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Heavy metals in the Danube floodplain related to the Yugoslavian conflict

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Abstract
In the frame of a research program of the Lower Danube River System a specific sub-program was implemented in the Danube floodplain. Three aspects were considered: one related to the longitudinal gradients (upstream - downstream), another one to transversal (successional) gradients, and a third one to temporal differences (present vs. reference period). The sampling program characterized the large space and time scale specific to the investigated regional system, covering the landscape heterogeneity. An upstream to downstream decreasing gradient was found in the case of new deposited sediment. The longitudinal gradient was less clear when biotic compartments were considered. Higher heterogeneity in metals' distribution and the effects of local pollution played an important role in this case. At the local landscape scale, successional and hydroconnectivity gradients were related in a complex manner to metals concentration. The main driving force of this relation was the hydrological regime, controlling directly and indirectly the metals' behavior in abiotic compartments. Plants reflected to some extent these differences, whereas animals with relatively high mobility did not reflect them. Compared to the available reference data, it was observed that in some compartments (fish) an increase of contamination took place, in other cases there was a decrease or a species and metal dependent variation.

Introduction
The Lower Danube River System (LDRS) includes the river stretch of 1080 km, between Black Sea and the upstream part of Iron Gate I man made reservoir and the associated floodplains, inner and coastal deltas. LDRS is a regional complex of ecosystems (landscape). The floodplain consists of riparian and insular local landscapes (1). The biogeochemical cycling of elements in local landscapes includes three types of processes (2): within ecosystem cycling, flows between the ecosystems of a landscape, and flows between landscapes. It is necessary to study the biogeochemical flows between as well within ecosystems to obtain insights into the effects of interactions among ecosystems for their biogeochemical functioning, and for the functioning of the landscape as a whole (3). Biogeochemical studies of fluvial floodplains from this perspective are relatively few (e.g. 4). However, from an applied point of view, the capacity of fluvial wetlands to improve water quality by removing nutrients, trace metals, and sediments from hydrological flows is widely recognized (5,6). Most agree that riparian wetlands are important in maintaining water quality on a short time bases, but there is no consensus about their effectiveness over longer periods of time (7). Much of what is known about the retention role of wetlands is based on changes in concentrations above and below river reaches containing wetlands (8), and there is a paucity of long term data on the fate of pollutants in wetlands (9).

Prior to the Yugoslavian conflict, the data collected during two well-designed expeditions carried out by the Cousteau team (10) and by Dutch and Bulgarian experts (11, 12) have proved and confirmed that, in spite of several hot spots associated with industrial sources and discharges of main tributaries, there was still no severe contamination of the Danube river at abiotic level (13). Studies of metals cycling at ecosystem scale (14) and, more recently, at local landscape scale (15) have been implemented in the Danube floodplain and coastal Delta, but evaluations of the metals retention capacity of wetlands have not been reported by now.
Here we present results concerning the role of Danube floodplain in the cycling of metals. The paper is structured by the following hypotheses:
1. Zn, Cu, Cr, Cd, and Pb concentrations decreases in the floodplain from upstream to downstream,
2. There is a net retention of metals in the floodplain on an annual base
3. Within a local landscape the concentrations are related to successional gradients.
The Yugoslavian conflict that occurred during the last part of the investigations raised the need for assessing its effects on LDRS (16, 17). In this context, we considered a fourth hypotheses, namely:
4. The concentrations have increased in the floodplain after the conflict.
The conceptual model adopted for studying the biogeochemistry and effects of metals in LDRS is presented in figure 1.

Fig. 1 Conceptual framework for the study of biogeochemistry and effects of metals in LDRS. Hypotheses 1 refer to the gradient between landscape 1 and n., hypotheses 2 refer to the net retention of metals in a landscape, hypotheses 3 refer to the mechanisms of the metals retention, and hypotheses 4 refer to the differences between reference state (before Yugoslavian conflict) and current state of LDRS floodplain. Legend: SES = socio-economic system, continuous black arrows = metal flows, dashed black arrows = effects, white arrow = state transition.

Methods
Hypotheses 1
Eleven floodplain landscapes located between km 100 and km 790 of the Danube river were sampled in summer 1999 for abiotic and biotic compartments (9 replicates minimum) of their ecosystems (levees, internal depressions, marshes, and shallow lakes). Sampling was done from different ecosystem types located on levees and in depressions (e.g. natural / planted forests, grasslands). Special considerations was given to the samples expected to reflect a short time increase of metals concentration in flooding water: new deposited sediment, willow adventive roots, amphibian juveniles, fish.

