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Assessment of the contamination of riparian soil and vegetation by trace metals — A Danube River case study

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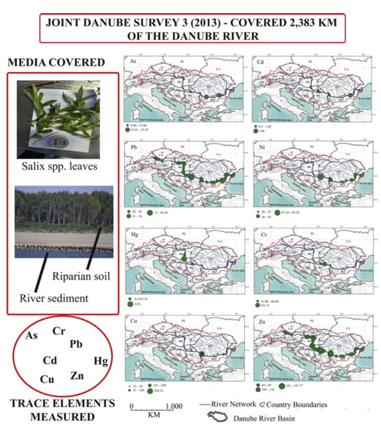
HIGHLIGHTS

- The effect of river ecosystem pollution on riparian soil and vegetation was studied.
- The study was on a large spatial scale, covering over 2386 km of the Danube River.
- A correlation between the metal content in sediment, soil and plants was found.
- The sediments and riparian soils are influenced by similar environmental factors.
- The accumulation of trace elements by riparian plant species is species-specific.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to assess the spatial distribution of arsenic and heavy metals (Cd, Cr, Cu Hg, Ni, Pb and Zn) in a riparian area influenced by periodical flooding along a considerable stretch of the Danube River. This screening was undertaken on soil and plant samples collected from 43 sites along 2386 km of the river, collected during the international Joint Danube Survey 3 expedition (ICPDR, 2015). In addition, data on the concentration of these elements in river sediment was used in order to describe the relationship between sediment, riparian soil and riparian plants. A significant positive correlation (Spearman r, for $p < 0.05$) was found for trace metal concentrations in river sediment and soil ($r = 0.817$). A significant correlation between soil and plants ($r = 0.438$) and sediment and plants ($r = 0.412$) was also found for trace metal concentrations. Elevated levels of Cd, Cr, Cu, and Ni were found at certain sites along the Serbian stretch, while elevated concentrations of Hg were also detected in Hungary, of Pb along the Romanian stretch and of As along the Bulgarian stretch (the Lower Danube). These results point to the presence of naturally-occurring metals derived from ore deposits in the Danube River Basin and anthropogenic metals, released by mining and processing of metal ores and other industrial facilities, which are responsible for the entry of metals such as Cu, Ni and Zn. Our results also indicated toxic Cd and Zn levels in plant

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samples, measured at the Hercegsznato site (Middle Danube, Hungary), which highlighted these elements as a potential limiting factor for riparian vegetation in that area. The distribution of the analysed elements in plant material also indicates the species-specific accumulation of trace metals. Based on our results, the Lower and Middle Danube were found to be more polluted in terms of the analysed elements.

1. Introduction

Water resources in Europe are affected by a complex mixture of stressors resulting from a range of drivers, including water scarcity, urban, industrial and agricultural land use, hydropower generation, and climate change (Hering et al., 2015; Navarro-Ortega et al., 2015). This is valid for water-dependent riparian ecosystems as well. As riverine pollution can cross national borders, continuous assessment of pollutants in water, sediments, and biota, as well as in riparian soils and vegetation is important as part of the wider picture. Several surveys have contributed to information on heavy metals in the Danube water, sediment and biota, e.g. the Environmental Programme for the Danube River Basin (1995–1996) and the Danube Regional Project Component 4.2 (2007). Consequently, chemical pollution from diffuse sources has been identified by current European legislation as one of the main stressors affecting the quality of rivers (EC, 2000). Despite strict government standards on environmental protection (air, water and soil), many sites along the Danube River are affected to varying degrees by pollution, especially in industrial and agricultural areas. These sources of pollution are diverse and the precise origin of the contaminants is often difficult to determine due to the multiple discharge points, e.g. the discharge of urban effluent, industrial effluent, mining excavated material, fertilizers and pesticides (Mikkelsen and Vesho, 2000). In addition, background geochemical loads can be considerable in regions where the parent rock layers contain hazardous and basin-specific pollutants such as heavy metals.

