional
crumbling of coarse grained gneiss particles of colloidal size settling very slowly without
the application of flocculants (rich in non-sericitized clay stones), when transported in
a vessel or in the stream. For this reason, it is recommended to build the sedimentation
sump as close to the wet separation plant as possible.

Table 1. Sedimentation velocity of coarse particles in 1000 cm$^3$ of water used in wet separation

<table>
<thead>
<tr>
<th>Sampling date</th>
<th>Decanter components</th>
<th>Turbid and clear water volumes [cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 hour</td>
</tr>
<tr>
<td>Outlet</td>
<td>coarse residue</td>
<td>100</td>
</tr>
<tr>
<td>December 1998</td>
<td>total residue</td>
<td>915</td>
</tr>
<tr>
<td></td>
<td>clear water</td>
<td>85*</td>
</tr>
<tr>
<td>Outlet</td>
<td>coarse residue</td>
<td>80</td>
</tr>
<tr>
<td>January 1998</td>
<td>total residue</td>
<td>870</td>
</tr>
<tr>
<td></td>
<td>clear water</td>
<td>130</td>
</tr>
<tr>
<td>50 m downstream</td>
<td>coarse residue</td>
<td>15</td>
</tr>
<tr>
<td>January 1999</td>
<td>total residue</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>clear water</td>
<td>985*</td>
</tr>
</tbody>
</table>

*water above sediment in graduated glass was not completely clear

Table 1 shows the background for the explanation of regulating the sedimentation
sumps with adequate dimensions for removal of suspended matter from water before be-
ing drained into the stream. In the sedimentation sumps adequately designed, built and
maintained it is possible to decrease the suspended matter content to the value of 25 mg/dm$^3$,
as observed in the water samples upstream the quarry.

DESIGNING SEDIMENTATION SUMPS

Draining murky water from the wet separation into the Kamenjača stream is a fundamen-
tal threat to water quality. Clarity of water has been a long-standing water quality criterion
[4]. The quarry owner must remove solid matter suspended in the waste water used in
the operation process. The sale prices of the quarry products are relatively low. The same
applies to investments and maintenance of equipment for removal of waste matter from
the water: descender, desilter, centrifuges and tools for using the flocculator (alumina,
ferrochloride, lime and similar chemicals), a device used for acceleration of settling. The
quarry has enough space for sedimentation sumps. It is necessary to see the possibilities
for clearing the murky water by using the sedimentation sumps mentioned.

In addition to dimensions of the particles suspended, an important effect on
the sedimentation velocity of solid particles belongs to the density difference existing
between suspended particles/fluid and fluid viscosity [7]. This is further proved by the
Stockes formula for laminar streaming of liquids with suspended matters.
\[ v_t = \frac{g \cdot (\rho_c - \rho) \cdot d_c^2}{18 \mu} \]  

where:

- \( v_t \) – sedimentation velocity of individual particles in given conditions [m/s],
- \( g \) – gravity acceleration [m/s\(^2\)],
- \( \rho_c \) – density of suspended particles [kg/m\(^3\)],
- \( \rho \) – fluid density [kg/m\(^3\)],
- \( d_c \) – particle diameter [m],
- \( \mu \) – dynamical viscosity of suspension [Pa s].

Figure 3 shows idealized rectangular sedimentation sump that will serve for computation of relevant basin dimensions securing laminar streaming and necessary detention of water in the basin. The entrance zone in which a mass of water with suspended particles is distributed and forming a laminar flow is marked 1. Sedimentation of particles occurs in Zone 2, through which the water flows to the exit/drain Zone 3, where the clarified water converges. Separated sediments accumulate in Zone 4. From there, sediments are removed by cleaning the basin bottom in accordance with the regime of work of the separation, i.e. sedimentation basins.

Decisive particle for dimensioning the sedimentation sump is the one entering at point a, settling along the entire length of the sump and reaching the point b after a certain period of time. Trajectory of sedimentation of such a particle represents the resultant of the streaming velocity vector \( v_o \) and vector of the sedimentation velocity \( v_t \) \[^4\]. Thus, all particles sinking with velocity \( v_t > v_o \) settle in the sedimentation basin (Zone 4) and do not reach the draining Zone 3 (Fig. 3).

For the given inflow of waste water from wet separation \( Q = 0.020 \) m\(^3\)/s, height of sedimentation sump \( h_o = 0.5 \) m and minimal time of retention in the sump \( t_o = 10800 \) seconds, it is possible to calculate the surface of the sedimentation sump \( A \), the volume of
the sump \( V \) and the velocity of the particle flow through the sedimentation sump \( v_o \) (Fig. 3) using the following formulae:

\[
\begin{align*}
    v_o &= h_o / t_o \\
    t_o &= V / Q \\
    A &= V / h_o \\
    v_o &= Q / A
\end{align*}
\]

On the basis of the above parameter values, i.e. the rectangular horizontal sump, the values of all other parameters are calculated using the above formulae as follows:

\[
\begin{align*}
    V &= Q \cdot t_o = 0.020 \cdot 10800 = 216 \text{ m}^3 \\
    A &= V / h_o = 216 / 0.5 = 432 \text{ m}^3
\end{align*}
\]

CONSTRUCTION OF SEDIMENTATION SUMPS AND POSSIBILITY OF CHANGING THEIR FUNCTION

Excavation of sedimentation sump gneiss using the existing equipment, in engineering and financial view, is always favorable for the quarry owner. However, securing a permanent use of correctly dimensioned structures for removal of suspended matter after a relatively short period of quarry life is of particular economic importance. According to Sport Encyclopaedia published by Miroslav Krleža Lexicographic Institute [9], the size of sport basins is most often \(25 \times 18 \times 2.2\) m or \(33.33 \times 20 \times (2.20\) to \(0.90\) m) or \(50 \times 25 \times 2.20\) m. For this reason, architects are advised to apply the sizes above for sedimentation sumps as well as to provide the sizes for future sports/recreation facilities.

The terrain configuration and the surface area owned by the quarry between the Kamenjača stream and the wet separation plant are suitable for laminar flow without the use of additional pumps. Therefore, an average content of solid particles in the water cleared by sedimentation, desired frequency of cleaning the sediment from the sumps to sediment gathering places for additional drying (Fig. 4) and standard sizes of sports pools have a decisive influence on designing sedimentation sumps.

Available useful substance surface is sufficient for one future sports pool having standard dimensions of \(50 \times 25 \times 2.20\) m and two smaller pools covering an area of \(25 \times 18 \times 2.20\) m. A part of the alluvial lagoon sediment area can later be used for fish breeding. If two necessary sumps, and a likely third one similar in size, are situated in a future large basin instead of the sediment collection site with fine grains (using existing equipment in the useful substance), an excavation approximately \(55\) m long, \(3.5\) m deep and \(30\) m wide will be rationally performed, then divided into two equal parts \(13\) m wide \((w)\) with a dividing \(4\) m wall of natural gneiss rock. Drain pipes will be installed at the bottom of the sumps to drain water through the settled sediment, particularly the coarser one, at the entrance closer to the second part of the sump (up to \(10\) m). Following is the verification of the length and width of sumps:

\[
\begin{align*}
    A &= l_o \cdot V; \\
    l_o &= A / w = 432 / 13 = 33.3 \text{ m}, \text{ or } 55 \text{ m respectively.}
\end{align*}
\]
In this way, the useful volume of each sump equals $55.13 \times 3.30 \text{ m} = 2360 \text{ m}^3$. If $0.020 \text{ m}^3/\text{s}$ of murky water flows through for a maximum of 10 hours a day, the total comes to $720 \text{ m}^3/\text{day}$. The same volume of water can flow out 24 hours/day, i.e. $Q_1 = 0.0083 \text{ m}^3/\text{s}$. In this case the average velocity of water $v_o$ on the spillway into the Zone 3 (Fig. 2) at the level of the spillway top (adjusted according to requirement) with 0.20 m water in the sump is determined as follows:

$$v_o = \frac{Q_1}{A_i} = \frac{0.0083}{13 \cdot 0.20} = 0.00319 \text{ m/s} \quad (10)$$

The space available in the sump for settling of sediment is:

$$V = l_c \cdot w \cdot h_s = 55 \cdot 13 \cdot 1.8 = 1237.5 \text{ m}^3 \quad (11)$$

The height of the sediment:

$$h_s = H - h_c - h_o = 3.5 - 0.2 - 0.2 = 3.10 \text{ m} \quad (12)$$

where:

$H$ – total depth of excavation [m],

$h_c$ – decrease of sump depth due to drain pipes [m],

$h_o$ – height of spillway in the sump that will be adjusted according to requirements [m],

$w$ – width of sump.

It is necessary to verify the laminar flow in the sumps of given dimensions and velocity of flow, because only the flow along constant streamlines secures effective settling of suspended particles.

The equation for calculating the Reynolds number is used here. For a rectangular sump, this number must be less than 580, which is the critical value characterizing the transition from turbulent to laminar flow regime [1].
where:

\( v_p \) – average velocity in the sump, 0.00319 m/s;

\( R \) – hydraulic radius – ratio between surface of flow and circumference of flow in the sump,

\[ R = A/O = w \left( h_o/w + 2h_o \right), \text{ as } h_o < w, R = h_o = 0.2 \text{ m}; \]

\( \mu \) – value of water viscosity with suspended fine particles, 0.002 Pa s;

\( \rho \) – water density with suspended fine particles, 1800 kg/m\(^3\).

The above calculation confirms the laminar flow, because the value of the Reynolds number is 344 only. For this reason, the planning consists of a standard-sized pool measuring 50×25×2.20 m for two sumps, and two sports pools measuring 25×18×2.20 m for drying the sediment.

Based on laboratory-determined average inflow water drift content of 0.133 m\(^3\) per 1 m\(^3\) of water, \(720 \times 0.133 = 95.76 \text{ m}^3/\text{day} \) is being settled. Filling of the sedimentation sump with such dimensions by the sediment from water with known content would last \(2216.5/95.76 = 23.15 \text{ days}\).

Interruption in using one sedimentation sump after a period of 23 days and its emptying from sediment into two supporting basins until next use after the following 23 days (until the second sump is filled), necessitates a moderate frequency of cleaning out the sumps.

If the spillway (i.e. spill-over point) of the sump is adjusted to the height of 3.10 m in relation to the top of the drain pipe on the bottom of the sump, the sump can receive the following amount of murky water in its space \(V_2\) (up to the spillway):

\[ V_2 = 55 \times 13 \times 3.10 = 2216.5; \text{ thus, the filling of this space would last } t_2 \text{ as follows:} \]

\[ t_2 = \frac{V_2}{Q} = \frac{2216.5}{0.020} = 110825 \text{ s or 30.78 hours.} \] (14)

The value \( t_2 \) is longer than 3 days of wet separation work (10 hours a day). This secures a several times more complete settling of the sediment with respect to the conditions of earlier assumed value of \( t_0 = 10800 \text{ s}, \) because:

\[ \frac{t_2}{t_0} = \frac{110825}{10800} = 10.26; (t_2 >> t_0) \] (15)

During the time of original filling of the sump lasting \( t_2 = 110.825 \) seconds, the sediment volume is expected to be \( V_3 = V_2 \times p_n = 2216.5 \times 0.085 = 188.40 \text{ m}^3, \) corresponding to the following height of sediment in the sump:

\[ h_2 = \frac{V_3}{A_2} = \frac{188}{55 \times 13} = 0.26 \text{ m} \] (16)

This is also the time it takes to open the valve on the drain pipe and for gradual draining of water. Due to the water being filtered into drain pipe through the sediment (which is an effective filter), clearer water is expected in the drain pipe than on the spillway.

**ADDITIONAL PROTECTION OF THE WATER FLOW**

In order to protect the Kamenjača water flow from the finest solid matter in a more complete manner, a shallow lake (lagoon) with a surface of about 10 000 square meters is also
planned downstream the sumps (Fig. 4). The surface of the future lagoon is covered with humus that will be removed with existing equipment and transported to the final surfaces of excavation to be used as green areas. Following the removal of humus from the bottom of the lagoon, significant infiltration of water into the water bearing alluvium is expected, as well as an increase of underground water level in the downstream wells in Mikleuška housing estates, which is an additional positive effect of the lagoon.

If ecologists have justified objections to the quality of water tested at the drainage point from the lagoon into the stream, it is recommended to reuse the lagoon water in wet separation.

SEDIMENT DISPOSAL

Figure 4 shows the layout of sedimentation sumps, the future lagoon contours and contours of locations for disposal of sediments. Two sediment disposal locations are planned, since a segregation of suspended particles in sedimentation sumps according to grain size is expected. Sedimentation of coarser grains that have value on construction materials market (for civil engineering purposes) is expected to be found at the first 10 to 15 m of the sump. Sediment predominately containing the finest particles is expected in the remaining part of the sump. Therefore, as shown in Figure 4, two collecting places for sediments drying on the sun are planned; one for the sediment with coarser grains to be sold on the market, and another for the finest particles used in forming the water flow in the lagoon, filling the quarry pits and for leveling final excavation surfaces before being covered with humus and plants.

The coarser fraction from the sedimentation sumps will be additionally dried in a specially arranged gathering place before being supplied to customers, while the drained water will be taken to the active sedimentation sump. Sediments of finest particles (mud) will be additionally dried in the basins, where an additional drain similar to the above described is recommended.

The lagoon water will be directed towards the spillway into the stream by a longer channel that will gradually form by the mentioned mud of finest particles settling in the sedimentation sumps. To achieve a more effective settling method for the finest particles in the lagoon and to remove the remainder of colloidal matter in the water after the flow through the sedimentation sump in the layout, a canal for laminar flow of water will be designed and built. The study [8] envisions a concept of facilitating the basin for gathering sediments for standard size swimming pools, and the lagoon for fish spawning, both advantageous in view of economic effects.

