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Results of the monitoring program in the Lower Danube River System in relation with Yugoslavian conflict

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Abstract
During and after the last year's Yugoslavian conflict the Romanian government has implemented a complex monitoring program in order to evaluate the effects of the conflict in the Lower Danube River System. The site organization included the Lower Danube river and floodplain, the Danube Delta, and the Black Sea coast. The analyzed stable contaminants were heavy metals, chlorinated organic pollutants and heavy hydrocarbons. The most sensitive system was the Iron Gate 1 lake, showing high values of stable contaminant and short life chemicals in the water column especially during April 1999. An important increase in stable pollutants concentration took place in the Danube's sediments, compared to a reference (before war) period. In the floodplain, a general decreasing gradient of pollutants from upstream to downstream was found, overlaid by local gradients related to succesional aspects. In the Danube Delta, the contamination was related to the hydroconnectivity gradients. Planctonic and benthic communities have shown some peculiar changes in the Danube Delta lakes compared to the reference period. On the Black Sea coast a contamination with oil occurred in May and June 1999. An important increase of the heavy metals and hydrocarbons concentration occurred in the top layer of sediments, especially in the areas located near Danube mouths.

Introduction
The Lower Danube River System (LDRS, figure 1) has worked until late 60's this century and still works, in spite of many deep changes occurred in the last decades, as the key component of the second largest (2857 km length) river in Europe, serving as buffer system between the river catchment and the sea, and is also important footprint for the economies of the riverine countries: Romania, Yugoslavia, Bulgaria, Republic of Moldavia and Ukraine (1).

Sustainable management of LDRS requires an operational interface (Decision Support System - DSS) enabling us to balance the spatio-temporal relationships and the mass and energy exchanges between the natural capital (major part in LDRS structure) and the socio-economic systems (2). Key components of any coherent DSS are the knowledge and data generation subsystems, and the complementary specific information subsystems (SIS) dealing with specific categories of natural capital and socio-economic components (3,4), such as LDRS. A SIS should include information concerning mechanisms and processes of
structural and functional dynamics of the system, and describing its productive and carrying capacity, together with data showing the variability of the key state variables and driving forces (5). Different research institutes from Romania in cooperation with research institutes from other riparian countries are involved in the Applied Research Projects under the Danube Environment Program (1), as part of the knowledge generation subsystem, and a network of governmental institutes is involved in the data generation (monitoring) activity.

The Yugoslavian conflict from spring 1999 acted as a potentially important driving force on LDRS, and raised the need for assessing its effects (6). Consequently, during and after the Yugoslavian of the last year conflict the Romanian government has implemented a complex monitoring program (7) in order to provide the needed dat for LDRS SIS. The institutional infrastructure included four institutes, three with main responsibilities in data generation (ICIM, INDD, and IRCM, acronyms as in authors addresses), and one with main responsibilities in knowledge generation and human resources formation (UB-DES). It was thus recognized that the acute problems related to the conflict provide an opportunity for critically analyzing the structure of current LDRS' SIS, for optimizing the monitoring system, and for differentiating new research directions.

This paper focus on the assessment of the ecotoxicological effects of the conflict based on the current SIS for LDRS, presents results concerning the short term effects, discuss these effects in the context of other impacts occurred in LDRS, and makes recommendations for an improved design of the SIS and DSS.

The study of the short term effects was structured by two hypotheses:
1. The concentrations of toxic pollutants have increased in LDRS after the conflict.
2. The structure of planktonic and benthic communities has changed after the conflict.

Methods
Hypotheses 1
Sampling of abiotic (water, soil/sediment) and biotic (fishes, benthic fauna, other compartments specific to the floodplain – as described in 8) was done at 91 locations (most of which are presented in figure 1) grouped in four impact areas depending on their distance from conflict zone, as follows:
- 8 stations on the Danube in impact area 1 (Iron Gates lakes, km 1080 – km 840)
- 22 stations on the Danube in impact area 2 (upstream floodplain, inner Danube Delta, and downstream floodplain, km 840 – km 78)
- 11 riparian systems in impact area 2 (each one with 3-4 stations on the transversal gradient)
- 26 stations in impact area 3 (Core Danube Delta, and Razelm – Sinoie lagoon)
- 22 stations in impact area 4 (continental plateau of N-V Black, 8 transects from N to S with stations on the depth gradient).

