Environmental assessment of pollution with detergents in the Prut River Basin, Romania
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Abstract. This study focuses onto the assessment of the impacts and associated risks posed onto natural water bodies by detergent-containing wastewaters in the Prut river basin in North-Eastern Romania. The focus of this assessment on detergents as a specific wastewater component is motivated by the environmental hazards that detergents cause when entering natural eco-systems, as well as by the rapid development of the living conditions in the studied area. The assessment of environmental impacts and associated risks is performed using a methodology that considers risk as a function of risk magnitude (environmental impacts) and the probability of occurrence. The assessment focuses onto four types of activities (industry, wastewater treatment plants - WWTPs, municipalities and services) in four counties of the Prut River Basin and it is based on surface water quality data that was collected in 2007. The results have shown that the highest impacts and associated risks are present in Vaslui and Galati counties (the southeast part of the Prut river basin) mostly because of the high probabilities that polluting agents would exceed the maximum allowed concentrations for detergents.

Key words: environmental impact assessment, risk assessment, water resources management, detergents.

Introduction. Integrated water resources management (IWRM) is the practice of making decisions and taking actions in a sustainable manner while, considering multiple viewpoints of how water should be managed, being often lengthy and involving many stakeholders. These decisions and actions relate to situations such as river basin planning, organization of task forces, infrastructure development, controlling reservoir releases, regulating floodplains, and developing new laws and regulations. One of the principles underlying the Water Framework Directive, and which is in line with those of sustainable development, is that water management must be achieved at the river basin scale (Water Framework Directive 2000).

According to the principles of the Water Framework Directive (WFD) and of the IWRM given by Global Water Partnership (GWP) through the Dublin Principles (GWP 2000), the sustainable water management should be based onto an integrated approach, which considers, beside the political commitment and the legal backgrounds, aspects related to multi- and trans-disciplinary research and training, public participation, communication and cooperation, infrastructure development, strategic planning and operational practices, to name just a few. Furthermore, these efforts should be coordinated considering the natural and human components of the water cycle (supply, use, discharge / recycling) and the water resources management process should be organized at a river basin level, as presented in Fig. 1 (Teodosiu 2007; Teodosiu et al 2009a).
The water-related challenges are enhanced in the new European Union member countries, like Romania, by historic water quality problems in connection to outdated or inexistent wastewater treatment infrastructure, as well as major drawbacks in the cooperation and coordination between the relevant stakeholders (Teodosiu 2007). These problems are also related to the fast economic and industrial growth, urbanization and extension of existent water-supply and sewage systems in many rural areas, which pose even greater burdens onto natural water resources. In this complex context, beside infrastructure upgrading and development, water management strategies, programs and instruments are urgently needed in order to ensure the long-term sustainability of water resources.

This contribution focuses onto the assessment of the impacts and associated risks posed onto natural water bodies by detergent-containing wastewaters and it is part of a much broader research effort which aims at developing integrated management instruments that would support decision making processes in water resources management.

The focus of this assessment on detergents as a specific wastewater component is motivated by several reasons. Firstly, there are serious environmental risks associated with detergent disposal via wastewaters into natural water bodies due to their intrinsic toxicity and the effect of their properties (surfactants) onto aquatic biota (Kowalska 2008), as well as their synergic effects with other types of pollutants in the aquatic environment (McWilliams et al 2001) like migration, dispersion or bioaccumulation. Although most of the surfactant constituents of detergents are broken down during biological wastewater treatment, their metabolites can have completely different chemical properties and increased toxicity. Secondly, most of the detergents used in households are often associated with other personal care products which represent a serious problem to both wastewater treatment facilities and aquatic ecosystems, due to their endocrine disrupting effects and mutagenic and carcinogenic potential on aquatic life. This is furthermore enhanced by the third reason, which represents the increased quality of life in both rural and urban areas of the study area, as well as by the increasing connectivity of households, services and industries to sewage systems, which, unfortunately is not always backed-up by upgraded treatment infrastructure.

The study consists in the integrated environmental and risk assessment of the occurrence of surfactants in wastewaters coming from various sources within the Prut River Basin, located in the North-Eastern part Romania.
Integrated environmental impact and risk assessment methodology. The actual trends of integrating environmental impact assessment procedures into the risk assessment (Lexer et al 2006) have been suggested as a tool to help decision making process within water resources management. Risk assessment is usually defined as the process that evaluates the likelihood that adverse ecological effects are occurring, or may occur, as a result of exposure to one or more stressors (Kuitunen et al 2007; Robu & Macoveanu 2010; Sandham & Pretorius 2008). This approach has been extensively used, but there are limited studies that integrate both environmental impact assessment and risk assessment to evaluate the complex impacts and risks related to surface water resources.