CONCLUSION

A public utilities company from Kutina regularly takes away fecal matter and solid waste from the quarry. No cases of uncontrolled effusion of lavatory content, gas or machine oil into the stream were recorded. Equally so, no amounts of settled matter in the precipitation water flowing into the stream from open surfaces of the quarry and poor rock heaps higher than those in the water flowing from ploughland and forest paths were observed. Additional measures securing the surroundings from these and other dangers have been successfully implemented. The process of purifying water used for washing equipment and stone in the wet separation has not yet been planned and implemented in the quarry.
Guidelines for construction of sedimentation sumps and the lagoon for removal of suspended matter are given in the study [8]. The prescribed clearness of water at the drain into the stream has to be adhered to. Further investigation of properties of particles suspended in water, systematic monitoring of the efficiency of sedimentation of particles with different coarseness in the sedimentation sumps and in the lagoon, leading to improved process during construction and use of these facilities are also recommended. We can also recommend the facilitation of a third sump, at the point of the northern sediment-gathering location, as well as special forming of the lagoon shape in order to secure a more effective settling.

If ecologists make justified objections relating to the quality of water tested at the draining point from the lagoon into the stream, it is then recommended to reuse the lagoon water in the wet separation.

In spite of the fact that no dissolved harmful matter has been found in the water samples used in wet separation or in the precipitation water falling and flowing over excavations, useful substances and waste heaps, special care in excavation is recommended in order to avoid erosion and drawn sediments during precipitation. Regular tests in chemical laboratories are strongly recommended. Any stronger clouded waters in the quarry should be directed to the lake (lagoon) downstream the sumps for sedimentation of colloidal particles and systematic control of water quality.

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THE TECHNOGENIC AND GEOGENIC MAGNETIC SUSCEPTIBILITY OF MOUNTAIN FOREST SOILS ON EXAMPLE OF FOREST DIVISION KAMIENNA GÓRA

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Keywords: Heavy metal content, magnetic susceptibility, parent rock, Sudety Mountains.

Abstract: The Sudety Mountains are located close to industrial areas of Germany, Poland and the Czech Republic and are the most polluted Polish mountains. Among air pollutants such as SO$_2$, NO$_x$, fly ashes from local and transboundary power plants emission have a significant input. In determination of soil pollutants, magnetic susceptibility measurements find application. The use of magnetic measurements as a proxy for chemical methods is possible because air pollutants and magnetic particles are interrelated. The major sources of air pollution in the Sudety Mountains are fly ashes from burning process of fossil fuels. This paper presents content and distribution of heavy metals in soil profiles, depending on their natural or industrial origin and the results of magnetic susceptibility measurements.

INTRODUCTION

The area of Forest Division Kamienna Góra covers 15526 ha and belongs to Region (VIII) of the Sudety Mountains, which are among the oldest mountain ranges in Europe. In morphological structure a distinguishing diversity of landscapes as an effect of rich geological history of this area is found. The soils of that region have weathering origin from shallow profile in higher part of mountains to middle and deep profile in subsidence.

The most of forest soils of that region contain considerable amounts of heavy metals such as lead, zinc and cadmium, the highest concentrations of which are observed in upper horizons. The magnetic susceptibility (MS) measurements found application in monitoring and assessment of the level of contamination of soils, especially by airborne pollutants. Magnetic iron particles are associated with hazardous pollutants such as heavy metals and as component of the industrial dust, are finally deposited on soil surface. Research of soil magnetic susceptibility of Poland shows diversity. Higher values of magnetic susceptibility (MS) are noted in soils of Southern Poland along the border with Slovakia, the Czech Republic and Germany, from Krakow through Upper Silesia to Lower Silesia. The reason for such spatial distribution of MS is emission of iron compounds related to burning processes of hard and brown coal. Metallurgy as well as coke plants and cement industry (Opole region) have significant influence on high values of MS, es-
especially on areas of Krakow and Upper Silesia. In the Sudety Mountains region, technogenic influence on MS values is lower, particularly under organic horizons of soil profile. Diversification of parent rocks such as basalts, amphibolites, serpenticites and phyllites, rich in ferrimagnetics affect magnetic susceptibility enhancement. Distribution of MS in soil profiles changes regardless of the soil type, but the fly ashes chemical content and level of deposition [8]. The aim of this work is to find relation between influence of parent rock and fly ash pollution on magnetic susceptibility of forest soils.

OBJECTS AND METHODS

Six profiles of soils localized in Forest Division Kamienna Góra were examined. Each evolved on different parent rock, under different forest stand and in different terrain configuration (height above sea level, slope gradient and orientation). The diagnosis of the soil profiles was done according to Polish Forest Soil Classification 2000 [2] and World Reference Base for Soil Resources 1998 [12].

Profile No. 1 (Skeleti-Protoalbic Cambisol). Located in the West Sudety Mountains at 1000 m a.s.l, northern orientation, slope gradient 6–8°, parent rock – phyllite shale. Type of humus: mor. Forest stand: die-back spruce stand after ecological disaster.

Profile No. 2 (Skeleti-Dystric Cambisol) Located in the West Sudety Mountains at 800 m a.s.l., western orientation, slope gradient 20°, parent rock – amphibolite. Type of humus: moder. Forest stand: beech timber forest.

Profile No. 3 (Skeleti-Haplic Podzol (Rustic)) Located in the Middle Sudety Mountains at 720 m a.s.l., southern orientation, slope gradient 25°, parent rock – porphyry. Type of humus: mor. Forest stand: spruce stand with a single admixture of beech.

Profile No. 4 (Dystric Cambisol) Located in the Middle Sudety Mountains at 520 m a.s.l., south-western orientation, slope gradient 12°, parent rock – “kwadrowe” sandstone. Type of humus: moder. Forest stand: spruce stand with a single admixture of beech, larch, and pine.

Profile No. 5 (Skeleti-Dystric Cambisol) Located in Middle Sudety Mountains at 550 m a.s.l., north-western orientation, slope gradient 15°, parent rock – conglomerate of alkali magma rocks. Type of humus: moder. Forest stand: beech stand.

Profile No. 6 (Rendzic Leptosol (Cambic)) Located in the West Sudety Mountains at 700 m a.s.l., south-western orientation, slope gradient 10°, parent rock – dolomite covered by magma rock – mantle. Type of humus: moder. Forest stand: spruce stand with a single admixture of beech and sycamore seed trees.

The six soil profiles were examined for physic-chemical parameters and magnetic susceptibility measurements (mass specific susceptibility [χ]) for each horizon. Soil samples were air dried and sieved through 1 mm screen in the laboratory to separate the soil skeleton. Particle size analysis was determined by sieve and aerometer methods by Casagrande’a in Prószynski modification (Tab. 1). Coarse fragment content in soils was determined in the field. Grain size and granulometry were determined according to classification of Polish Society of Soil Science. Soil pH in distilled water and 1 M KCl were determined by potentiometric method. Organic carbon was determined by modified Tiurin method (Tab. 2). Heavy metal content was determined by AAS method after the mineralization in mixture of 70% HClO₄ and concentrated HNO₃. Elements such as Ni and Cr were determined by ICP technique. All detail parameters regarding physic-chemical
properties of the presented profiles and wide description of forest habitats are published in Atlas of Forest Soils in Poland [1].

Magnetic susceptibility is defined as a ratio of the material magnetization to the external magnetic field. Paramagnetic materials reach positive values of magnetic susceptibility whilst diamagnetic negative values [10]. The magnetic susceptibility (MS) was measured using the MS2 Bartington sensor in laboratory. It was expressed as the mass specific susceptibility (SI units of $\chi\cdot10^{-8}$ [m$^3$·kg$^{-1}$]) (Tab. 3), which is the volume susceptibility divided by the density of the material. The content of heavy metals in different horizons of soil profiles expressed in mg·kg$^{-1}$ is strongly modified by density of horizons. To determine the correlation coefficient between magnetic susceptibility and heavy metals content in whole profile, factor D was applied. The volume density (D) expressed in g·cm$^{-3}$ was worked out in the Department of Forest Soil Science of the Agricultural University of Cracow [1]. For calculation $D = 1.3773 \cdot e^{-0.0547}$ was assumed, where x – organic carbon content in %, which include samples with C$_{org.}$ content below 0.29% (Tab. 2).

Dust fall data were obtained from Forest Research Institute in Warsaw for three summer seasons (1988, 1989, and 1992) and winter season (1989). For comparison, dust fall results from neighbouring Forest Divisions (Śnieżka, Wałbrzych) are enclosed (Tab. 5) [3].

RESULTS AND DISCUSSION

Diversity of parent rock of examined soils is related with geological structure of the Sudety Mountains and present as follow: phyllite shale, amphibolite, porphyry, sandstone, conglomerate of alkali magma rocks and dolomite. The mechanical analyses were completed in laboratory and the soil horizons present textural classes from sand (S) (25–50 cm in profile No. 6) to silt loam (SiL) (7–26 cm and 26–76 cm in profile No. 5) according to USDA classification.

All soil profiles have low pH in uppermost horizons (below 4.5 in H$_2$O). Besides parent rock, climate and form of the organic matter, industrial pollutions have influence on low pH reaction. High amounts of anthropogenic Pb in organic horizons (O), (Tab. 3), significantly decrease activity of microorganisms and decomposition of organic matter, what reflects the high content of organic carbon in uppermost horizons.

The magnetic susceptibility varies depending on horizon and parent rock. Comparison of coefficients of correlation between (MS) and heavy metals content expressed in mg·kg$^{-1}$ and mg·dm$^{-3}$ shows that expression of Cd, Pb, Fe and Mn in mg·dm$^{-3}$ does not affect the tendency (correlation coefficient are positive) (Tab. 2).

In the profiles No. 1 and No. 2 both technogenic and geogenic influence on magnetic susceptibility are observed. As opposed to the rest of soil profiles, magnetic susceptibility has the lowest values in upper horizons (Tab. 3).

Profile No. 1 (Skeleti-Protoalbic Cambisol) formed on phyllite shale, is rich in magnetic minerals. The highest content of iron, zinc and manganese accompanies the highest values of magnetic susceptibility in soil profile. Distribution of (MS) in soil profile suggests geogenic character. Correlation coefficients for Pb and Cd have negative values but for Fe, Zn, Mn, Ni, positive (Tab. 2).

Profile No. 2 (Skeleti-Dystric Cambisol) formed on amphibolite, rich in magnetic minerals, presents lithogenic character of magnetic susceptibility. High content of iron in
Table 1. Grain size distribution and chemical properties of soils

<table>
<thead>
<tr>
<th>No. profile</th>
<th>parent rock</th>
<th>Depth [cm]</th>
<th>Level</th>
<th>% fraction [mm]</th>
<th>C_{avg} [%]</th>
<th>pH (H_2O)</th>
<th>pH (KCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;1</td>
<td>1.0–0.1</td>
<td>0.1–0.02</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>1</td>
<td>phyllite shale</td>
<td>1–8</td>
<td>Of</td>
<td>0</td>
<td>31.76</td>
<td>3.4</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8–21</td>
<td>Of/Ees</td>
<td>40</td>
<td>13.29</td>
<td>3.4</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21–56</td>
<td>BbrBfe</td>
<td>80</td>
<td>39</td>
<td>0.1–0.02</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>56–110</td>
<td>BbrC</td>
<td>90</td>
<td>40</td>
<td>0.1–0.02</td>
<td>3.5</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>amphibolite</td>
<td>1–8</td>
<td>O/Ah</td>
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<td>14.99</td>
<td>3.8</td>
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<td>25–70</td>
<td>Bbr</td>
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<td>5.2</td>
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<td>4.1</td>
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<td></td>
<td>70–120</td>
<td>BbrC</td>
<td>90</td>
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<td>5.3</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>porphyry</td>
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<td>3.5</td>
<td>2.7</td>
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<td></td>
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<td>Ees</td>
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<td>3.3</td>
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<td>5.84</td>
<td>4.1</td>
<td>3.7</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>“kwadrowe” sandstone</td>
<td>1–6</td>
<td>Ofh</td>
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<td>23.52</td>
<td>3.7</td>
<td>2.9</td>
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<td>3.8</td>
<td>3.1</td>
</tr>
<tr>
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<td></td>
<td>11–64</td>
<td>Bbr</td>
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<td>4.1</td>
<td>4.1</td>
<td>3.8</td>
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<tr>
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<td></td>
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<td>30</td>
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<td>4.8</td>
<td>3.6</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>conglomerate alkali magma rocks</td>
<td>2–7</td>
<td>Of/A</td>
<td>30</td>
<td>16.3</td>
<td>3.7</td>
<td>3.0</td>
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<td>7–26</td>
<td>ABbr</td>
<td>40</td>
<td>1.12</td>
<td>4.2</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26–76</td>
<td>Bbr</td>
<td>40</td>
<td>4.1</td>
<td>4.1</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>76–120</td>
<td>BbrC</td>
<td>90</td>
<td>4.1</td>
<td>4.1</td>
<td>3.8</td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td>dolomite covered magma rock-mantle</td>
<td>0–10</td>
<td>Ah</td>
<td>20</td>
<td>10.37</td>
<td>4.4</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10–25</td>
<td>ABbr</td>
<td>20</td>
<td>1.33</td>
<td>5.7</td>
<td>4.7</td>
</tr>
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<td></td>
<td></td>
<td>25–50</td>
<td>IICca</td>
<td>90</td>
<td>7.9</td>
<td>7.9</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 2. Correlation coefficients (r) between magnetic susceptibility and heavy metals content in soil profiles expressed in [mg·kg\(^{-1}\)]/[mg·dm\(^{-3}\)]

<table>
<thead>
<tr>
<th>No. profile</th>
<th>Fe</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.53/0.50</td>
<td>-0.65/0.56</td>
<td>-0.64/0.71</td>
<td>0.45/0.63</td>
<td>0.62/0.61</td>
<td>-0.06/0.30</td>
<td>0.71/0.72</td>
</tr>
<tr>
<td>2</td>
<td>0.85/0.63</td>
<td>-0.58/-0.40</td>
<td>0.36/0.80</td>
<td>-0.58/0.60</td>
<td>0.74/0.63</td>
<td>-0.45/0.34</td>
<td>0.72/0.83</td>
</tr>
<tr>
<td>3</td>
<td>-0.55/-0.90</td>
<td>0.99/0.99</td>
<td>0.99/0.92</td>
<td>0.96/-0.81</td>
<td>-0.22/-0.57</td>
<td>0.45/-0.70</td>
<td>0.84/-0.48</td>
</tr>
<tr>
<td>4</td>
<td>-0.19/-0.50</td>
<td>0.99/0.99</td>
<td>0.99/0.99</td>
<td>0.94/-0.20</td>
<td>-0.08/-0.50</td>
<td>0.90/-0.53</td>
<td>0.62/-0.37</td>
</tr>
<tr>
<td>5</td>
<td>-0.69/-0.90</td>
<td>0.99/0.99</td>
<td>0.99/0.99</td>
<td>0.83/-0.97</td>
<td>-0.91/-0.96</td>
<td>0.53/-0.91</td>
<td>-0.43/-0.92</td>
</tr>
<tr>
<td>6</td>
<td>0.63/0.30</td>
<td>0.99/0.99</td>
<td>-0.49/-0.60</td>
<td>0.44/0.14</td>
<td>-0.62/-0.77</td>
<td>0.87/0.56</td>
<td>0.58/0.25</td>
</tr>
</tbody>
</table>
the profile have stronger influence on (MS) than high content of lead in organic horizon. Correlation coefficients in this profile are positive for iron, cadmium and nickel and negative for lead. (Tab. 2).