Hypotheses 2
In order to estimate the metal budget of a floodplain landscape the research was focused on Fundu Mare Island. This is a 21.11 km² island remained under natural flooding regimen located between km 175 and 183. Landscape structure and ecosystems surfaces used to estimate metals fluxes at the island scale are presented in (18). We considered the following fluxes:
- input and output by flooding water in dissolved and abiotic particulate form. These fluxes were estimated in a two years study (1996-97) Annual water mass balance was performed based on hydrological conditions for inflow, outflow, precipitation and evapotranspiration as described in (18). Sediment input was estimated by measuring sedimentation rates after the hydrological events. Sediment output was indirectly estimated by the difference between sediment load in flooding water and sedimentation (erosion was not estimated). Dissolved metals in the flooding water was measured on a monthly bases, and total metals in new deposited sediment after each
hydrological event.

- output by wood and fish harvesting. Annual wood and fish biomass export on a surface unit are
general estimations for the Danube floodplain ecosystems (19). Metals concentrations in wood
were not directly estimated, but through analyses of branches and twigs fallen in litter traps
(sampling in 1996-1997) Metals concentrations in fish were obtained separately for muscle and
liver (sampling in 1999, see hypotheses 4) and average body concentration was calculated.
Metals input by biotic compartments and natural biotic metals export were not estimated.

Hypotheses 3

A transect of 800 m length was established in the Fundu Mare Island and studied in 1996-1997. The
transect consisted of five stations, starting from the shore (S), crossing a mature forest located on a
high levee (L), a natural forest from the nearby depression (D), a marsh (M1, M2), and ending near a
lake (Lk1). Another transect in the same island started at the Danube, went along a channel (C1, C2)
and crossed five lakes (Lk 1 to 5, each one with two or three stations) connected by short channels.
Top (8cm) soil/sediment was sampled monthly in the Danube floodplain in 5 to 9 replicates,
depending on the ecosystem type. Plant species (20), terrestrial invertebrates (carabids, Ciubuc,
unpublished data) were sampled monthly / fortnightly during the growing season in the ecosystems
crossed by the first transect and identified to species level by specific methods. Dominant species
were analyzed for total metals in whole body (carabids) or aboveground parts (plants).

Hypotheses 4

Metals concentrations in compartments sampled before Yugoslavian conflict (defined as reference
state) were compared with concentrations in same compartments sampled after the conflict (current
state). From the abiotic compartments we used new deposited sediment. Sampling of floodplain water
during or immediately after the conflict was not performed. The biological compartments were those
expected to rapidly reflect (within several months) changes in the quality of Danube water, namely
young individuals of fishes (Abramis brama, Cyprinus carpio, Lucioperca lucioperca, Esox lucius) and
amphibian juveniles (Rana sp.). Annual plants (Xanthium sp. young individuals) and carabids
(Harpalus (pseudophonus) rufipes) were also included in order to see whether the potentially
contaminated new deposited sediment influences their concentration of metals on a short time bases.
The sampling program for characterizing the current state was common with hypotheses 1. Because
reference data for fishes were not available from our studies, we used those provided by Wachs (21).
Our reference data were limited to Fundu Mare island and several neighboring landscapes, and were
obtained in the frame of the studies dealing with hypotheses 2 and 3.

Analytical procedures

Water samples filtered glasfibre were analyzed for the dissolved metals content after 0.45 μm filtration
by graphite atomic absorption spectrometry. Solid samples were analyzed for their total metal
concentration by wet digestions and furnace or graphite atomic absorption spectrometry. Details of
sampling methods and analytical procedures are presented elsewhere (15, 22). From the analyzed
metals here are presented Zn, Cu, Cr, Pb, and Cd. Concentrations are in ppm on a dry weight bases,
excepting for those in fish, which are given in ppm on a fresh weight bases, and for water (ppb).