Sampling was performed between April and August 1999. Sampling and analytical methods were specific to each compartment and were those used in the Trans-National Monitoring Network (Standard Operation Procedures; 9), including all precautions specific to trace analyses. Data quality and comparability was ensured by intercalibration between partners, some of them being included in international intercalibration programs (9). Analyzed substances included heavy metals (Zn, Cu, Cr, Pb, Cd, and Ni), organochloric compounds (pesticides and PCBs), polyaromatic hydrocarbons (PAHs), and total hydrocarbons (only in water and sediment). During the conflict were also analyzed short-lived substances (dichloretan, chloroform) in water samples from impact area 1.

Hypotheses 2
Planktonic and benthic communities were analyzed in the Danube River (9 stations) and Danube Delta (18 lakes). Comparison between investigated ecosystems and with reference period was performed using as indicators species richness, Shannon diversity, and number and biomass abundances of selected taxons.
Fig. 1 Position of Lower Danube River System in the Danube Basin, and location of its major hidrogeomorphic units (grey boxes, from 1 to 9). Squares shows the position of the sampling points.
Results

Hypotheses 1

The most affected by conflict was Iron Gate 1 lake (impact area 1), especially because of pollution with heavy metals and stable organic pollutants (PCBs, and PAHs). On an annual average base heavy metals concentrations in water have increased 2-20 times in water compared to the reference values (before conflict), and on a short time bases up to 60 times. As an extreme example, Pb has increased from 1.4 ppb (January 1999) to 81 ppb (July 1999). Highest concentrations were recorded for all other metals in April 1999. Concentrations of metals in water were higher than acceptable ones under Romanian legislation (table 1). Concentrations of metals in sediments were also higher than reference data (table 2). Acceptable Romanian limits for sediment (Cd 3 ppm, Zn 300 ppm, on a dry weight bases; other analyzed metals of ecotoxicological interest not included – Ord. of Ministry of Environment 756/1997) were exceeded. PAHs concentrations in sediments increased 75-170 times in 1999 compared to average of 1998. Compared to data from 1992 (10), PCBs concentration in sediments were 100-400 times higher in 1999.

<table>
<thead>
<tr>
<th>Impact area</th>
<th>Time period</th>
<th>Zn</th>
<th>Cu</th>
<th>Cr</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1996-98</td>
<td>19-96</td>
<td>10-26</td>
<td>8-17.6</td>
<td>0.2-22.4</td>
<td>4.3-55.8</td>
</tr>
<tr>
<td></td>
<td>1999 Apr-Jul</td>
<td>38.5-1155</td>
<td>8.2-74.6</td>
<td>23.2-78.7</td>
<td>1.1-5.6</td>
<td>16-72</td>
</tr>
<tr>
<td></td>
<td>Aug 1999</td>
<td>20-33</td>
<td>5.4-26.8</td>
<td>8.3-15.9</td>
<td>0.2-3.4</td>
<td>14.5-21.1</td>
</tr>
<tr>
<td>2</td>
<td>1996-98</td>
<td>22-206</td>
<td>11.5-32.5</td>
<td>7.5-45</td>
<td>0.5-9.4</td>
<td>8.7-40</td>
</tr>
<tr>
<td></td>
<td>1999 Apr-Jul</td>
<td>20-72.7</td>
<td>10.5-53</td>
<td>8.9-82</td>
<td>0.25-10.4</td>
<td>7.4-62.8</td>
</tr>
<tr>
<td></td>
<td>Aug 1999</td>
<td>11-77</td>
<td>19-32.3</td>
<td>7.9-25.1</td>
<td>0.8-2.7</td>
<td>11.4-26.5</td>
</tr>
<tr>
<td>Admissible conc. (STAS 4708-1988)</td>
<td>30</td>
<td>50</td>
<td>50</td>
<td>3</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 1 Metals distribution in Danube water (range, ppb) over the period of investigation (Apr.-Aug. 1999) in the first two impact areas, compared with the reference period (1996-1998).