Profile No. 3 (Skeleti-Haplic Podzol (Rustic)) shows enhancement of magnetic susceptibility in the upper horizon (69.6·10⁻⁸ m³·kg⁻¹) (Tab. 3). Parent rock (porphyry) is not rich in magnetic minerals; measurements in lower horizons gave results in range from 26 to 32·10⁻⁸ m³·kg⁻¹. Lead content is highest in the surface horizon, correlation coefficient between content of this element in all horizons and magnetic susceptibility is equal to 0.99, which suggests technogenic origin of Pb in this profile.

In the profile No. 4 (Dystric Cambisol), the highest magnetic susceptibility (130.9·10⁻⁸ m³·kg⁻¹), (Tab. 3) has the organic horizon (Ofh). Parent rock (“kwadrowe” sandstone) is poor in magnetic minerals. Slope orientation (SW), which is in main direction of pollution influx and high Pb and Cd contents in upper horizon, suggests technogenic origin of these elements in soil profile. Correlation coefficient for magnetic susceptibility and lead and cadmium content equals 0.9 and confirms technogenic character of magnetic susceptibility.

Table 3. Magnetic susceptibility (χ), volume density (D) and heavy metals content in soil profiles

<table>
<thead>
<tr>
<th>Profile</th>
<th>Depth [cm]</th>
<th>Level</th>
<th>χ·10⁻⁸ [m³·kg⁻¹]</th>
<th>D [g·cm⁻³]</th>
<th>Heavy metals x D [mg·dm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>1</td>
<td>1–8</td>
<td>Of</td>
<td>105.4</td>
<td>0.24</td>
<td>2036.2</td>
</tr>
<tr>
<td></td>
<td>8–21</td>
<td>Oh/Ees</td>
<td>138.8</td>
<td>0.67</td>
<td>13986.6</td>
</tr>
<tr>
<td></td>
<td>21–56</td>
<td>BbrBle</td>
<td>119.4</td>
<td>1.38</td>
<td>57021.6</td>
</tr>
<tr>
<td></td>
<td>56–110</td>
<td>BbrC</td>
<td>181.0</td>
<td>1.38</td>
<td>52164.0</td>
</tr>
<tr>
<td>2</td>
<td>1–8</td>
<td>O/Ah</td>
<td>224.6</td>
<td>0.61</td>
<td>17044.1</td>
</tr>
<tr>
<td></td>
<td>8–25</td>
<td>A</td>
<td>445.4</td>
<td>1.18</td>
<td>43008.8</td>
</tr>
<tr>
<td></td>
<td>25–70</td>
<td>Bbr</td>
<td>357.7</td>
<td>1.38</td>
<td>50011.2</td>
</tr>
<tr>
<td></td>
<td>70–120</td>
<td>BbrC</td>
<td>289.6</td>
<td>1.38</td>
<td>47720.4</td>
</tr>
<tr>
<td>3</td>
<td>1–17</td>
<td>Ofh</td>
<td>69.6</td>
<td>0.35</td>
<td>3713.8</td>
</tr>
<tr>
<td></td>
<td>17–38</td>
<td>Ees</td>
<td>26.2</td>
<td>1.22</td>
<td>13645.3</td>
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<tr>
<td></td>
<td>38–49</td>
<td>Bh</td>
<td>28.7</td>
<td>1.00</td>
<td>15528.8</td>
</tr>
<tr>
<td></td>
<td>49–70</td>
<td>Bfe</td>
<td>31.5</td>
<td>1.38</td>
<td>17470.8</td>
</tr>
<tr>
<td></td>
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<td>BC</td>
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<td>1.38</td>
<td>18285.0</td>
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<td>4</td>
<td>1–6</td>
<td>Ofh</td>
<td>130.9</td>
<td>0.38</td>
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<td>ABbr</td>
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<td>9894.6</td>
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<td>BbrC</td>
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<td>1.38</td>
<td>17829.6</td>
</tr>
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<td>5</td>
<td>2–7</td>
<td>Oh/A</td>
<td>115.1</td>
<td>0.56</td>
<td>10491.8</td>
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<td></td>
<td>7–26</td>
<td>ABbr</td>
<td>28.4</td>
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<td>26825.4</td>
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<td>26–76</td>
<td>Bbr</td>
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<td>BbrC</td>
<td>23.5</td>
<td>1.38</td>
<td>37784.4</td>
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<td>0–10</td>
<td>Ah</td>
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<td>0.78</td>
<td>21553.6</td>
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<td>ABBbr</td>
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<td>IIICa</td>
<td>1.3</td>
<td>1.38</td>
<td>6927.6</td>
</tr>
</tbody>
</table>
In the profile No. 5 (Skeleti-Dystric Cambisol), highest magnetic susceptibility (115.1·10^-8 m^3·kg^-1) (Tab. 3) is in horizon Oh/A. Parent rock (conglomerate of alkali magma rocks) is poor in the magnetic minerals. Slope orientation (NW), highest Pb content in the upper horizon and high correlation coefficient (0.9) between content of this element and magnetic susceptibility suggests technogenic origin of lead in this profile.

In the profile No. 6 (Rendzic Leptosol (Cambic)), the highest magnetic susceptibility (108·10^-8 m^3·kg^-1) (Tab. 3) is in the horizon Ah and decreases with depth. Parent rock (dolomite covered by magma rock – mantle) is poor in magnetic minerals. Slope orientation (SW) is compliant with direction of long-range pollution influx from industry regions. The highest Pb content in upper horizon and correlation coefficient between content of this element in the profile and magnetic susceptibility suggest technogenic origin of lead in this profile (Tab. 2).

Research conducted in South of Poland on 42 forest soil profiles shows comparable results regarding distribution of heavy metals (Pb, Zn, Cd) in O/A horizons and their technogenic origin [6]. Correlation coefficients for Pb content and magnetic susceptibility are high in profiles developed on parent rocks poor in magnetic minerals (dolomites, sandstones, porphyries). In profiles developed on parent rock rich in magnetic minerals, they have negative values (Tab. 2). However, lead content in uppermost organic horizons is highest in all profiles, which suggests anthropogenic origin of this element, in profiles rich in magnetic minerals (Profile 1, 2), does not affect significantly magnetic susceptibility values.

Technogenic character of magnetic susceptibility in uppermost organic horizons is result of fly ashes deposition (Profiles 1, 2, 3, 4, 5, 6; Tab. 4). Geogenic character of magnetic susceptibility in examined soil profiles is confirmed by higher values in parent rocks compared to the uppermost organic horizons (Profiles 1, 2; Tab. 4). Pedogenic processes also affect (MS) in researched soils, it concerns accumulation horizons (B) of soils, formed on poor in ferromagnetics parent rocks (Profiles No. 3, 4, 5, 6; Tab. 4). Relocation and transformation of iron compounds and then other elements may significantly affect magnetic susceptibility of a soil profile.

The magnetic properties of soils change due to the industrial and urban dust deposition. Most of industrial dusts contain significant fraction of ferrimagnetic particles that are produced during various high temperature technological processes or combustion of fossil fuels [8]. High magnetic susceptibility in uppermost horizons of forest soil profiles are related to species composition of forest stands. Norway spruce is the dominant species in the Forest Division Kamienna Góra and has the highest ability to retain air pollution compared to other tree species [11].

<table>
<thead>
<tr>
<th>Magnetic susceptibility character</th>
<th>Profile No. and parent rock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 phyllite shale</td>
</tr>
<tr>
<td>Technogenic</td>
<td>X</td>
</tr>
<tr>
<td>Geogenic</td>
<td>X</td>
</tr>
<tr>
<td>Pedogenic</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>2 amphibolite</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>3 porphyry</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>4 “kwadrowe” sandstone</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>5 conglomerate alkali magma rocks</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td></td>
<td>6 dolomite covered magma rock-mantle</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>
Lead, in spite of other emitted heavy metals, has the highest enrichment coefficient which is connected with physic-chemical properties and specific surface of ash from power station chimneys. Specific surface for chimney ash from the power station “Turów” is 3.96 \text{m}^2\text{g}^{-1} and is higher than fly ash 2.28 \text{m}^2\text{g}^{-1} [4]. These factors have influence on higher Pb content (compared to Zn content) in uppermost horizon of soil profiles and bogs of southern Poland, where the majority of power plants is located.

Table 5. Monthly dust fall over Forest Division Kmienna Góra area [g·m\(^{-2}\text{-month}^{-1}\)], based on Forest Research Institute data [3]

<table>
<thead>
<tr>
<th>Years</th>
<th>Śnieżka mean</th>
<th>Śnieżka max</th>
<th>Śnieżka month</th>
<th>Kamienna Góra mean</th>
<th>Kamienna Góra max</th>
<th>Kamienna Góra month</th>
<th>Walbrzych mean</th>
<th>Walbrzych max</th>
<th>Walbrzych month</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989</td>
<td>1.431</td>
<td>16.025</td>
<td>VIII</td>
<td>1.536</td>
<td>5.962</td>
<td>V</td>
<td>2.051</td>
<td>7.072</td>
<td>V</td>
</tr>
<tr>
<td>1989/90</td>
<td>2.010</td>
<td>3.890</td>
<td>XII</td>
<td>1.733</td>
<td>9.781</td>
<td>X</td>
<td>1.792</td>
<td>4.886</td>
<td>II</td>
</tr>
</tbody>
</table>

Mean natural content of Pb in Polish soils is 18 mg·kg\(^{-1}\). In all profiles the content of Pb is highest in the uppermost organic horizons. Because of low migrations of this element, its natural distribution in soil profile reflects its content in parent rock. A reason of high values of Pb in soil profiles of the Sudety Mountains area is transboundary pollution influx from Germany and the Czech Republic, which was shown by Zwoździak [13]. Low households emission significantly contributes to air pollution in winter. The main directions of pollution influx in the Sudety Mountains are SW and W. The flow of air pollution from Germany is confirmed by data of magnetic susceptibility of soils along the Polish-German border. On the Southern part of the border, along the Śeniawa – Gubin line, magnetic susceptibility values range from 277–500·10\(^{-8}\) m\(^3\)·kg\(^{-1}\) and along the Słubice – Woliński National Park line from 50–200·10\(^{-8}\) m\(^3\)·kg\(^{-1}\) [9]. Higher Pb content over Zn in uppermost horizons of mountain soils is confirmed by Skiba for the Karkonosze Mountains [5]. Study of peat bog localized in Izerska Mountain Pasture showed in 0–5 cm layer: Zn content from 17.6 mg·kg\(^{-1}\) to 58.6 mg·kg\(^{-1}\) and Pb content from 72.4 mg·kg\(^{-1}\) to 201 mg·kg\(^{-1}\) and confirming relation between these elements [7]. Zinc is one of the most mobile metals in soil, due to its exchangeable forms and relations (compounds) with organic matter. The highest content of this element as well as of cadmium was found in ABbr horizon of Profile No. 6 (Tab. 3). Research conducted on Izerska Mountain Pasture showed high fluctuations of Zn content in the period from 800 to 2000 A.D. Significant increase of Pb and Cd content after 1800 A.D. was related to industrial development period [7].

Cadmium is an element strongly dispersed in rocks (higher concentrations are in alkali magma rocks and slates) and its average content is in the range of 0.03–0.22 mg·kg\(^{-1}\). In soils with pH range of 4.5–5.5, cadmium is very mobile whereas in higher pH values are immobilized. Natural content of this element in soil depends on its presence in the parent rock, but high anthropogenic influence causes its increase in soils. The highest content of Cd is in horizon ABbr (10–25 cm) profile No. 7 (Rendzic Leptosol Cambic). For the rest of soils, the highest content is noticed in surface organic horizons which suggest the anthropogenic origin of this element.
CONCLUSIONS

Magnetic properties of investigated soils reflect various influence of parent rock on the magnetic susceptibility values. In the examined profiles, the elements are of both lithogenic and anthropogenic origin. Sedimentary rocks, such as dolomite and “kwadrowe” sandstone (profile No. 4 and 6), have low concentration of magnetic minerals compared to metamorphic rocks such as amphibolite and phyllite shale (profile No. 1 and 2). Magnetic susceptibility of the examined forest soils has geogenic character in profiles No. 1 and No. 2, where anomalies of MS distribution are observed. Distinguishing between technogenic and geogenic magnetic susceptibility is possible because of the content and spatial distribution of heavy metals in soil profiles. In organic horizons, especially subhorizons Of and Oh, on the whole researched area, magnetic susceptibility had technogenic character and heavy metals (especially lead) occurred in relatively high amounts. Content of lead in upper horizons is higher than zinc content, which is characteristic for soils in the Sudety Mountains – region which is under influence of the fly ashes deposition. Ecological hazard for studied soils results from high Pb content and low pH reaction in organic horizons.