In a previous article Barjoveanu et al (2010) provided a full description of the integrated environmental and risk assessment methodology (EIRA), as well as the arguments for its application as an instrument for water resources management. A brief overview of this methodology together with its particular aspects related to this case study is presented below.

The EIRA methodology considers the environmental risk as a function of magnitude of environmental impacts and their probability of occurrence (Eq. 1). For assessing the environmental impacts, the steps of prioritizing among different environmental components was skipped, as we refer only to surface waters, the importance units in equation 2 being set to a value of 1000. Furthermore, the environmental quality parameter in eq 2 which measures the magnitude of impacts is calculated by comparing the measured concentrations of considered pollutant (detergents in our case) with their respective maximum allowed concentrations (MAC), leading thus to a non-dimensional measure of the environmental impacts magnitude, as presented in Eq. (3).

\[ ER_j = EI_j \cdot P_j \]  
where: \( ER_j \) – environmental risk for environmental component \( j \) (-); \( EI_j \) – environmental impact on environmental component \( j \) (-); \( P_j \) – probability of impact occurrence on environmental component \( j \) (%).

\[ EI = \frac{IU}{EQ} \]  
where: \( EQ \) – environmental quality parameter (-); \( IU \) – importance units (-).

\[ EQ = \frac{MAC}{MC} \]  
where: \( MAC \) – maximum allowed concentration of quality indicator(s) (-); \( MC \) – measured concentration of quality indicator(s) (-).

The impact on surface water (\( EI_{sw} \)) represents an average of the impacts caused by different polluters that occur in wastewater and, in this case the method was applied considering only one wastewater quality indicator (detergents concentration) in quantifying the environmental impacts, as presented in Eq. (4).

\[ EI_{(sw)}^{det\,ergents} = \frac{IU_{sw}}{EQ_{(sw)}^{det\,ergents}} \]  

\[ \]

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where: \( EQ_{\text{sw/detergents}} \) – quality of *surface water*, considering the quality indicator *detergents* (-); \( IU_{\text{sw}} \) – significance units obtained by *surface water* (-).

The environmental impact assessment of the wastewaters entering the natural system was performed considering the detergents concentrations of the effluents from the industries, wastewater treatment plants, municipalities’ and services’ activities, that discharge wastewaters in the Prut River, that are monitored by Prut Water Directorate. This indicator (detergents) was considered based on the fact that it induces significant environmental impact and risks onto the natural water bodies. The next step was to quantify the risks that arise, considering the results of environmental impacts (Eq. 1).

The probability units \( (P_j) \) of impact occurrence were calculated using historic data series that allowed for calculating the frequencies of events during which 70% of the maximum allowed concentrations (MAC) was reached, which represents the attention threshold for a polluting event (Eq. 5). The value of MAC for detergents when discharging in natural water bodies, as regulated by the national legislation, through the Government Decision no. 352/2005 (GD 2005) is 0.5 mg/L.

\[
P = \frac{n}{m} \quad (5)
\]

where: \( P \) – probability of impact occurrence on environmental component surface water (%); \( n \) – number of attention thresholds reached over the data series (-); \( m \) – total number of measurements of the data series (-).

The initial method developed by Robu (2005) and improved by Robu et al (2005) used a classification scale for comparing the environmental impacts and the associated risks induced to different environmental components, based on the calculation of the impacts and risks for the same quality indicators, but for different environmental components.

Because only one environmental component (surface water) is considered in this assessment, the scale proposed by the method developers could not be used as a reference. In these conditions, a new approach for analyzing the results should be used. In this case study, four Romanian counties (Botosani, Iasi, Vaslui and Galati), covered by the Prut River its tributaries were considered for an assessment of the pollution with detergents in terms of environmental impacts and associated risks.