<table>
<thead>
<tr>
<th>Impact area</th>
<th>Time period</th>
<th>Zn</th>
<th>Cu</th>
<th>Cr</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1997</td>
<td>58</td>
<td>38</td>
<td>26</td>
<td>0.7</td>
<td>32.4</td>
</tr>
<tr>
<td></td>
<td>1999 Apr-Jul</td>
<td>122-47</td>
<td>72-144</td>
<td>64-114</td>
<td>2-8.5</td>
<td>35.5-153</td>
</tr>
<tr>
<td></td>
<td>Aug 1999</td>
<td>162-346</td>
<td>61-74</td>
<td>69-77</td>
<td>2.3-3.3</td>
<td>19.5-137</td>
</tr>
<tr>
<td>2</td>
<td>1997-98</td>
<td>46.5-299</td>
<td>42-56</td>
<td>22-76</td>
<td>0.3-4.7</td>
<td>13-37.5</td>
</tr>
<tr>
<td></td>
<td>1999 Apr-Jul</td>
<td>69-143</td>
<td>24-109</td>
<td>15-76</td>
<td>1.2-7.3</td>
<td>23-69.8</td>
</tr>
<tr>
<td></td>
<td>Aug 1999</td>
<td>55.8-235</td>
<td>28-102</td>
<td>34-100</td>
<td>1-4.5</td>
<td>18.2-69.8</td>
</tr>
<tr>
<td>1,2</td>
<td>1992 (10)</td>
<td>73-2000</td>
<td>19-290</td>
<td>35-310</td>
<td>0.35-4.7</td>
<td>23-420</td>
</tr>
</tbody>
</table>

Tab. 2 Metals distribution in Danube sediment (annual average or range, ppm).

In the second impact area the concentrations increase in Danube was not so obvious, especially in the case of sediments, but was still visible in the case of Cr, Cd, and Pb in water, with maximum values measured in April-May 1999 (table 1, 2). Most of the contaminated sediment seem to have been retained in Iron Gate lakes, even if some of them have reached the floodplain (see next paragraph). Organic pollutants did not show temporal or spatial patterns attributable to the conflict, excepting for total hydrocarbons, which showed high concentrations in water (up to 34.7 ppm) at the confluence with Timoc river (a river draining part of the conflict area). High concentrations of total hydrocarbons were also measured downstream Arges and Ialomita rivers (7-9 ppm), exceeding the acceptable concentrations under Romanian legislation (0.1 ppm).

Results concerning heavy metals in floodplain are presented elsewhere (8). We mention here only the main findings relevant to hypotheses 1. Heavy metals concentrations in new deposited sediment decreased from upstream to downstream Danube reaches, but did not show an increase compared to reference data (however, the reference data were limited to
few floodplain landscapes). Transversal gradients of concentrations in sediment were also found. In some biotic compartments (fish species locally migrating between Danube river and floodplain) an increase of contamination with metals took place (not statistically tested due to lack of raw reference data), in other cases there was a decrease or a species and metal dependent variation. Maximum admissible concentrations in fish (Zn 50 ppm, Cu 5 ppm, Cd 0.1 ppm, Pb 0.5 ppm on a fresh weight bases; Ord. of Health Ministry 975/1998) were exceeded. Reference data for organic pollutants were not available, and consequently no conclusions can be drawn. It is worth noticing that organochloric compounds had difficult to interpret distribution pattern in new deposited sediment along the upstream – downstream gradient. PAHs had maximum values (up to 68 ppm d.w.) in floodplain landscapes located at the confluence of Danube with Jiu river, a highly polluted one, and their concentration decreased in landscapes located more to downstream.

In the Danube Delta lakes and Razelm-Sinoie Lagoon no metal concentration increase was found compared to the reference period, excepting for some lakes directly connected to the Danube which had a higher average metal concentration in water in 1999 compared to 1998. Highest metal concentration in water during 1999 were found in April-May in all lakes. Organic pollutants did not show an increase in water or sediments compared to the reference period. No reference data were available for biotic compartments.

On the Black Sea Coast (Southern Romanian part) a contamination with oil occurred in May and June 1999, which cannot be explained by the conflict, as it was not noticed in the Delta. However, at the Danube mouths an important increase in metals and total hydrocarbons in water and sediments occurred. Total hydrocarbons increased in sea water 1.36 times at Danube mouths compared to the reference period (1995-1998), but 2.5 times in southern littoral waters (far from Danube mouths). Heavy metals increased on a short time bases 2.5-6.3 times compared to the reference period, with maximum increase in the case of Pb (up to 50.9 ppb), and on an annual average base 1.1 - 1.7 times, with maximum increase for Cd. In sediments the metal concentration increase on a short time base ranged between 1.34 and 1.69 times, with maximum increase for Cd, and on a annual average base between 1.1 and 1.72 with maximum increase for Ni.