REFERENCES


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Sudety są położone w pobliżu centrów przemysłowych Niemiec, Polski i Czech i są najbardziej zanieczyszczonymi polskimi górami. Pośród takich zanieczyszczeń jak SO₂ i NOₓ istotną rolę odgrywają emisje pyłów lotnych pochodzących z lokalnych i przygranicznych elektrowni. W oznaczaniu stopnia zanieczyszczeń gleb znajdują zastosowanie pomiary podatności magnetycznej. Zastosowanie tego rodzaju pomiarów jako wsparcie metod chemicznych jest możliwe dzięki wspólnym relacjom między cząstekami magnetycznymi i samymi zanieczyszczeniami. Głównym źródłem zanieczyszczeń powietrza w rejonie Sudetów są popioły lotne pochodzące z procesu spalania paliw kopalnych. Praca przedstawia skład i rozmieszczenie w profilach glebowych metali ciężkich, w zależności od ich naturalnego bądź przemysłowego źródła pochodzenia oraz wyniki pomiarów podatności magnetycznej.
HEAVY METALS AND SELECTED PHYSICOCHEMICAL PROPERTIES OF RENDZIC LEPTOSOLS OF THE PONIDZIE REGION (SOUTHERN POLAND)

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Keywords: Rendzic Leptosol, chemical properties, heavy metals, Nida Basin.

Abstract: The aim of the study was to characterize and compare physicochemical properties of Rendzic Leptosols formed in the Nida Basin. The highest heavy metal contents were observed in surface horizons. Average heavy metal contents were (mg kg⁻¹): Zn – 59.9, Cu – 24.9, Pb – 23.4, Cr – 15.4. These values are typical of Rendzic Leptosols and moderate to heavy soils. The soils under study were characterized by high pH values, large content of organic matter, CaCO₃, high saturation of sorption complex with basic cations. The soils did not show greater differences in chemical properties.

INTRODUCTION

The vast, sloping south-westwards Nida Basin is a part of the Śląsko-Małopolska Upland and is characterized by an exceptional diversity of physicogeographical conditions. The formation of Limestone-Rendzic Leptosols was facilitated by transgression and regression of Cretaceous seas leading to the sedimentation of several hundred-meter deep series of limestones, chalk rocks and marls [10, 13]. Recurrent short-term return of a shallow sea to the area of the present Nida Basin in Tertiary period left a series of lithotamnic limestones, marls, glauconite sands and gypsum in the changing sedimentation condition zone [3, 8]. Gypsum accumulation and weathering processes promoted the formation of Sulfate-Rendzic Leptosols [4, 11]. The gypsum series occurring in the Ponidzie Region are characterized by a marked regularity and cover a large compact area. They are built mainly of three types of gypsum: selenite, compressed coarse-crystalline gypsum and shaley gypsum [13, 18].

The goal of the present study was to characterize and compare physicochemical properties of Cretaceous, Tertiary and Sulfate-Rendzic Leptosols formed in this area.

MATERIAL AND METHODS

This study investigated in detail 5 profiles of Rendzic Leptosols occurring in the Nida Basin. The profiles of Rendzic Leptosols (Fig. 1, Tab. 1) were sampled in 2004 in the follow-
ing mesoregions: the Wodzisław Hummock (profile no. 1 near the town of Tomaszów),
the Solec Basin (profile no. 2, near the town of Łatanice), the Pińczów Hummock (profile
no. 3 near the town of Zakamień), the Połaniec Basin (profile no. 4 near the town of Kije
and profile no. 5 near the town of Śladków Mały).

![Fig. 1. Localization of soil profiles on the background of physicogeographical units
1 – no profile, 2 – forest area, 4 – grounds area 5 – physicogeographical units 6 – road](image)

Soil pits were dug to bedrock and 4–6 samples were collected from defined soil
horizons for laboratory analyses. Air-dried samples were analyzed for particle-size dis-
tribution in the skeletal and gravel sands fraction by sieve analysis, and in the dust and
floating fraction by aerometric method of Casagrande modified by Prószyński, pH in H₂O
and in 1 M KCl was determined by a potentiometric method, CaCO₃ content by Sheibler
calcimeter method, organic carbon content in mineral horizons by Tiurin method and in
organic horizons by Alten method, total nitrogen content after sample mineralization by
Kjeldhal method using a Kjeltec Auto 1030 autoanalyzer, hydrolytic acidity by Kappen
method in 0.5 M Ca(CH₃COO)₂ solution, sum of basic exchangeable cations S was ass-
sayed in 0.5 M NH₄Cl, pH 8.2. Based on the sum of basic cations (S) and hydrolytic acidity
(Hh), sorption capacity T and soil saturation with alkali V were calculated. Trophic
index of forest soils ITGL was calculated based on weighed sum (Iₚₚₕₚₚₕ) of the following
indices: dust fraction ($I_{\text{dust}}$), floating fraction ($I_{\text{fz}}$), pH ($I_{\text{pH}}$), basic exchangeable cations ($I_{\text{cat}}$) calculated per a volume unit, stage of organic matter decomposition ($I_{\text{CN}}$) in relation to genetic mineral horizons of the soil under study, determined according to procedures proposed by Brożek [2]. Total contents of microelements and heavy metals in selected soil samples were determined by ICP-AES method using a Jobin-Yvon spectrometer, model JY 70 PLUS. Samples were dissolved in *aqua regia* solution: HCl-HNO$_3$, after prior incineration of organic substance at 480° C. 4 samples of the water collected in the vicinity of the profile 2 and 3 (Łatanice and Zakamień) were analyzed of the content for ions SO$_4^{2-}$ and S$^2-$ using photometer IF 205 SLANDI.

**STUDY AREA**

The Solec Basin is a spacious depression filled with Miocene sea deposits (mostly lithotamnic limestones and Thorton gypsums) formed on Cretaceous marls. The Solec Basin formations are complex and the basin is characterized by large fluctuations of relative altitude (to 50 m). Interesting gypsum series in the western part of the basin form a structural escarpment 35 m deep. Floor parts are formed by coarse-crystalline gyspums, middle part by coarse-crystalline transforming into cryptocrystalline gypsum with blade cleavage while approaching the surface [18]. Karst processes and phenomena developing in gyspums (sinks, ravines, and small caves) are an example of the most beautiful gypsum karst in Poland.

The Płaniec Basin is a flat-bottomed tectonic subsidence. The basin is filled by Miocene gyspums (interesting karst phenomena), silt and sands partially covered with Quaternary Sarmatian sediments encountered near the villages of Borkowo and Chrabkowo.
The Pińczów Hummock (Wójczańsko-Pińczowski) is a horst uplifted in Tertiary Period rising to an altitude of 293 m a.s.l. The hummock prominently dominates over the Nida Valley. It is covered by lithotamnic limestones ("Pińczów stone" – produced in Pinczów), marls and upper Cretaceous gaize, the same as in the adjacent basins, while the substratum contains marl and upper Cretaceous gaize. A middle part of the Pińczów Hummock is visibly lowered, and large areas are covered by glacial sands and moraine clays forming an accumulation plain.

The Wodzislaw Hummock is a flat anticline of Cretaceous chalk rocks in the eastern part covered by loess. Loess covers the surface of the hummock but does not form a continuous cover. The loessial terrains are diverse owning to features of older substratum and Pleistocene and Holocene erosion processes.

RESULTS AND DISCUSSION

Soils occurring in the Nida Basin closely reflect lithology of the parent rock, with prevailing lithogenic Limestone-Rendzic Leptosols, autogenic Cambisols, Chernozems, Haplic Podzols, and Fluvisols [11, 16].

The Rendzic Leptosols under study differed in the underlying parent rock and land use on its surface (arable land: profile 2 and 4, and land used for forest crops: profiles 1, 3, 5). They belonged to Cretaceous-Rendzic Leptosols (profile 1, 4), Tertiary-Rendzic Leptosols (profile 5) and Gypsiri-Rendzic Leptosols (profile 3 and 2), characteristic of this terrain [4, 6] (Tab. 1). Depth of these soils ranged from 35 to 68 cm. Mineral horizon Cca or Cce was usually strongly skeletal and contained weathered rock debris (12–76% of fraction > 1 mm), often transforming in the lower part into a massive rock (Tab. 2).

Depth of humic horizon was much greater in Sulfate-Rendzic Leptosols and ranged between 30 and 50 cm. Granulometric composition of the fine fractions of soils under study comprised normal dust, medium clay, heavy clay and sporadically strong clayey sand (profile 5). They contained 20–68% of sand fraction, 13–44% of dust and 19–58% of floating particles.

The pH values of soils were in the range of 6.0–8.5. Horizons located directly above the parent rock had a slightly basic pH due to its influence (Tab. 3). The pH value decreased towards the surface, what can be attributed to the formation of organic acids able to chelate basic ions and to migrate towards the bottom of the profile. The pH value of organic horizon (pH in KCl) ranged from 6.2 to 7.4 and depended, among other things, on plant communities overgrowing the surface.

The soils contained different amounts of calcium carbonate which is another factor, apart from grain size distribution and parent rock, distinguishing the soils. Calcium carbonate content in surface horizons ranged between 1.6 to 13.8% and increased downwards in the profile to 67.2%.

The chemical analysis of waters collected in the nearness of profiles Gypsiri Rendzic Leptosols (the profile No. 2 and 3), a kind of fertile soil, showed the content of $S^{2-}$ crossing 0.05 mg·dm$^{-3}$. The content of ions $SO_4^{2-}$ was very high and fluctuated from 390 mg·dm$^{-3}$ (Łatanice) to 420 mg·dm$^{-3}$ (Zakamień), considerably exceeding the average content for natural waters which is situated within the range 10–80 mg·dm$^{-3}$ [7].

Waters about the high content of ions $SO_4^{2-}$ are characterized by low pH values. However, pH analyzed samples of the water showed the insensible reaction with values in the section 7.40–7.92.
It’s the result of the dissolution reaction of the gypsum and the reduction of the solvable sulphate under of the organic matter:

$$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \text{ and}$$

$$\text{SO}_4^{2-} + 2\text{C}_{org}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-.$$ 

These soils contained marked amounts of organic matter almost independently of the type of land use. The highest contents of organic carbon were observed in mollic horizon of Gypsiri-Rendzic Leptosols (3.96–5.32%), and the lowest in Ah horizon of Tertiary-Rendzic Leptosols (profile 5). The content of organic carbon in all profiles quickly decreased with depth.

The Rendzic Leptosols under study contained humus of calcimorphic type (kalcamull). C:N ratio in mineral horizons ranged from 3.3 to 13 and decreased with depth. Nitrogen content $N_{TOT}$ was the highest in humic horizon of Rendzic Leptosols used for growing forest crops and fluctuated between 0.95–1.10. Hydrolytic acidity was low and amounted to from 6.5 cmol(+)⋅kg$^{-1}$ in O horizon to 0.1 cmol(+)⋅kg$^{-1}$ in Cca horizon. Sorption capacity was high, the sum of exchangeable cations was in the range of 23.9–104.8 cmol(+)⋅kg$^{-1}$. Sorption complex was saturated mainly by Ca$^{2+}$. These values are slightly higher than those reported by Ciarkowska [4, 5] for Gypsum Brown and Red-Rendzic Leptosols [15]. The highest values were characteristic of Gypsiri-Rendzic Leptosols in profile 3. Saturation of sorption complex of these soils was very high exceeding 87.1% (to 99.8%). Based on the features of soils expressed by trophic index ITGL, it can be inferred that these soils are hypertrophic and eutrophic (ITGL > 36.1, Tab. 1). Current richness of this habitat suggests a highland forest Lwyż-N with a potential vegetation represented by subcontinental dry-ground forest *Tilio-Carpinetum* (Tracz. 1962).

