STUDY OF SPATIAL AND TEMPORAL VARIATIONS OF SOME PHYSICOCHEMICAL PARAMETERS OF THE LOWER SIRET RIVER

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Abstract. The present paper presents the variability of some physicochemical parameters of the Siret river. Measurements were made partially by responsible authorities in charge with water management and by the environmental laboratory of the European Centre of Excellence for the Environment (ECEE) of Dunarea de Jos University of Galati. The monitoring was carried out for three years in order to observe the seasonal variation of the characteristics of the Siret river and their influence on some physicochemical parameters. Our results show that physical parameters of the lower Siret river are affected by anthropogenic activities as well as by seasonal variations of water flow and temperature. The study shows the complexity of these correlations and the necessity of a global, multi-parametric monitoring in order to establish the real impact and the relative contribution of natural and anthropogenic causes.

Keywords: physicochemical parameters, water debit, the Lower Siret river.

AIMS AND BACKGROUND

The present work aims at evaluating the relative extent of possible anthropogenic effects by some physicochemical parameters on the Lower Siret river and at discriminating between natural and anthropogenic effects. Their spatial and temporal distribution was analysed in order to find the most probable pollution sources along the river within the above-mentioned area.

The Siret hydrographic basin is one of the most important in Romania covering integrally or partially 13 counties.

Presently there are no special statistics in Romania concerning the efficiency of water use in industry or agriculture. Concerning the identification of significant pressures the main problem is the lack of monitoring data, especially data for the identification of priority substances. In the official studies the area belonging to the Galati county including villages, industrial and agricultural pollution sources is almost non-existing.

* For correspondence.
**Experimental**

*Sites.* Three sampling stations were established along the Siret river, taking into account the length of the river and their position relatively to sources of pollution (Fig. 1).

![Fig. 1. Hydrographic basin of the Siret river with the distribution of industrial and agricultural sources](image)

Another criterion was that the distribution should be relatively even along the river. We have selected three stations (see Fig. 1): (S1) – Cosmesti (45°51’ N and 27°18’ E); (S2) – Lungoci (45°34’ N and 27°30’ E), and (S3) – Sendreni (45°24’ N and 27°56’ E). The map in Fig. 1 shows also the distribution of potential anthropogenic activities which might affect the water quality.

*Methods.* The data were produced by ECEE laboratory or taken from official sources. The sampling was carried out monthly during three years (2005–2007) based on officially approved monitoring techniques. The water samplings were prepared in our laboratory for the analysis. At each sampling time and at each sampling station the following chemical and physical parameters were measured: pH, biological oxygen demand (BOD₅), chemical oxygen demand (COD). For
water flow and temperature official records of National Administration of Romanian Waters were used. The seasonal averages for the physical parameters are presented in Table 1. For the acidity (measured by pH) we have used the official records and compared them with our data. The dissolved oxygen, temperature, and pH were measured on site by means of a portable oxygen-meter, type WTW Multi350i. For the COD determination a method was performed that is analogous to EPA 410.4, US Standard Methods 5220 D. All reagents used were p.a. (Merck). Determination of BOD during 5 days was testing using a standard method SM 5210 2005-09HA.

Table 1. Seasonal values of water debit, temperature and pH

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Season</th>
<th>Sampling stations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow water</td>
<td>m³ s⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>spring</td>
<td></td>
<td></td>
<td>90.28</td>
</tr>
<tr>
<td>winter</td>
<td></td>
<td></td>
<td>201.33</td>
</tr>
<tr>
<td>summer</td>
<td></td>
<td></td>
<td>230.72</td>
</tr>
<tr>
<td>fall</td>
<td></td>
<td></td>
<td>119.21</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>spring</td>
<td></td>
<td></td>
<td>5.44</td>
</tr>
<tr>
<td>winter</td>
<td></td>
<td></td>
<td>13.44</td>
</tr>
<tr>
<td>summer</td>
<td></td>
<td></td>
<td>20.49</td>
</tr>
<tr>
<td>fall</td>
<td></td>
<td></td>
<td>6.83</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>spring</td>
<td></td>
<td></td>
<td>7.62</td>
</tr>
<tr>
<td>winter</td>
<td></td>
<td></td>
<td>7.73</td>
</tr>
<tr>
<td>summer</td>
<td></td>
<td></td>
<td>7.82</td>
</tr>
<tr>
<td>fall</td>
<td></td>
<td></td>
<td>7.98</td>
</tr>
</tbody>
</table>

Sources of pollution. The main categories of pressures on physical parameters of the river within the studied area are produced by: sewage, industrial units, agricultural farms, municipalities with improper functioning of the wastewater treatment plants.