**Study area.** The Prut river basin (Fig. 1) is located in the North-Eastern part of the Danube basin. Its total area of 27,500 km\(^2\) covers the territory of three countries: Ukraine, Romania and the Republic of Moldova. In the Romanian part, Prut basin is managed by the Prut Water Directorate and includes in its patrimony: 52 reservoirs (with a total volume of 707 million m\(^3\), divided in: 36 complex reservoirs, 11 temporary storages and 5 polders), 854 km of regularizations, 1073 km of dikes, 73.3 km of bank consolidations, 6 derivations-upstream waterways and 11 pumping stations (DAP 2008). The Prut River (952.9 km) is the second longest tributary of the Danube River and it forms the border between Romania and Republic of Moldova. The Barlad River is the most important left-side tributary of the Siret River. The study area is Prut-Barlad catchment (Fig. 2) that lies, almost entirely, on Botosani, Iasi, Galati and Vaslui counties and partially on Neamt, Bacau and Vrancea counties.
Distribution of river basin by counties is different depending on the existing drainage system and the establishment of the watershed between catchments of Siret and Prut Rivers (Teodosiu et al 2009b), such as counties Botosani, Iasi, Vaslui, Galati have a rate of 90-100% and Bacau, Neamt and Vrancea in smaller proportions (Table 1).

Table 1

Demographic and land planning facts (DAP, 2008)

<table>
<thead>
<tr>
<th>No.</th>
<th>County</th>
<th>Area (km²)</th>
<th>% from total area on the river basin</th>
<th>Population</th>
<th>% from total population</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Botosani</td>
<td>4782</td>
<td>23.60</td>
<td>414042</td>
<td>18.85</td>
<td>Area being monitored</td>
</tr>
<tr>
<td>2.</td>
<td>Iasi</td>
<td>4564</td>
<td>22.52</td>
<td>692546</td>
<td>31.53</td>
<td>by the Prut Water Directorate</td>
</tr>
<tr>
<td>3.</td>
<td>Vaslui</td>
<td>5318</td>
<td>26.24</td>
<td>455550</td>
<td>20.74</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Galati</td>
<td>4328</td>
<td>21.35</td>
<td>612485</td>
<td>27.88</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Neamt</td>
<td>172</td>
<td>0.85</td>
<td>13566</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Bacau</td>
<td>946</td>
<td>4.67</td>
<td>7481</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Vrancea</td>
<td>157</td>
<td>0.77</td>
<td>920</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>20267</td>
<td>100</td>
<td>2196590</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
According to the objectives of this study only the impacts and risks on surface water were considered and the situation of discharging agents existing in 2007 year was highlighted. The study analyzed the contributions of different polluters in four counties that match various sectors of Prut River. From the upstream of Prut river - Botosani County, from the middle area - Iasi and Vaslui counties, and from the downstream of the river was considered Galati County. A total number of 133 agents with various activity types were considered in the impact and risk assessment of the pollution with detergents were inventoried.

After a general inventory of the total number and types of wastewater discharging agents, the focus was to apply the environmental impact and risk assessment for those agents that recorded exceedences of the MAC (64 cases from the total of 133). Furthermore, the polluters were grouped into 5 categories, with the following remarks: wastewater treatment plants (WWTP) refer to discharges that come from the main towns (urban/rural areas) from these four counties, after passing through a wastewater treatment facility, while municipalities refer to town/localities or other administrative activities (hospitals, high schools, etc) within the basin that discharge wastewater directly into natural water bodies, without any treatment. With very few exceptions, most of the wastewater treatment plants within the Prut river basin are outdated as in infrastructure presents very poor performance in terms of removal efficiencies (Barjoveanu et al 2010).

The analyzed industries for assessing the pollution with detergents cover a wide range of activities (building materials and equipments, metallurgic industry, thermal energy production and distribution, furniture industry, food industry, beverage industry, pharmaceuticals, textile industry, supermarkets) that discharge "pre-" or completely untreated effluents with various compositions in the natural water bodies. The "services" category of wastewaters is also relevant within Prut catchment by the detergents loads discharged especially from the waste management sites and the vehicles maintenance and services.

In Table 2, a classification of the total number of wastewater discharges exceeding the MAC by activity types and by county, based on the 2007 yearly average concentrations of detergents is presented. Although in the Prut river basin agricultural activities and food processing industries are well developed, our assessment includes only 3 such activities because of the limited available data.

<table>
<thead>
<tr>
<th>No. County</th>
<th>No. of wastewater discharging units analyzed/ with MAC exceedences*</th>
<th>WWTP</th>
<th>Municipalities</th>
<th>Industry</th>
<th>Services</th>
<th>Agricultural and zootechnical activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Botosani</td>
<td>27/17</td>
<td>8/6</td>
<td>12/10</td>
<td>5/0</td>
<td>2/1</td>
<td>-</td>
</tr>
<tr>
<td>2. Iasi</td>
<td>31/15</td>
<td>7/3</td>
<td>7/6</td>
<td>13/3</td>
<td>2/1</td>
<td>2/2</td>
</tr>
<tr>
<td>3. Vaslui</td>
<td>39/16</td>
<td>6/3</td>
<td>12/7</td>
<td>13/1</td>
<td>8/5</td>
<td>-</td>
</tr>
<tr>
<td>4. Galati</td>
<td>36/16</td>
<td>6/5</td>
<td>12/7</td>
<td>6/1</td>
<td>11/3</td>
<td>1/0</td>
</tr>
</tbody>
</table>

*the number of wastewater discharging units with exceedences of MAC have been marked with bold.