The highest contents of heavy metals in soils were observed in the surface horizons, which is in line with literature data [1, 5, 11, 15, 17]. Total contents of zinc in the study

<table>
<thead>
<tr>
<th>Profile No</th>
<th>Horizons</th>
<th>Depth [cm]</th>
<th>&gt; 1.0</th>
<th>1.0–0.1</th>
<th>0.1–0.05</th>
<th>0.05–0.02</th>
<th>0.02–0.005</th>
<th>0.005–0.002</th>
<th>&lt; 0.002</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ah</td>
<td>1–15</td>
<td>3.0</td>
<td>21.0</td>
<td>17.0</td>
<td>28.0</td>
<td>10.0</td>
<td>7.0</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>CcaA</td>
<td>15–29</td>
<td>2.0</td>
<td>3.0</td>
<td>4.0</td>
<td>3.0</td>
<td>10.0</td>
<td>9.0</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>Cca</td>
<td>29–55</td>
<td>38.0</td>
<td>25.0</td>
<td>21.0</td>
<td>14.0</td>
<td>13.0</td>
<td>8.0</td>
<td>20.0</td>
</tr>
<tr>
<td>2</td>
<td>Ah</td>
<td>0–31</td>
<td>2.0</td>
<td>41.0</td>
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<td>7.0</td>
<td>12.0</td>
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<td></td>
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<td></td>
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<td>49–52</td>
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<td>Ah</td>
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<td></td>
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<td>20–30</td>
<td>31.0</td>
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<td>9.0</td>
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<td>Ah</td>
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<td>11.0</td>
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<tr>
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<td>4.0</td>
<td>9.0</td>
<td>6.0</td>
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Table 3. Some chemical properties of the investigated soils

<table>
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<tr>
<th>Profile No</th>
<th>Horizons</th>
<th>Depth [cm]</th>
<th>pH</th>
<th>pH KCl</th>
<th>CaCO&lt;sub&gt;3&lt;/sub&gt; [%]</th>
<th>C&lt;sub&gt;tot&lt;/sub&gt; [cmol(+)-kg&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>N&lt;sub&gt;tot&lt;/sub&gt; [%]</th>
<th>C:N</th>
<th>Hh [cmol(+)-kg&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>S [%]</th>
<th>T [%]</th>
<th>V [%]</th>
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<th>Cu [mg·kg&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>Pb [mg·kg&lt;sup&gt;-1&lt;/sup&gt;]</th>
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soils ranged from 10.2 to 134.8 mg·kg⁻¹ (mean 59.9), of copper from 5.9 to 89.9 mg·kg⁻¹ (mean 24.9), lead from 4.8 to 55.6 mg·kg⁻¹ (mean 23.4), chromium from 5.7 to 30.7 mg·kg⁻¹ (mean 15.4). These values are typical of Rendzic Leptosols and for heavy and medium-heavy soils [2, 4, 12, 17] Heavy metal contents in Rendzic Leptosols under study did not exceed permissible levels [9, 12]. Slight enrichment in copper (60–81 mg·kg⁻¹) was observed only in the mineral horizon of Gypsiri-Rendzic Leptosols, thus, this soil can be included into class I, i.e. soils with elevated Cu content for medium-heavy soils (where permissible content is 100 mg·kg⁻¹).

Information about the heavy metal content in the soils of Pińczów district [14] indicates that the concentration of these elements in the soils is relatively small. Values in soils to 10 cm are shaped as follows: Zn (14.8–178.8, mean 64.1 mg·kg⁻¹), Cu (1.8–23, mean 10.1 mg·kg⁻¹), Pb (5.1–93.3, mean 17.2 mg·kg⁻¹), Cr (0.13–1.5, mean 0.47 mg·kg⁻¹). The slight enrichment of superficial soil levels in heavy metals has an industrial character (The Pińczów Building Stone Works Joint Stock Company, Gypsum Industrial Plant “Dolina Nidy” S.A.) [11, 14].

CONCLUSIONS

1. The soils under study belong to the following subtypes: Cretaceous-Rendzic Leptosols, Tertiary-Rendzic Leptosols and Gypsiri-Rendzic Leptosols. They are skeletal soils of medium depth.

2. The soils are distinguished by high pH values, marked content of organic matter and CaCO₃, and high saturation of sorption complex with basic cations. They do not show much diversity in terms of the studied chemical properties.

3. Average contents of heavy metals in the Rendzic Leptosols were estimated (at mg·kg⁻¹): Zn – 59.9, Cu – 24.9, Pb – 23.4, Cr – 15.4). These values are reported to characterize unpolluted soils.

REFERENCES

METALE CIĘŻKIE ORAZ WYBRANE WŁAŚCIWOŚCI FIZYCZNE I CHEMICZNE RĘDZIN PONIDZIA (POŁUDNIOWA POLSKA)

Celem prezentowanej pracy jest charakterystyka i porównanie właściwości chemicznych oraz zawartości metali ciężkich w rędzinach kredowych, trzeciorzędowych, siarczanowych wykształconych w obrębie Niecki Nidziańskiej. Najwyższe zawartości metali ciężkich stwierdzono w poziomach powierzchniowych. Przeciętna zawartość metali ciężkich wynosi (w mg kg⁻¹): Zn – 59,9; Cu – 24,9; Pb – 23,4; Cr 15,4) i są to wartości typowe dla rędzin i gleb średnio ciężkich i ciężkich. Badane gleby odznaczają się wysokimi wartościami pH, znaczną zawartością materii organicznej, CaCO₃, wysokim wysyceniem kompleksu sorpcyjnego kationami o charakterze zasadowym i nie wykazują większego zróżnicowania w obrębie badanych właściwości chemicznych.
THE INFLUENCE OF THE METHOD OF RECLAMATION AND SELECTION OF TREE SPECIES FOR AFFORESTATION ON CHANGES IN LANDSCAPE DEGRADED BY FIRE

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Keywords: Landscape, fire-site, forest soils, enzymatic activity, reclamation.

Abstract: The paper analyses the influence of the method of reclamation on changes in the landscape degraded by fire. The analyses involved experimental areas (I, II, III) in which various ways of preparing the soil were used (soil excluded from mechanical cultivation; full mechanical cultivation; ploughing furrows) in cultures of the Scots pine (Pinus sylvestris L.) and the Grey alder (Alnus incana (L.) MOENCH). The analyses also included a natural succession (NS) area and a control area (L) marked out in a natural forest complex directly bordering the burned area. The analyses showed that after 12 years of recultivation, the burned landscape was regaining the state of structural and functional biological balance. Cultivation of grey alder substantially stimulated the enzymatic activity of the analyzed soil, thus showing its beneficial influence on the landscape potential and justifying the use of this species as a preceding crop when rehabilitating the burned area. Various ways of preparing the soil had no substantial influence on noticeable, long-term changes in the functioning of the analyzed landscape.

INTRODUCTION

Disturbances in the functioning of landscape resulting from complete forest fires are rapid and frequently irrevocable [9]. One of the main landscape elements which undergoes degradation is the soil [7, 8]. Positive restoration effects of after-fire landscapes can be achieved by soil revitalization and by the application of plantings with species suitable for specific site [12, 15].

The basis of the functioning of the landscape is the continuity of matter circulation and energy flow between individual elements of the landscape [6]. Soil microorganisms belong to the most active landscape components which determine its quality and the activity of enzymes secreted into the soil environment provides a good indicator of their metabolic potentials. Enzymatic processes reflect disturbances in the matter circulation and energy flow by landscape elements caused by environmental stress factors [5].

The objective of the performed experiments was to assess the influence of the method of restoration and tree species selection for afforestation on the transformations of the
landscape degraded by a forest fire on the basis of selected soil parameters determining processes of energy flow and matter circulation in a landscape system.

OBJECT AND METHODOLOGY

The performed investigations were carried out on a fire site situated in the north-central part of the Noteć Primeval Forest, in the region of the Potrzebowice Forest District (52°53’N, 16°10’E) on podzolic soils (Podzols) under different types of reclamation programs. The reclamation operations were performed by the Department of Soil Silviculture of the Poznań Agricultural University [4]. The experimental surface of 7.5 ha was established in 1994, two years after a Scots pine stand approximately 60 years of age was completely burned down. The dimensions of plots, henceforth referred to as ‘experimental plots’, were as follows: 25 x 20 m (500 m²). The investigations comprised the surface of natural succession (NS) as well as surfaces on which three extremely different methods of soil preparation (I, II and III) were employed in plantations with Scots pine – Pinus sylvestris L. (S) and Grey alder – Alnus incana (L.) MOENCH – (O). The plantings were carried out using two-year old seedlings [4]. The soil on the experimental plot I was excluded from mechanical cultivation and its preparation was limited to digging a hole with a spade in which the seedling was placed. This method enabled leaving the organic-mineral horizon intact. In the case of the experimental plot II, full mechanical tillage was performed carrying out shallow ploughing to the depth of 30 cm using a disk plough. Consequently, the residues of the soil organic horizon were removed completely and they were uniformly mixed with the mineral layer. On the experimental plot III, furrows were ploughed every 1.5 m with of a forest LPZ-75 plough equipped with 2 mouldboards and their bottoms were additionally loosened to the depth of 40 cm using a subsoiler. Seedlings were planted in the belts prepared in the above-described way. The organic horizon was completely removed from the area of furrows and, following the turning over of the ploughed furrow-slice, it was left between rows earthed up with part of the mineral soil. The succession plot (NS) and control area (L) were established on an un-cleaned clear-cut area situated at the distance of approximately 70 m from the forest fragment which survived the forest fire. The residues which were left after clear cutting were neither removed nor cut. No artificial regeneration was carried out on this plot so that all plants growing there were the result of spontaneous plant succession in the region of the forest fire.

The investigations on selected plots were conducted in 2004–2006. The presented paper discusses research results obtained following 12 years of reclamation operations on the forest fire site.

In June 2006, soil samples were collected from the depth of 0–10 cm and 10–20 cm from five points on each of the selected experimental plots and selected physical, chemical and biochemical properties were determined in each of them in five replications. Identical soil samples were collected from the natural forest complex unaffected by the forest fire situated in direct neighborhood of the forest fire site and which acted as the control plot (L). The following parameters were determined in soil samples with disturbed and intact structure: texture composition using Bouyoucos method in Prószyński’s modification, specific density by pycnometric method [17], bulk density using Nitzsch’s vessels of 100 cm³ volume, soil porosity calculated on the basis of density assays, soil moisture content by drier-gravimetric method, pH in 1 mol·dm⁻³ KCl, organic carbon and total ni-
trogen using Vario Max analyzer as well as ammonium nitrogen and nitrate nitrogen [ISO 14255]. The biochemical analyses comprised the following determinations: the activity of dehydrogenases with a TTC (triphenyl tetrasolium chloride) substrate [20], acid phosphatase (Pac) and alkaline phosphatase (Pal) [19], urease [21] and protease [11]. The activity of dehydrogenases was given in cm$^3$ H$_2$ necessary to reduce TTC to TFP (triphenyl phormosan); of phosphatases – in mmols of p-nitrophenol (PNP) produced from sodium 4-nitrophenylphosphate; urease – in mg N-NH$_4^+$ formed from hydrolyzed urea; protease – in mg tyrosine developed from sodium caseinate.

Statistical analysis was carried out using the Statistica 6.0 PL program.

RESULTS AND DISCUSSION

Different methods of soil preparation, after 12 years of their application on the forest fire site, failed to exhibit an unambiguous effect on the analyzed soil physical properties (Tab. 1). Soils on the examined experimental plots showed almost identical texture (the content of clay fraction ranged from 1–3%) and specific density (2.64–2.65 Mg·m$^{-3}$). Soil moisture content on the majority of the plots ranged from 0.03–0.04 m$^3$·m$^{-3}$ to 0.05 m$^3$·m$^{-3}$ on O II, O III and NS experimental surfaces.

Table 1. Basic physical properties of investigated soils

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<th>Depth [cm]</th>
<th>Moisture [m$^3$·m$^{-3}$]</th>
<th>Specific density [Mg·m$^{-3}$]</th>
<th>Bulk density [Mg·m$^{-3}$]</th>
<th>Porosity [m$^3$·m$^{-3}$]</th>
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</table>

/*S – *Pinus silvestris*,  O – *Alnus incana*,
NS – natural succession,  L – control area

Distinct differences were observed only in porosity and, closely connected with it, soil bulk density. In the soil top layer (0–10 cm), porosity and bulk density values ranged from 0.46 m$^3$·m$^{-3}$ and 1.42 Mg·m$^{-3}$ (S I) to 0.57 m$^3$·m$^{-3}$ and 1.14 Mg·m$^{-3}$ (S III), respectively. In the subsurface layer (10–20 cm), the values of the parameters were lower and comparable. Plot O II (grey alder plantings) constituted an exception where, following
complete mechanical tillage, residues from the organic layer were totally mixed thoroughly with the mineral layer, causing significant homogenization of the 0–20 cm layer and, consequently, leading to high porosity (0.48 m$^3$·m$^{-3}$), at 1.37 Mg·m$^{-3}$ density. Such an effect failed to occur on plot S II (Scots pine plantings), though.

The obtained results indicate that a tree species used for plantings was a factor modifying porosity and bulk density. It could have been associated with the individual impact of a tree species on the composition of a microbiological complex settling tree roots and decomposing the plant material. A tree species significantly influences soil soluble C concentration and, as a result, affects soil porosity and bulk density [8, 14]. In alder plantings (O I – O III), the values of soil porosity in the 0–10 cm layer were higher (0.50–0.51 m$^3$·m$^{-3}$) than in pine plantings (S I and S II) (0.46–0.49 m$^3$·m$^{-3}$). In comparison to leaf fall, needle fall contains less N and more lignin. The coniferous substrate, rich in waxes, resins and lignin, is more resistant to decomposition due to its high initial lignocellulosic index which plays a decisive role in the rate of its microbiological transformation [10]. As to the 0–10 cm layer, the porosity bearing the closest similarity to that of an intact forest habitat (0.46 m$^3$·m$^{-3}$), was found in the soils of plot S II and the NS (natural succession) plot, which were totally different with regard to the extent of interference in the soil cover.

A surprisingly low bulk density (1.14 Mg·m$^{-3}$) and the highest porosity were observed in the soil from plot S III (Tab. 1). As regards the pine crops, the soil from plot S III had the highest organic carbon content. However, it was noticeably lower than in the soil in the forest habitat not disturbed by fire (L) (Tab. 2). A positive impact of the reclamation system on transformations in the landscape destroyed by fire can be observed, among others, in soil humus formation. The method of soil preparation is a factor influencing soil biological activity contributing to the improvement and stability of soil colloidal-mineral complex, which, in turn, guarantees a long-term effect of favorable changes in the soil physical condition. Malicki [13] points out that mechanical interference in a soil environment exerts only a slight influence on the development of soil physical properties. This claim is corroborated by numerous reports found in the literature on the subject. Among others, Biskupski and Sienkiewicz [3] showed that methods of soil preparation for sowing highly diverse as to their intensity changed soil density and moisture content only to a limited extent. On the other hand, experiments carried out by Olejarski [15] revealed that the method of soil preparation on fire sites had a significant impact on the development of the physical state, in particular, on the water properties. However, it should be emphasized that Olejarski [15] also presented results of other investigations which showed that, in certain conditions, the method of soil preparation fails to cause tangible, long-term changes in soil physical conditions.