RESULTS AND DISCUSSION

The average water flow of the Siret river within the studied area (Fig. 2) is roughly 300 m³/s and slightly increases from upstream (continuous line with crosses) to downstream (dotted line with ‘x’ markers), although at winter times and during most of the year 2007 the flow is constant along the river. Some important increases are observed each year but no meteorological data were available, that would allow us to connect the debit increases to heavy rains, snow melts or freshets. One can say, however, that July 2005 was associated with floods.
The temperature (Fig. 3) varies with the season, as expected. Generally, the temperature increases from upstream to downstream during summer, while cold seasons are characterised by an opposite variation.

![Fig. 2](image2.png)

**Fig. 2.** Water debit variation during 2005–2007 for the three stations: S1 – continuous line, S2 – dashed line, S3 – dotted line. S1 is the most upstream station (Cosmesti), S2 is the middle station (Lungoci) and S3 is the downstream station (Sendreni) (see Fig. 1 for details)

The third physicochemical parameter which was included in our study is the acidity (or alkalinity) described by pH (Fig. 4). The variation of the pH along the river is not regular; most of the time the river is more acid upstream, with some exceptions. There is no clear seasonal variation. Interestingly, there is a marked decrease in the pH in May 2005, relatively smaller decreases in July 2005, June 2006 and March 2007, all of them coinciding with increases in the water flow. The observed anticorrelation between pH and flow is clearer when each station is considered separately. However, there are other three pH variations which are not related to flow variations: one is the decrease in September 2005 seen at S1 while the other two are seen in June 2007 and October 2007 for the whole river. Increases of pH seen in the second part of the years at S2 and S3 could be due to agricultural run-off of ammonia compounds.
The acidification observed in April–May 2005 is associated with an increase in the water flow. In this case, the increase in the acidity of the water could be explained assuming that the flow increase is caused by heavy rains or by snow melt and taking into account that rainwater and snow are more acid than surface waters. Even natural, unpolluted rainwater has a pH of about 5.6, which comes from the natural presence of CO$_2$, NO$_2$, and SO$_2$ found in the troposphere$^6$.

Figure 5 shows that BOD$_5$ generally increases from upstream to downstream. There are also exceptions from this general rule, as it is, for instance, in July 2007. The downstream station records several peaks in the BOD$_5$. In July 2005 this is associated with the raise in the flow. A similar peak is observed also for the other two stations. This particular increase in the BOD$_5$ could be explained by the fact that a high water flow is accompanied by a larger nutrient and biological content of the river from natural sources, i.e. an increase in the BOD$_5$. Other flow increases have no effect on the BOD$_5$. The other peaks can be individually related to different chemical compounds. For instance the February 2006 peak at station S3 can be related to a similar outstanding peak in NH$_4^+$, while the peak in June 2007 could be associated to the extremely high value of TP at the same station. However, these might be simple coincidences and no conclusion can be drawn based only on these individual observations. The depletion of BOD$_5$ seems to be due to the microbial decomposition of the organic matter that accumulates in this particular area$^5$. 

**Fig. 4.** Acidity variation during 2005–2007 for the three stations: S1 – continuous line with crosses, S2 – dashed line with diamonds, S3 – dotted line with ‘x’ markers

**Fig. 5.** BOD$_5$ variation during 2005–2007 for the three stations: S1 – continuous line with crosses, S2 – dashed line with diamonds, S3 – dotted line with ‘x’ markers
The COD (Fig. 6) displays an increase from S1 to S3, which is more obvious than for BOD\(_5\). There is an exception in the summer of 2005, coinciding with the peaks in the water debit, when the COD is higher at the upstream station. Another interesting observation is a significant decrease at all stations in April 2005 that coincides with a similarly marked decrease in NO\(_3^-\). The temperature is known to influence the pH, alkalinity and dissolved oxygen concentration in water. A lower temperature favours greater dissolution of dissolved oxygen in water\(^5\). Thus we should expect a higher COD in winter than in summer. This is not seen on our results. The comparison between COD and debit shows, on the other hand, a correlation between the two parameters. Although data from only two years are available, a seasonal variation of the COD can be observed, with generally smaller values in cold times, probably associated to small water debit values.

![Fig. 6. COD variation during 2005–2007 for the three stations: S1 – continuous line with crosses, S2 – dashed line with diamonds, S3 – dotted line with ‘x’ markers](image)

CONCLUSIONS

Our results show that physical parameters of the Lower Siret river are affected by anthropogenic activities as well as by seasonal variations of debit and temperature. The study shows the complexity of these correlations and the necessity of a global, multi-parametric monitoring in order to establish the real impact and the relative contribution of natural and anthropogenic causes.

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