Results

Hypotheses 1

Metals concentrations in new deposited sediment have shown in 1999 a decreasing longitudinal (km
800 to km 100) and transversal (marsh to levee) gradient for Zn (from 384 to 32, figure 2A), Cu (114-
10), Cr (114-10), and Cd (3.54-0.59), but not for Pb (which ranged between 9 and 87, with maximal
values in the 400-600 km river stretch). Concentrations in soil presented a smaller range of variation
than concentrations in new deposited sediment (Zn from 60 to 200, Cu 23-86, Cr 23-105, and Cd
0.50-2.48), excepting for Pb (5-96). Concentrations in marshes soil increased from upstream to
downstream, and in levees soil did not show clear variation trend. Concentrations in biotic samples
generally had patterns difficult to interpret. In figure 2B-D we present the most relevant cases. Zn and
Pb concentrations in Salix sp. adventive roots decreased from upstream to downstream. Amphibians
and certain plants species had highest metal concentrations just downstream of km 690.

Hypotheses 2

Figure 3 presents the estimated metal budget for Fundu Mare Islands. Total retention of the studied
metals is 29.5855/year. These results must be taken cautiously, because erosion (presumably an
important export pathway, 23) was not estimated. Important differences occur between metals
(table1) as well as between metal forms. The retention is due manly to sedimentation during floods,
and to a much smaller extent to wood and fish harvesting. There seems to take place a net export of Zn, Cr, and Cd in dissolved forms, which, from ecotoxicological point of view, is a very important aspect.

Fig. 2 A Longitudinal and transversal distribution patterns of Zn in new deposited sediment in Danube floodplain in 1999. The diagram represents projection of the regression surface fitted to the raw data. (x axis – km from Danube mouths; y axis – distance from Danube shore; white to black squares – increasing concentration of metal; the arrow shows the direction of concentration increase.

B, C, D Distribution of metals in amphibians (B) and plants (C, D, selected metals and species) from the Danube floodplain (current state) along the longitudinal gradient.

Tab. 1 Cumulated inputs, outputs, and the estimated retention rates of each metal (t/year and %).

<table>
<thead>
<tr>
<th>Metals dissolved</th>
<th>63.002 t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals in suspended sediment</td>
<td>31.246 t</td>
</tr>
<tr>
<td>Metals in biotic compartments</td>
<td>NE</td>
</tr>
<tr>
<td><strong>TOTAL INPUTS:</strong> 94.248 t</td>
<td></td>
</tr>
</tbody>
</table>

| 55.58 t, 6-8 hours, all ecosystems |
| 3.78 t, 10-14 days, all ecosystems |
| 3.76 t, 3-5 months, depression, marsh, lakes |
| 1.08 t, 6 hours = 14 days, all ecosystems |
| NE, erosion, > 1 year, shore |
| 0.2 t, > 1 year, wood harvesting, levees |
| 0.02 t, > 1 year, wood harvesting, depressions |
| 0.0011 t, 3-6 months, fish harvesting, lakes |
| **TOTAL OUTPUTS:** 64.663 t |

Fig. 3 Metals budget (all metals, t/year) in Fundu Mare Island. Time scale of metals retention and the involved ecosystems are also indicated. **Legend:** NE = not estimated.
Hypotheses 3
Annual average concentrations of Zn, Pb, and Cu in soil increased along the successional gradient starting in the shallow lakes and ending with the mature forest located on levee (figure 4; Cd not included because concentrations were near the detection limit). Cr concentrations in soil/sediment increased from the ecosystems of the mentioned successional gradient towards the island channel, Danube and shore ecosystems. Concentration range is reported elsewhere (15, 24). Depressions ecosystem had the most important role in metals retention, despite their relatively small surface in the landscape (figure 4B). Central lakes (Lk2, 3) had smaller metal concentration in sediment than extreme ones (located at the beginning and the end of the hydroconnectivity gradient), a pattern which is different from what was found along Danube Delta hydroconnectivity gradients (smallest concentrations at the end of the gradient, 25). Metals in plants did not present a consistent trend along the successional gradient excepting for Cu, whose average concentrations in dominant plant species decreased towards the levee (figure 4A). Concentrations in carabids species sampled in levee, depression and marsh ecosystems during the not-flooded period did not significantly differ from one ecosystem to another (annual average of Zn 101, Cu 34, Cd 2.45, Pb, 14.45, Cr not determined).

Fig. 4 PCA diagram obtained using the annual average concentrations (factors 1 and 2 with eigenvalues and explained variance indicated in axis titles) showing metals distribution in the ecosystems soil of Fundu Mare island (arrows show the direction of increasing metal concentration), and distribution graphs of three other parameters not included in the analyses - metals in vegetation (A - standardized average concentrations), sedimentation, and metals inputs by sedimentation (B - per cent of total input). Legend: S = shore, L = levee, D = depression, M1, 2 = marshes, Lk1-5 = lakes, C1,2 = channels; increasing code number of station indicates increasing distance from Danube.