Soils on the fire site were characterized by lower acidity than the soil on the forest site unaffected by the fire (experimental plot L). The above mentioned differences ranged from 0.20 to 0.70 pH unit in 1 mol·dm$^{-3}$ KCl (Tab. 2). On all the examined plots, pH$_{KCl}$ values were lower in the top soil layer (0–10 cm) than in the layer extending from 10 to 20 cm. Differently decomposed forest litter, usually occurring in the form of surface organic layer, favors acidification because it contains non-neutralized humus substances as well as soluble fractions of humic acids. Moreover, nitrification, which is the outcome of enhanced mineralization, is one of the factors which increase the acid load in the surface layers of forest soils. The applied methods of reclamation of the forest fire site failed to exert any practical influence on changes in the reaction of those soils (Tab. 2).
Following 12 years of reclamation, the content of organic carbon and total nitrogen in soils of the plots affected by the fire was statistically significantly lower by about 20–60% in comparison with the soil from the control plot (Tab. 2). Our earlier investigations [14] carried out after 10 years of reclamation showed that levels of the above-mentioned constituents in soils damaged by the fire were by 50–80% lower than in the unaffected soil in the site directly neighboring with the fire site. The observed increases in levels of organic carbon and total nitrogen in consecutive years of the experiments confirm growing self-regulating capabilities of the landscape damaged by the fire and show that the applied methods of reclamation were effective. The new active humus found in the sterile soils acts as a stimulator of the continuity of processes of matter circulation and energy flow which take place between individual elements of the landscape [2, 6].

In the case of soils situated in the area affected by the fire on plots with the Scots pine plantings, the $C_{org}$ and total N resources were significantly lower than in the cultivations with Grey alder and on the NS plot (natural succession). Statistically confirmed differences were observed primarily in the top soil layer (Tab. 2). Different methods of soil preparation after 12 years of their application on the fire site failed to show an unequivocal impact on organic carbon and total nitrogen contents in soils. In Scots pine plantings, the highest quantities of $C_{org}$ and total N were recorded in the soil from the experimental plot III on which furrows were ploughed up, while in the alder plantings – in the soil from plot I (the soil where no mechanical tillage was used).

The quantities of organic carbon and total nitrogen determined in the top layer of the examined soils were several times higher than those found in the 10–20 cm layer (Tab. 2).

The values of the C:N ratio observed in the soils from the plots S III, O II and NS were significantly higher in the 0–10 cm layer than in the 10–20 cm layer. The differences

<table>
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<tr>
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<th>pH</th>
<th>$C$ [g⋅kg$^{-1}$]</th>
<th>$N$ [mg⋅kg$^{-1}$]</th>
<th>C:N</th>
<th>$N-NH_4^+$</th>
<th>$N-NO_3^-$</th>
</tr>
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<tbody>
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<td>32.83b</td>
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<td>0.90c</td>
<td>23.8d</td>
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<td>21.5c</td>
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<td>20.6c</td>
<td>47.09c</td>
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<td>48.72c</td>
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<td>18.4c</td>
<td>32.46b</td>
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<td>0.54b</td>
<td>18.4c</td>
<td>36.09b</td>
<td>8.79b</td>
</tr>
</tbody>
</table>

Values in the column followed by the same letter are not significant at $p < 0.05$, “t” – test
noted on the other plots (S I, S II, O I and O III) were statistically non-significant (Tab. 2). The highest values of the C:N ratio were registered in the soil of the NS plot: 29.0 in the 0–10 cm layer and 22.5 in the 10–20 cm layer while the lowest ones were found in the soil from plot O II: 13.2 in the 0–10 cm layer and 9.9 in the 10–20 cm layer. On the other plots, the values of this parameter reached the same level as those in the soil of the control plot (L) (Tab. 2). Greater fluctuations in the metabolic rate were observed in the alder plantings (C:N ranging from 9.9 to 20.6) than in the pine crops (C:N from 20.3 to 23.8).

The contents of N-NH₄⁺ and N-NO₃⁻ in soils on plots where Grey alder was cultivated were similar to those determined in the control soil (experimental plot L), whereas in soils from the plots with Scots pine planting as well as on the NS (natural succession) plot, they were significantly lower, by approximately 30–40%, than in the control soil (Tab. 2). In alder cultivating, the symbiosis between the tree roots and nitrogen-fixing Actinomycetales contributes to soil enrichment with the available forms of this element and enables nitrogen uptake by a plant.

The above mentioned results indicate that alder plantings exerted a positive impact on the resource-functional (material, storage, transport) potentials of the landscape after the fire which increase the system capability for biotic productivity and realization of abiotic processes [1, 18]. On the other hand, in Scots pine cultivations as well as on the NS plot, the soil still remains an accumulative ecosystem which immobilizes nitrogen, hence in the process of biomass production it will continue to exhibit increased demand for nitrogen. It should further be emphasized that the investigations carried out two years earlier, after 10 years of reclamation operations of the degraded landscape [14], revealed that within the forest fire site, irrespective of the employed regeneration species, quantities of mineral nitrogen (N-NH₄⁺ and N-NO₃⁻) in soils were by about 70–80% smaller than in the soil of the forest environment unaffected by the fire. In addition, it is worth stressing that the content of these constituents on plots with Grey alder plantings was significantly higher in comparison with Scots pine stands. The above data prove that the destroyed cultural landscape, i.e. the forest fire site before the reclamation process, with the passage of time managed to regain its capacity to counteract changes in its structure and character of functioning of its elements caused by the fire and transformed into a harmonious cultural landscape [16]. Methods of soil preparations employed in the process of the reclamation of the fire site did not influence in a significant manner the content of N-NH₄⁺ and N-NO₃⁻ in the soil. The content of the ammonia form of nitrogen in the examined soils was several times higher than that of the nitrate form (Tab. 2), which was related to the low soil pH limiting nitrification (Tab. 1).

The activity of dehydrogenases, acid phosphatase, alkaline phosphatase and protease in the soils on experimental plots with Grey alder was similar to the level of the activity of these enzymes determined in the soil on the control plot (L), whereas on plots where Scots pine was growing as well as on the NS (natural succession) plot, it was significantly lower, approximately 1.5 to 3.0 times than in the control soil (Tab. 3). In the case of urease, it was found that the activity of this enzyme in soils on all plots affected by the forest fire was identical with that in the control soil which is in keeping with the results reported by Januszek et al. [7] and corroborate once more that urease is resistant to external factors and the only factor limiting its activity is substrate (urea) availability. The above data confirms that following 12 years of after-fire reclamation operations of the affected landscape, especially on the experimental plots with alder plantings, it was
possible to achieve the condition of relative dynamic biological equilibrium which is essential if the landscape system is to function properly [6]. The observed high relative soil enzymatic activity on plots with alder plantings was accompanied by a significantly higher content of organic carbon and total nitrogen (Tab. 2). These results indicate that alder plantings enhance the reclamation potentials of landscape area, including such partial potentials as: self-regulation and resistance, buffering, environment-forming as well as resource and functional procedures as expressed in the form of, among others, the capacity of the landscape to produce and store energy in the form of organic matter [18].

Table 3. Enzymatic activity of soils (Dh – dehydrogenases in cm³ H₂·kg⁻¹·d⁻¹, Pac – acid phosphatase and Pal – alkaline phosphatases in mmol PNP·kg⁻¹·h⁻¹, U – urease in mg N-NH₄⁺·kg⁻¹·h⁻¹, P – protease in mg tyrosine·kg⁻¹·h⁻¹)

<table>
<thead>
<tr>
<th>Plots</th>
<th>Depth [cm]</th>
<th>Dh</th>
<th>Pac</th>
<th>Pal</th>
<th>U</th>
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<td></td>
<td>0–10</td>
<td>2.21c</td>
<td>14.63c</td>
<td>5.42d</td>
<td>2.35b</td>
<td>6.21b</td>
</tr>
<tr>
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<td>1.23a</td>
<td>8.63b</td>
<td>2.95a</td>
<td>0.79a</td>
<td>3.68a</td>
</tr>
<tr>
<td></td>
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<td>1.98b</td>
<td>9.56b</td>
<td>4.34c</td>
<td>2.28b</td>
<td>7.53b</td>
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<tr>
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<td>4.47a</td>
<td>2.59a</td>
<td>0.76a</td>
<td>4.08a</td>
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<td>S II</td>
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<td>9.32b</td>
<td>4.75c</td>
<td>2.72b</td>
<td>8.05b</td>
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<tr>
<td></td>
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<td>6.42a</td>
<td>2.12a</td>
<td>0.84a</td>
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<td>8.39e</td>
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<td>2.72a</td>
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<td>6.15b</td>
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</table>

Values in the column followed by the same letter are not significant at p < 0.05, “t” – test

No significant effect of the method of soil preparation on its enzymatic activity was noted.

The activity of the examined enzymes in top layers of soils was several times higher than in the 10–20 cm layer (Tab. 3) which is associated with profile humus distribution and declining quantities of the carbon substrates in the soil available for microorganisms and enzymes.

Summing up the obtained results, it can be said that following 12 years of reclamation the examined after-fire landscape is reaching the condition of biological structural and functional equilibrium. At the same time, it should be emphasized that landscape, as an energetically open system where boundary exchange of energy and matter takes place continually, is permanently exposed to the action of natural and anthropogenic factors. What is important from the ecological point of view is the stability and durability of the capability for self-regulation developed in the result of the performed reclamation procedures which characterizes harmonized cultural landscapes. This indicates that it is...
necessary to continue research on changes of biochemical parameters stimulating processes of matter circulation and energy flows between landscape elements from the point of view of estimation of the long-term effect of reclamation operations on functioning of the examined landscape.

CONCLUSIONS

1. The increasing contents of organic carbon and total nitrogen in the examined soils in consecutive years of investigations confirm the growing self-regulating capability of the landscape damaged by the fire and the effectiveness of the performed reclamation program.

2. The distinct positive impact of the reclamation program on experimental plots with alder plantings justifies the use of this species as the pioneer crop for fire site regeneration.

3. The determined significant increase in the organic carbon content in the soil on experimental plots with Grey alder stimulated favorable changes in the activity of enzymes catalyzing the most important transformations of soil organic matter. This confirms that alder plantings increased the self-regulating, resistance, buffering as well as resource-functional potentials of the examined landscape.

4. Plantings with Grey alder exerted a significant influence on the increase of mineral forms of nitrogen in the soil corroborating their positive impact on the resource-functional potentials of the landscape subjected to the reclamation program.

5. It is evident from the performed investigations that the applied enzymatic tests also signal changes taking place in the landscape system under the influence of the applied tree species which makes complex recognition of the course of the regeneration processes of forest ecosystems damaged by fires possible and can be utilized to develop optimal programs of management of large-area fire sites.

6. Different methods of soil preparation 12 years after their application on the examined fire site failed to exhibit a significant influence on the determined soil properties. This means that the employed methods of soil preparation did not cause tangible, long-term changes in the functioning of the examined landscape.

REFERENCES


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WPŁYW METODY REKULTYWACJI I WYBRANYCH GATUNKÓW DRZEW DO ZALESIEŃ NA ZMIANY KRAJOBRAZU ZDEGRADOWANEGO PRZEZ POŻAR

W pracy analizowano wpływ sposobu rekultywacji na przekształcenia krajobrazu zdegradowanego przez pożar. Badaniami objęto powierzchnie doświadczalne, na których zastosowano odmienne sposoby przygotowania gleby (gleba wyłączona z uprawy mechanicznej, pełna uprawa mechaniczna, wyoranie bruzd) w uprawach sosny zwyczajnej (Pinus silvestris L.) i olszy szarej (Alnus incana (L.) MOENCH) oraz powierzchnię naturalnej i powierzchnię kontrolną wytypowaną w naturalnym kompleksie leśnym bezpośrednio sąsiadującym z pożarzyskiem. Badania wykazały, że po 12 latach rekultywacji krajobraz popożarowy uzyskuje stan strukturalnej i funkcjonalnej równowagi biologicznej. Nasadzenia olszy szarej w istotny sposób stymulowały aktywność enzymatyczną badanych gleb, co wskazuje na ich korzystny wpływ na potencjał krajobrazu i uzasadnia stosowanie tego gatunku jako przedplonu przy odnawianiu pożarzyska. Odmienne sposoby przygotowania gleby nie miały istotnego wpływu na uchwytne, długofalowe zmiany funkcjonowania badanego krajobrazu.
THE REMOVAL OF Cr(VI) FROM THE AQUEOUS SOLUTION BY GRANULAR FERRIC HYDROXIDE (GFH)

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COMMUNICATION

Keywords: Granular ferric hydroxide (GFH), adsorption isotherms, batch tests, column tests, chromium.

Abstract: In this work, sorption of chromium on granular ferric hydroxide (GFH) has been investigated using batch and column techniques. The adsorption behavior of Cr on GFH, depending on pH, contact time and sorbent amount were studied. The equilibrium adsorption capacity of GFH for Cr was measured and extrapolated using Freundlich isotherms. Metal ions bounded to the GFH could be recovered by alkaline solution, and the GFH can be recycled. The sorption capacity of GFH was 25.0 mg/g. The ion exchange of chromium on GFH follows pseudo-first-order kinetics. The intraparticle diffusion of chromium on GFH presents the limiting rate. The results indicated practical value of this method for industry and also provide strong evidence to support the proposed thesis about the adsorption mechanism.

INTRODUCTION

Chromium(VI) is released into the environment through a large number of industrial operations, including metal finishing industry, leather, tanning, textile and pulp processing factories [9].