The reported concentration increases (for all impact areas, excepting the floodplain) could not be tested for statistical significance, because average composite samples were analyzed for the characterization of both reference and current state.

Hypotheses 2
No significant changes occurred in the planktonic and benthic communities of the Danube River and of the Danube Delta lakes, excepting for zooplankton in Danube Delta lakes. Compared to 1998, in 1999 the zooplankton species richness decreased to less than half, and the biomass was 3-10 times lower (depending on lake). However, as no increase in contamination occurred in Delta lakes (see hypotheses 1) and no changes were remarked in impact area 1 (where a contamination increase occurred), these changes have probably other causes than the conflict, which clarification requires further investigations.

Discussion, Conclusion, Recommendations
Despite the lack of statistical tests, we consider that there are important arguments for considering the contamination increase of LDRS as real and attributable to the conflict in the case of impact area 1. For other areas further investigations are necessary in order to sustain the above statement. In. On the other hand, the evaluation of the ecotoxicological effects should be performed in the context of other changes of LDRS. There are remarkable quantitative accounts of the structural and qualitative changes occurred, mainly in the last 3-4 decades, in the major categories of ecosystems of the LDRS (11). The main processes affecting the physical and chemical characteristics of the water systems (water quality) belonging to the LDRS, were the eutrophication and water salinity transitions (11). If the first
process has a general relevance for the entire LDRS, including the North-Western Coast of the Black Sea, the second one is specific for the Razim-Sinoe lagoon system. Pollution with heavy-metals, pesticides and other pollutants accompanied these changes of the water quality at the LDWS scale, but by the date of the conflict pollution with ecotoxicologically relevant contaminants did not represent a major problem compared to structural changes and eutrophication (12). The arising question is whether the observed increase in contamination will have significant long-term effects on the functioning of LDRS. Long term and large distance effects could follow at the LDRS scale taking into consideration the ability of aquatic and riparian communities to multiply the flow density of metals (13, 14). A definite answer can be obtained only through long-term research and monitoring of the system.

In this context, we would like to mention that in order to improve the data and knowledge quality, in last years have started to be developed both conceptual frame and methodology to establish, according with the diversity of ecological structure at the national and macroregional scale, long term ecological research and monitoring programs. Most East-European countries develop their own network of sites for long term studies (2) as part of the International Long Term Ecological Research (ILTER) network. Three local landscapes from LDRS have been proposed to be included in the Romanian network (15): Danube Delta Biosphere Reserve, Small Island of Braila (part of the Inner Danube Delta), and Ciuperceni wetlands (part of upstream floodplain).

Specific directions that we recommend to be followed for better understanding of the ecotoxicological effects are:

*At the level of the data generation subsystem*
- the improving of the current monitoring systems by i) extending the number of analyzed compartments in order to include biological ones such as fishes, ii) extending the number of analyzed parameters in order to include the chemicals for which no reference data were available iii) adapting the sampling program at least in the case of several stations within each impact area in order to have replicate data and allow statistical tests for differences between averages at different time periods.
- the design and application of an integrated monitoring in ILTER included sites
- enhancement of the co-operation between the institutes involved in both monitoring and research (7)

*At the level of knowledge generation subsystem*
- the following research priorities: i) assessing the retention time of ecotoxicologically important pollutants in Danube floodplain and Delta ii) assessing the relative importance of this retention compared to the upstream-downstream flows (these two directions belongs to the field of landscape biogeochemistry, in which recent advancement of the studies at river system and catchment scale took place -16, 17), iii) application of GIS techniques for the identification of LDRS by specific and dynamic structural and functional models, and iv) development and improvement of mathematical modeling techniques for specific decision making and management issues, in particular for estimating the time retention of toxic pollutants, the effects of this retention of the structure of key trophodynamic modules, and the effects of this retention on other services provided by LDRS subsystems

*At the level of the specific information systems*
- designing and developing a GIS based formal structure of LDRS’ SIS (18)
- building the interface and guidelines for information system management

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