Hypotheses 4
Fishes sampled in 1999 had higher metal concentrations (table 2) than in the reference system (21). Significance level of the differences could not be assessed to lack of raw reference data. Amphibian juveniles did not show any significant difference between current and reference state, excepting for Cd (higher concentrations in reference state, table 2). Zn, Cu, and Cr concentrations in new deposited sediment were higher in the reference state than in current state (214.75 vs. 99.62 Zn, 130.72 vs. 42.85 Cu, and 141.81 vs. 36.24 Cr). Cu concentrations in Xanthium sp. were higher in current state (16.25 vs. 2.71). Cu and Cd concentrations in H. rufipes were higher in reference state (26.15 vs. 13.97 Cu, and 1.81 vs. 0.77 Cd), but Pb concentrations were higher in current state (24.33 vs. 5.40). All other average metals concentrations in the analyzed compartments did not significantly differ in current state compared to reference state.
Tab. 2 Average and range of metal concentrations in fish species (n = 60, Danube river), and amphibian juveniles (n = 9, Fundu Mare island) in reference (before conflict, RS) and current (after conflict, CS) system (* = significant difference RS vs. CS, Mann-Whitney test; NA = not available).

<table>
<thead>
<tr>
<th></th>
<th>Fish (four species, ppm f.w.)</th>
<th>Amphibian juveniles (Rana sp., ppm d.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Av.</td>
<td>Min</td>
</tr>
<tr>
<td>Zn</td>
<td>13.00</td>
<td>5.91</td>
</tr>
<tr>
<td>Cu</td>
<td>0.76</td>
<td>0.34</td>
</tr>
<tr>
<td>Cr</td>
<td>0.17</td>
<td>0.06</td>
</tr>
<tr>
<td>Cd</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>0.13</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Discussion and conclusions

The distribution pattern of metals in new deposited sediment suggests the presence of strong sources of pollution upstream of the investigated area, which might coincide with those occurring during the conflict. The decrease of metal concentration in *Salix* sp. adventive roots is consistent with the decreasing concentration gradient in Danube water at the conflict time (16). Willow adventive roots develop during long floods, coinciding in 1999 with the conflict. Km 690, downstream of which are located the landscapes with high metal concentrations in plants and amphibians is the point of Danube confluence with Jiu river, a highly polluted one. Hypotheses 1 is generally not confirmed, excepting for deposited sediment in 1999. Additional research is needed to check this pattern in normal (without conflict pollution sources) conditions.

Our metal budget underlines the important role of riparian landscapes as mechanical filters, which is in agreement with published literature (e.g. 23). Saturation of wetlands with respect to metal retention, and net export of dissolved metals was previously found in the treatment wetlands (26). Zn, Cr and Cd export is plausible because of their higher mobility than Pb and Cu under low redox conditions (27). Hypotheses 2 is confirmed in this particular case (Fundu Mare island), but additional research is needed in order to assess the export by erosion and check the possibility of extrapolating the results to other floodplain landscapes.

Increasing total concentrations in soil (the major storage compartment for metals) along the successional gradients was previously found in the case of nutrients (28). Undisturbed ecosystems are thought to change through succession from open systems with high flow-through compared to storage, to closed systems with large stores compared to inputs and outputs (29). The major natural driving force of these changes in the Danube floodplain is hydrological regimens (30), which seems to control also metals cycling at landscape level by facilitating inputs, outputs, and, at ecosystem level, by redox control of metals speciation. There are arguments in favor of hypotheses 3, but future research is needed to elucidate in detail mechanisms of the observed pattern and to characterize metals distribution in other kinds of ecosystems located on levees and in depressions. Heterogeneity of metals distribution in levee ecosystems of a local landscape might be responsible for the lack of clear longitudinal metal distribution pattern in floodplain levees remarked at hypotheses 1.

The concentration increase found in fishes might be due to the pollution sources associated to the conflict, because dissolved metals are rapidly uptaken from water by fishes (30). However, due to the lack of reference data for the period just before the conflict, we can not definitely conclude that this increase is due to the conflict.

Acknowledgements


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