Removal of Cr(VI) from wastewater is essential due to their toxicity. Two possible oxidation states for chromium are: Cr(III) and Cr(VI). Cr(VI) is a strong oxidant and potential carcinogen. It has toxic influence on plants, animals, humans and microorganisms and is associated with the development of various chronic health disorders, including organ damage, dermatitis and respiratory impairment [10].

Many previous works have attempted to find reasonable methods to remove heavy metals from wastewater, such as: electrochemical [6], chemical precipitation [1], adsorption [7].

As one of the most promising techniques for removal of chromium from industrial wastewater, adsorption technology has been employed for many years and effectiveness of various adsorbents has been demonstrated [8]. Jing Hu using maghemite nanoparticles to remove Cr(VI) reached the maximum adsorption at pH 2.5 [5]. A number of investigators have studied the removal of inorganic metal ions in particular chromium from aqueous solution using different adsorbents. Adsorption not only removes heavy metals from liquid phase but also allows regenerating and recycling them back into the industrial process.
A previous study [1–3] has shown that GFH is a promising material for the removal of arsenic and phosphorus from the natural water by adsorption. Badruzzaman showed that arsenate adsorption isotherm data were fitted with the Freundlich model [1]. Resulting $K_F$ values were 3.60 and 4.55 $\mu$g As/mg dry GFH. At pH 7.0 Driehaus [2] obtained an adsorption density 17 mg As/g dry GFH at an equilibrium liquid phase concentration of 10 $\mu$g/dm$^3$. The difference in adsorption capacity between Badruzzaman and Driehaus could be due to differences in initial concentration of As(V) or background water composition [1, 2]. Driehaus does not mention a pH buffer, but bicarbonate was used in his study [2].

Genz [3] investigated the advanced phosphorus removal by adsorption on activated aluminum oxide (AA) and GFH in water treatment, GFH showed a higher maximum capacity for phosphate and a higher affinity at low P concentrations compared to AA. The achieved loadings from 0.1 and 0.3 mg/dm$^3$ equilibrium of phosphorus concentrations at pH 8.2 amount to 7.9 and 12.3 mg/g for GFH and to 4.6 and 7.9 mg/g for activated aluminum. For reloading of phosphorus the regeneration of GFH by 0.6 M NaOH seems most effective by the volume ratio of NaOH to the bed volume 100:1. Since, typically between two and four bed volumes of regenerant are used in adsorption filters a much higher consumption of NaOH is used. It was also found that the adsorption process was influenced by the matrix pH, the contact time and the capacity of the GFH material.

In this study, GFH as a sorbent was investigated for the removal of Cr(VI) from wastewater, recovery of GFH, and presentation of Cr(VI) adsorption mechanism onto GFH. Another goal was to obtain significant data for the application of this technique on industrial scale and make comparisons of low-cost adsorbents for treating wastewaters with chromium(VI).

**MATERIAL AND METHODS**

*Adsorbent media*

GFH was obtained from Wasserchemie GmbH & Co. KG, Germany, applied in batch and fixed-bed column tests. The characteristic of GFH:

- water contents 36.5–42%,
- grain size 0.32–2 mm,
- grain density 1.5 kg/dm$^3$,
- Fe(OH)$_2$ contents 52–57%,
- flow rate 5–20 m/h,
- pH range 3.5–9.0,
- concentration of Fe in water < 0.2 mg/dm$^3$.

The results are presented on a dry GFH mass.

*Instrumentation*

A Unicam 919 atomic adsorption spectrometer (AAS Unicam, England) was used for chromium(VI) analysis. The primary wavelength was 357.9 nm. The gas used in burner was acetylene. Sensitivity of the method was 0.05 mg/dm$^3$. The possible negative effect of other metals presence was overcome by addition of a buffer. A pH meter CI-316 (ELMETRON, Poland) was used for pH measurement. Peristaltic pump (pp1B-05A ZALiMP, Poland) for column tests.
Chemicals
pH adjustment was done by 0.1 M NaOH or HCl.
Distilled water was used throughout the work. Stock solutions of 1000 mg/dm³ chromium(VI) was prepared by dissolving 2.8292 g of potassium dichromate (K₂Cr₂O₇) in distilled water. No other salts were added to adjust the ionic strength.
The pH-meter was calibrated using standard buffer solutions of known pH.

Batch experiments
Working solutions with chromium(VI) concentration of 5 mg/dm³ were prepared from the standard solution of potassium dichromate diluted to 250 cm³ with distilled water. To develop adsorption isotherms, the method of adding different quantities of adsorbent (0.1 g, 0.15 g, 0.2 g, 0.25 g, 0.3 g, 0.35 g, 0.4 g, 0.45 g, 0.5 g dry matter) to a constant solution volume at the same initial concentration of chromium was used. Experiments were repeated with different pH value (3.5, 4.0, 5.0, 6.95). pH value was corrected by 0.1 M HCl.

After adjusting pH and adding GFH, the contents of flasks were stirred for 7 h. This equilibration time was determined in a corresponding kinetic experiment. After stirring the sample was filtered, and only then the final concentration of chromium was measured.

Fixed bed column experiments
A glass column with a diameter 1.4 cm was filled with GFH on glass wool support to the high of 16.7 cm. Column was supplied with chromium wastewater for a period of 4 days continuously as fixed-bed down-flow reactors. Before starting to exploit the column, the solubility of filtering material was checked and in the range of pH accepted by Manufacturer very low solubility was observed (max. conc. of Fe < 0.03 mg/dm³). Chromium contained wastewater was pumped through the GFH column with a peristaltic pump, at the rate of 10 m/h. (This flow rate is the average between minimum and maximum given by Manufacturer). The contact time was 1 minute. The homogeneous surface diffusion model was used to describe the column batch data [5].

Regeneration studies
The loaded column was regenerated after the first loading with 0.6 M NaOH solution with the 100 cm³ portions of reagent. For reconditioning the column was rinsed with distilled water and pH was readjusted before reloading.

FUNDAMENTAL PRINCIPLE

The metal concentration on the sorbent increases until equilibrium is reached between the solid and liquid phases in the system. The concentration of metal on the medium is calculated as the difference between the original concentration of the solution and the measured concentration in the liquid phase after contact. The mass balance may be expressed as:

\[ m \left( N_e - N_o \right) = V \left( C_o - C_e \right) \]  

where \( N = 0 \), let \( x = V \left( C_o - C_e \right) \) so

\[ N_e = \frac{x}{m} \]
The $N_e$ value means the mass ratio of metal to sorbent. The most frequently used isotherm for the mathematical representation of this type of data is the Freundlich equation (3):

$$N_e = K_F C_e^{1/n}$$  \hspace{1cm} (3)

Equation (3) can be linearized as logarithm:

$$\log N_e = \log K_F + \left( \frac{1}{n} \right) \log C_e$$  \hspace{1cm} (4)

where:

- $V$ – volume of solution [dm$^3$],
- $x$ – mass of metal captured by media [mg],
- $C_o$ – initial liquid phase metal concentration [mg/dm$^3$],
- $C_e$ – equilibrium liquid phase metal concentration [mg/dm$^3$],
- $N_e$ – equilibrium metal concentration on media [mg/g],
- $m$ – mass of the media [g],
- $K_F$ – Freundlich isotherm constant [l/g].

**RESULTS AND DISCUSSION**

*Equilibrium adsorption isotherms*

The results obtained during the batch scale experiments are shown in Figure 1 for GFH at pH = 3.5, 4.0, 5, 6.95. Initial concentration of Cr(VI) $C_o$ was 5 mg/dm$^3$. The pH-value was lowered using 0.1 M HCl.

![Fig. 1. Correlation between final concentration of Cr(VI) and x/m ratio on GFH at various pH](image)

*Effect of pH on adsorption*

The effect of pH on the removal of chromium by its adsorption on GFH (0.15 g), is shown in Figure 2. It can be seen that pH of the solution plays a very important role in the adsorption of chromium. At pH = 6.95, GFH adsorption capacity was 2.59 mg/g, and at pH = 3.5 the capacity increased to 7.46 mg/g. A decrease in pH from 6.95 to 3.5 led to higher loading for adsorbents due to the more positively charged adsorbent surface at acidic pH.
Effect of GFH dosage on adsorption

Figure 3 shows the degree of removal of chromium from the solution at different doses of GFH and with different pH values. The GFH doses varied from 0.15 to 0.4 g. The experiment shows that for the maximum removal of 5 mg/dm$^3$ of chromium from 250 cm$^3$ sample requires a minimum GFH dosage of 0.4 g. The experimental results reveal that the chromium removal efficiency increases up to an optimum dosage beyond which the removal efficiency does not change. It is clear that the equilibrium concentration decreases with increasing adsorbent doses for a given initial chromium concentration, because by constant initial metal concentration, increasing adsorbent doses provides a greater surface area or adsorption sites [5].
Chromium removal behaviors
The chromium removal kinetic was established using in each case 36.30 g GFH. Experiments were repeated at different pH value in order to find out the equilibrium time. The reaction mixture consisted of 1 dm$^3$ of wastewater with initial concentration of 1400 mg Cr(VI)/dm$^3$ (this concentration was calculated proportional to the amount of GFH used in previous experiment). At fixed time interval a sample was withdrawn and analyzed. The result is shown in Figure 4 at pH = 5.68 and 3.5. The highest efficiency of chromium removal took place in 360 min, after which approximately 65% Cr was removed.

From the reported data it can be seen that the initial adsorption kinetics is very high (the trend is almost vertical) for all values of pH and that it rapidly decreases with time. Since the initial kinetics is mainly related to the external mass transfer resistance, the external diffusion is very rapid. Furthermore, we observed that adsorption capability becomes very low after 360 min, which means that GFH adsorption is close to saturation.

![Fig. 4. Cr(VI) removal kinetic curve in flow condition](image)

Kinetic model of adsorption
Experiments were performed in order to understand the kinetics of chromium removal on GFH. It is shown in Figure 5. The rate constant k, shown in Table 1 can be evaluated by the following pseudo-first-order expression:

$$\frac{dq}{dt} = k_{ad}(q_e - q)$$

Integrating equation (5) for boundary from time t = 0, and if at the time t the concentration falls to q, it gives:

$$\lg (q_e - q) = \lg q_e - \left(k_{ad}/2.303\right)t$$

<table>
<thead>
<tr>
<th>pH</th>
<th>The rate constant for reaction, k [1/h]</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.86</td>
<td>0.39</td>
<td>0.97</td>
</tr>
<tr>
<td>3.5</td>
<td>0.31</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 1. The rate constant for reaction values on different dosage GFH
Intraparticle diffusion model

The rate constant for intraparticle diffusion, $k_{id}$, can be evaluated by the following:

$$q = k_{id} \sqrt{t}$$

(7)

It is shown in Figure 6 and Table 2.

### Table 2. The rate constant for reaction values on different dosage GFH

<table>
<thead>
<tr>
<th>pH</th>
<th>The rate constant for intraparticle diffusion, $k_{id}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.86</td>
<td>4.08</td>
<td>0.96</td>
</tr>
<tr>
<td>3.5</td>
<td>6.30</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Adsorption capacity and desorption

To measure the adsorption capacity for GFH, the adsorption column was operated until the column capacity was exhausted (i.e. concentration in the influent $C_e$ was similar to the concentration in the inflow). It is shown in Figure 7. The GFH sorption capacity is 25 mg Cr/g of GFH.
CONCLUSION

GFH is an effective adsorbent for Cr(VI) removal, with relatively high adsorption capacity.

Lower pH values would be advantageous for adsorbent in terms of the possible loading. Small specific amount of residuals can be easily disposed of without additional treatment.

During long-term operation contamination growth and clogging of adsorption filters might occur. At this point a regeneration procedure might replace backwashing.

REFERENCES


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USUWANIE Cr(VI) Z ROZTWORÓW WODNYCH PRZEZ SORPCJĘ NA GRANULOWANYM WODOROTLENKU ŻELAZA (GFH)

POLYCHLORINATED DIBENZO-P-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs) COMPOUNDS IN SEDIMENTS OF TWO SHALLOW RESERVOIRS IN CENTRAL POLAND

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COMMUNICATION

Keywords: PCDDs/PCDFs, sediments, reservoirs.

Abstract: The objectives of this research were to 1) measure the concentrations of PCDDs/PCDFs in sediments from two reservoirs located in Central Poland, 2) illustrate the pollution level, and 3) identify sources affecting these contaminations. Sediment samples were collected during spring period of 2007 from Barycz Reservoir situated on the Grabia River and Lower Pond located on the Sokołówka River. Almost all of analyzed homologues were identified, except for two the most toxic congeners: 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, which were not observed. The total concentrations of PCDDs/PCDFs were 213.727 pg g⁻¹ for Barycz Reservoir and 536.266 pg g⁻¹ for Lower Pond, with dominant OCDD congener. WHO-TEQ concentrations based on TEF values ranged from 2.323 to 7.984 pg g⁻¹ for Barycz Reservoir and Lower Pond, respectively.

INTRODUCTION

Every year in Europe more than 30 000 chemicals in quantities of 1 Mg are produced and handled. Many of them are formed due to combustion processes or as manufacturing by-products. Some are highly reactive and toxic for living organisms in very low concentrations but possess relatively short lifetime; others, like polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), have been shown to be persistent in environment, bioaccumulative and hazardous for biota for several years [13].

PCDD/DFs form a group of synthetic organic chemicals that contain 210 structurally related individual congeners widely distributed in the environment. They have been detected in soil, surface water, sediments, plants, and animal tissue in all regions of the earth [6, 7, 9]. Because of their low volatility and low solubility in water they can be
strongly associated with particulates and thus most of them are contained in soil and sediments that serve as environmental reservoirs from which PCDD/DF may be released over a long period of time. They can also enter the aquatic environment by atmospheric transport and deposition, direct and indirect discharges and as a riverine input [13, 14, 16].