**Results and Discussion.** The integrated environmental impact and risk assessment method was applied to quantify the environmental impact and associated risk for the wastewater discharging agents in Prut catchments considering the detergents loads, using the yearly average values of this indicator for various types of wastewaters as presented in Table 2. The probabilities of occurrence of these impacts were calculated with the formula given by Eq. (5), as a frequency of discharge events that overcome 70% of MAC, over a data series that covered one year (2007). It was possible to compare the impacts and associated risks for each location and for every impact component, but due to the large
number of analyzed locations, the results were analyzed based on pollutant categories. Thus, initially the yearly average concentrations were regarded as events with specific correlated probabilities, as presented in the next figure (Fig. 3).

![Figure 3](image)

**Figure 3.** The correlation between detergents concentrations and MAC exceedence probabilities.

It may be observed that, even if the number of the analyzed organizations was almost the same, Galati County, being located in the most downstream side of the Prut River, presents the lowest values for detergents concentrations in wastewater discharges, but with high probabilities. Iasi and Botosani counties present a constant range of detergents concentrations, but the difference between these two counties is given by the distribution of the impacts magnitude at several locations. In Iasi County there are more locations where the MAC value was slightly exceeded, comparing with Botosani County.

Fig. 4 presents the results of the integrated quantification of impacts and associated risks induced by the wastewater discharges from industrial activities, municipalities, services from four different counties considering the detergents concentrations. These graphs show a comparison of the impacts and associated risks of these effluents discharged in different sectors of the Prut River and its tributaries, and it may be observed that the highest impacts and risks are caused by Vaslui County, followed by Botosani and Iasi counties, while the lowest impacts and risks are induced by Galati County.
Figure 4. Integrated quantification of environmental impacts and associated risks for each analyzed county.

A different manner for approaching the results interpretation (presented in Fig. 5) was a correlation of the highest environmental impacts and risks with their wastewater discharges flows, revealing that the low values for environmental impacts and risks for Galati County obtained in the previous analysis could be explained by high values of the wastewater discharges flows by the most significant polluters from this county, fact that could be assigned to the dilution process.

The integrated methodology allows a comparison of the impacts and risks structures based on effluents types from the analyzed counties, as presented in Fig. 6. It may be observed that the distribution of impacts and risks indicator is fairly uniform. There are two exceptions: the municipalities from Galati and Vaslui counties and industrial activities from Iasi and Galati counties. This is probably caused by the different effluent characteristics of the untreated or pre-treated effluents. On the other side, it may be observed that the dominant contribution of the analyzed wastewater discharging units is assigned to the industrial and services’ activities from Iasi and the municipalities’ wastewater discharges from Botosani County. In Galati county insignificant impacts, but high associated risks are reported, this means that measures for pollution prevention should be considered for the industrial discharging units.
Figure 5. The highest environmental impacts and risk values and the associated discharges flows.

Figure 6. Environmental impacts and risk contribution by activity type.
Conclusions. This study performed a critical quantification of environmental impact and associated risks induced into natural water bodies (tributaries of the Prut River), by different categories of wastewater effluents. The assessment has taken into consideration 5 types of activities: municipalities, WWTP, industrial and services from four Romanian counties (Botosani, Iasi, Vaslui and Galati). The integrated impact and risk assessment is based on a methodology that was adapted so as to allow the determination of impacts and risks of wastewater pollution sources upon one environmental component (surface waters) based on a single quality indicator – the detergents concentration.

The results have shown that all of the analyzed units that discharge wastewaters polluted with detergents present very high risks values for the surface waters. The highest contribution of the environmental impacts and risks onto surface water is in Vaslui County and Galati County (located in the most downstream side of the Prut River). This situation is given by the detergents concentrations in wastewater discharges, as well as by the high probabilities of exceedences occurrence, indicating poor wastewater treatment performance. In Galati County, the industrial activities reported insignificant impact, but high associated risks, this meaning that measures for pollution prevention should be considered for the industrial discharging units.

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