MATERIALS AND METHODS

Study areas
In this study we determined the concentrations of 17 PCDD/PCDF congeners in sediments collected from two shallow reservoirs: Barycz Reservoir and Lower Pond (Fig. 1). Sites were selected to represent the major land uses: agricultural – Barycz Reservoir, and urban (residential and commercial-industrial) – Lower Pond, based on dominant mapped land-use and personal observation of the surrounding area.

Fig. 1. Location of the sediment samples taken for the analysis

Barycz Reservoir (51°35’N; 19°12’E) is located in the middle course of the Grabia River (river basin 813 000 m²) between Barycz and Ldzań villages [12]. The total capacity of this reservoir is 2800 m² and mean depth 1.78 m. The reservoir was built for water retention and irrigation of agriculture.

Lower Pond is situated on the Sokołówka River (river basin 45 400 m²) which represent highly urbanized and industrialized catchment contaminated with heavy metals and organic compounds due to sewage and storm water disposal. The main channel was channelised by concrete slabs, to straighten the course and deepen the bed for the purpose of detention of storm waters. The total capacity of Lower Pond is 1080 m² and mean depth is 1.0 m [1, 17].
**Sampling**

Sediment samples were collected using sediment core sampler during the spring period of 2007 (06.04.2007). Samples were filled into amber containers and transported at 4°C to the laboratory. Afterwards the samples were freeze dried at -40°C, and put through 2000 μm mesh sieve.

**PCDDs/DFs analysis**

The dried sediments were extracted by ASE (Automatic System Extraction) 200 Dionex. The 2 g of sediment were spiked with $^{13}$C-labelled PCDDs/DFs standard of known quantity to monitor extraction efficiency. Extraction was performed at 150 atm (11 Mpa) at 175°C. Extracts were treated with a multilayer column packed with neutral silica and silica modified with 44% (w/w) and 22% sulphuric acid (SiO$_2$ – H$_2$SO$_4$), 3% KOH and 10% AgNO$_3$, prewashing by 150 cm$^3$ of hexane. Elution was performed with 200 cm$^3$ of hexane. The extracts were then reduced to approximately 100·10$^{-6}$ dm$^3$ and n-hexane was replaced by n-nonane and the internal standard was added [5].

For identification and quantification of 17 2,3,7,8-substituted PCDD/DF, HRGC/HRMS (HP6890, Hewlett Packard/Autospec Ultima, Micromass) fitted with DB-5MS columns (60 m x 0.25 mm i.d., film thickness 0.25 μm) was used. As an internal standard the perfluorokerosene (PFK) was used. The column oven temperature was programmed as follows: 150°C for 2 min, 20°C/min to 200°C (0 min), 1°C/min to 220°C for 16 min and 3°C/min to 320°C for 3 min. The injector temperature was 270°C. The MS was operated with a mass resolution of 10 000, and the electron impact ionization energy was 34.8 eV with an ion source temperature of 250°C. Helium was used as carrier gas at a flow rate 1.6 cm$^3$/min. Samples were quantified with an isotope dilution method [5].

**Quality assurance/Quality control**

The analytical method used was properly validated on the basis of internal reference materials and the analytical laboratory involved successfully passed the accreditation procedure in 2005.

Quantification was done by the external standard method using certified calibration standards. Each analytical batch contained a method blank, a matrix spike, and replicate samples. A reagent blank was used to assess artifacts, precision was verified by duplicate analyses and recoveries were estimated using samples spiked with PCDD/PCDF. Samples spikes were used also as an additional check of accuracy. Recoveries of $^{13}$C-labeled PCDD and PCDF congeners through the analytical procedure ranged from 74 to 146%.

**RESULTS AND DISCUSSION**

Results showed that almost all tetra- to octachlorinated PCDDs/PCDFs were identified, except for two the most toxic congeners: 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, which were not observed (Tab. 1 and Fig. 2). The maximum concentration was observed for octachlorinated PCDD congeners: 162.483 and 409.636 pg·g$^{-1}$ d.w. for Barycz Reservoir and Lower Pond, respectively (Tab. 1 and Fig. 2).
Table 1. Concentration of analyzed PCDDs/PCDFs in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007 [pg·g⁻¹ d.w.]

<table>
<thead>
<tr>
<th>Congener</th>
<th>Barycz Reservoir</th>
<th>Lower Pond</th>
<th>Barycz Reservoir</th>
<th>Lower Pond</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WHO-TEQ concentration</td>
<td></td>
<td>WHO-TEQ concentration</td>
<td></td>
</tr>
<tr>
<td>2378-TCDD</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>12378-PeCDD</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>123478-HxCDD</td>
<td>0.325</td>
<td>0.597</td>
<td>0.033</td>
<td>0.060</td>
</tr>
<tr>
<td>123678-HxCDD</td>
<td>1.254</td>
<td>1.266</td>
<td>0.125</td>
<td>0.127</td>
</tr>
<tr>
<td>123789-HxCDD</td>
<td>4.083</td>
<td>6.207</td>
<td>0.408</td>
<td>0.621</td>
</tr>
<tr>
<td>1234678-HpCDD</td>
<td>4.496</td>
<td>29.185</td>
<td>0.145</td>
<td>0.292</td>
</tr>
<tr>
<td>OCDD</td>
<td>162.483</td>
<td>409.636</td>
<td>0.049</td>
<td>0.123</td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>0.000</td>
<td>10.028</td>
<td>0.000</td>
<td>1.003</td>
</tr>
<tr>
<td>12378-PeCDF</td>
<td>0.639</td>
<td>4.738</td>
<td>0.019</td>
<td>0.142</td>
</tr>
<tr>
<td>23478-PeCDF</td>
<td>1.047</td>
<td>8.242</td>
<td>0.314</td>
<td>2.472</td>
</tr>
<tr>
<td>123478-HxCDF</td>
<td>3.158</td>
<td>7.143</td>
<td>0.316</td>
<td>0.714</td>
</tr>
<tr>
<td>123678-HxCDF</td>
<td>3.068</td>
<td>7.517</td>
<td>0.307</td>
<td>0.751</td>
</tr>
<tr>
<td>123789-HxCDF</td>
<td>2.228</td>
<td>2.472</td>
<td>0.223</td>
<td>0.247</td>
</tr>
<tr>
<td>234678-HxCDF</td>
<td>2.718</td>
<td>11.487</td>
<td>0.272</td>
<td>1.149</td>
</tr>
<tr>
<td>1234678-HpCDF</td>
<td>7.198</td>
<td>22.790</td>
<td>0.072</td>
<td>0.228</td>
</tr>
<tr>
<td>1234789-HpCDF</td>
<td>3.818</td>
<td>5.228</td>
<td>0.038</td>
<td>0.052</td>
</tr>
<tr>
<td>OCDF</td>
<td>7.211</td>
<td>9.732</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>Total</td>
<td>213.727</td>
<td>536.266</td>
<td>2.323</td>
<td>7.984</td>
</tr>
</tbody>
</table>

Fig. 2. Percentage content of analyzed homologues in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007

The total concentrations of PCDD/DF were 213.727 and 536.266 pg·g⁻¹ d.w. for Barycz Reservoir and Lower Pond, respectively, with the predominance of PCDD (182.641 and 446.891 pg·g⁻¹ d.w. for Barycz Reservoir and Lower Pond, respectively)
The total PCDD/DF TEQs concentrations were 2.323 and 7.984 pg TEQ·g⁻¹ dry weight for Barycz Reservoir and Lower Pond, respectively (Tab. 1 and Fig 4). The PCDF congeners were responsible for higher contributions to 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (WHO-TEQ) values (2.06 and 5.53 times higher than PCDDs for Barycz Reservoir and Lower Pond, respectively).

Fig. 3. Total PCDD/DF concentration in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007 [pg·g⁻¹ d.w.]

Fig. 4. Total PCDD/DF TEQ concentration in sediment samples collected from Barycz Reservoir and Lower Pond during spring period of 2007 [pg·g⁻¹ d.w.]
The composition of 7 PCDD congeners in sediments collected from Barycz Reservoir was in order: OCDD (76.02%), 1,2,3,4,6,7,8-HpCDD (6.78%), 1,2,3,7,8,9-HxCDD (1.91%), 1,2,3,6,7,8-HxCDD (0.59%), 1,2,3,4,7,8-HxCDD (0.15%), 1,2,3,7,8-PCDD and 2,3,7,8-TCDD (0.00%). Similar pattern was observed for Lower Pond sample: OCDD (76.39%), 1,2,3,4,6,7,8-HpCDD (5.44%), 1,2,3,7,8,9-HxCDD (1.16%), 1,2,3,6,7,8-HxCDD (0.24%), 1,2,3,4,7,8-HxCDD (0.11%), 1,2,3,7,8-PCDD and 2,3,7,8-TCDD (0.00%). The PCDFs composition was more diverse and ranged from 3.37% to 0.00% for the Barycz Reservoir sample and from 4.25% to 0.46% for the Lower Pond sample.

It could be stated that no previous measurements of PCDD/PCDF concentrations were undertaken in analyzed reservoirs, thus there are not available data for comparison. Nevertheless, the obtained concentrations of PCDDs/PCDFs in the studied area were more or less comparable to the values observed in other reservoirs worldwide. Chi et al. [2] reported that concentration of PCDDs in northern Taiwan reservoir ranged between 0.95 to 14.40 pg TEQ·g⁻¹. In a study of Rose and McKay [15] the concentrations ranged from 1 to 100 pg TEQ·g⁻¹. Research of Koh et al. [11] showed the PCDD/PCDF concentration values in sediment from the Hyeongsan River were between 190 to 290 pg·g⁻¹ d.w. El-Kady et al. [4] reported that total sum of PCDD/PCDFs in sediments of the River Nile was in the range from 239.67 to 755.09 pg·g⁻¹ d.w. A study of Kannan et al. [10] showed values from 68.7 to 1420 pg·g⁻¹ d.w. with TEQ concentration ranged from 3.00 to 62.1 pg·g⁻¹ d.w. Hilscherova et al. [8] reported concentration from 59 to 120 and from 2400 for PCDDs to 53600 pg·g⁻¹ d.w. for PCDFs for upstream and downstream of the Tittabawse River, respectively.

From the study obtained by Polish researchers carried out on soils in Poland total PCDD concentrations ranged from 6.8 to 41 pg·g⁻¹ d.w. and concentration of PCDFs was in range 3.9 to 19 pg·g⁻¹ d.w. and in all samples highly chlorinated PCDDs/DFs dominated (OCDD, 1,2,3,4,6,7,8-HpCDD, OCDF, 1,2,3,4,7,8,9-HpCDF, 1,2,3,4,6,7,8-HpCDF were found in all investigated soils). Total toxic equivalency was in the range of 0.023–5.9 pg TEQ·g⁻¹ d.w. [18].

Presented by authors values were several times lover that obtained in our study, nevertheless it could be stated that sediment samples are matrices that accumulate lipophilic substances and can receive inputs via various pathways including atmospheric deposition, industrial and domestic effluents, storm water, spills, and other. Thus they are the ultimate sink for micropollutants and it is estimated that about 97% of released POPs in a water column are retained in sediment [3].

The main sources of PCDDs/DFs in the analyzed samples include thermal processes such as grass and trash burning as well as heating of houses by small stoves fired with hard coal with added household wastes, and former use of agrochemical formulations consisting of impurities of PCDD/DF. Thus, this kind of pollution may play an important role at agricultural site (Barycz Reservoir). In comparison, as the main sources of PCDD/PCDF in the urban region (Lower Pond), energy and fossil fuel production, co-fired power boilers, and chemical industry can be considered. Moreover, congeners 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD are reported as closely related to incineration sources, and therefore can be linked to these processes. Congeners 1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8-HxCDD, in turn, showed similarities with the PCDD/DF homologues in pentachlorophenol (PCP), and thus their presence in the environment is explained as PCP-related contamination. The higher concentrations of OCDD/OCDF might be connected to the former
production and use of highly chlorinated polychlorinated biphenyl formulation – such as chlorofen [18].

The obtained results suggest that sediments from Barycz Reservoir and Lower Pond are contaminated with PCDD/PCDFs in a considerable rate. Industrial and urban characteristic of Lower Pond basin with combined overflows located along the Sokolówka River have influenced its higher sediment concentration.

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POLICHŁOROWANE DIBENZO-P-DIOKSYNY I POLICHŁOROWANE DIBENZOFURANY W OSADACH DENNYCH DWÓCH PŁYTKICH ZBIORNIKÓW POLSKI CENTRALNEJ

Celem niniejszych badań było: 1) zmierzenie stężeń PCDD/DF w osadach dennych dwóch zbiorników zaporowych zlokalizowanych w Polsce Centralnej, 2) zilustrowanie poziomu zanieczyszczenia powyższymi związkami oraz 3) identyfikacja źródeł wpływających na istniejący stan. Osady dennne pobrano w sezonie wiosennym 2007 r. ze Zbiornika Barycz usytuowanego na rzece Grabi i Stawu Dolnego zlokalizowanego na rzece Sokołówce. Niemal wszystkie spośród 17 analizowanych kongenerów PCDD/DF zidentyfikowano w badanych próbach, wyjątkiem były dwa najbardziej toksyczne związki: 2,3,7,8-TCDD i 1,2,3,7,8-PeCDD, których nie wykryto. Całkowite stężenie PCDD/DF w Zbiorniku Barycz wynosiło 213,727 pg g⁻¹ s.m. oraz 536,266 pg g⁻¹ s.m. w Stawie Dolnym, z dominującym stężeniem kongeneru OCDD. Stężenie mierzone jako WHO-TEQ wynosiło 2,323 i 7,984 pg g⁻¹ s.m., odpowiednio dla Zbiornika Barycz i Stawu Dolnego.