The ecosystems of a riparian zone are of particular interest for research, not only as ecotones (between aquatic and terrestrial types) with complex characteristics, but also as a source of accurate data for management. The mineral component of riparian soils originates mostly from river-deposited sediment, however during high waters there is the washout of organic litter from riparian sites by water (Mikkelsen and Vesho, 2000). This increases the heterogeneity of riparian soils by producing a bare soil surface in some areas. This phenomenon also increases plant diversity along the shore line by creating favourable conditions for the seeds of species that require a bare soil surface for germination (Bilby, 1988; Pusey and Arthington, 2003; Mikkelsen and Vesho, 2000; Steiger et al., 2005). The complexity of riparian ecosystems also makes them responsive to anthropogenic pressures, which is often hard to predict. Apart from influence of natural and anthropogenic stressors, these ecosystems are under the shared responsibility of different management units (e.g. water management, environmental management, agriculture, forestry, etc.), which complicates management practices. The Danube River Basin was considered to be one of the Earth's 200 most valuable ecoregions (Olson and Dinerstein, 1998), and it is listed among the world's top 10 rivers at risk (Wong et al., 2007). The Danube Delta is one of Europe's most important wetlands and was designated a Transboundary UNESCO World Heritage Site and a Man and Biosphere Reserve (IUCN, 1992; WWF, 1995).

Although the boundaries of a riparian ecosystem can be highly variable, in general they extend outwards from the river channel to the limits of flooding, and travel into the canopy of riverside vegetation (Sedell et al., 1991). Riparian zones are unique and dynamic systems because their size is directly proportional to water body size and site topography, e.g., steep slopes characteristic of small streams may limit the development of riparian vegetation, while aquatic systems with less extreme topography exhibit larger riparian boundaries (Bilby, 1988). Conversely, the influence of the riparian zone on the aquatic system decreases as water body size increases (Bilby, 1988; Agee, 1988). They can play a key role in the functioning of the aquatic ecosystem, affecting chemical, physical and biological processes (Naiman and Décamps, 1997; Pusey and Arthington, 2003). Vegetated riverine riparian areas influence chemical loads from diffuse industrial and agricultural sources (runoff) and reduce in-stream pollution during floods (Karr and Gorman, 1975; Kleiss et al., 1989). Riparian soil acts as an important sink for pollutants, especially heavy metals from river water or upland, by the process of adsorption and sedimentation (Zhang et al., 2011). In water ecosystems, soil is a complex, seasonally changing and dynamic component, thus representing an excellent media for monitoring heavy metal pollution because anthropogenic heavy metals are usually deposited in top soil.

The Danube is one of Europe's most important waterways. Along its course, it passes through nine countries: Germany, Austria, Slovakia, Hungary, Croatia, Serbia, Romania, Bulgaria, and Ukraine. Moreover, the Danube drains parts of Switzerland, Italy, Poland, the Czech Republic, Slovenia, Bosnia-Herzegovina, Albania, Montenegro, Moldova, and the Former Yugoslav Republic of Macedonia. Thus, the Danube River Basin (DRB) is considered to be the world's most international river basin, collecting water from the territories of 19 countries, and it forms an international border for eight of them. The DRB drains the areas of nine ecoregions (Illies, 1978). About 81 million people are connected by this complex hydrological system (Sommerwerk et al., 2010). The Danube flows through numerous industrial and urban centres and receives a significant amount of pollution due to the reception of urban and industrial waste, as well as agricultural land runoff (Schmid, 2004; Behrendt et al., 2005; Liška et al., 2008). Over the past 150 years, water quality has become a key issue for the Danube and the coastal zone of the Black Sea (Sommerwerk et al., 2009). Therefore, the adoption of the Convention on Cooperation for the Protection and Sustainable Use of the Danube River (Danube River Protection Convention) was driven by the strong intention of the Danube countries to intensify their water management cooperation in the field of water protection and water use.

With a view to obtaining a complex insight into the state of Danube water quality, surveys are carried out every six years in accordance with the river basin management planning period set out by the EU Water Framework Directive (WFD, Directive). The first Joint Danube Survey was carried out in 2001, the second in 2007, and the third in 2013. Comparable data on the entire course of the river has been provided, covering biological, chemical and bacteriological parameters. The JDS also introduced a comprehensive survey of hydromorphological parameters of the Danube using a single method. JDS3 was an international longitudinal survey that produced comparable and reliable information on water quality for the whole length of the Danube River, including the major tributaries on a short-term basis. The results of analysis of heavy metals in the surface water samples collected during JDS 1 and JDS 2 revealed metal concentrations above the set targets at only three sites (Hg at two sites downstream sites from Budapest, and Ni at the Timok-Danube confluence), whereas the concentrations of Cd, Cu, Ni, Zn and Pb were often elevated in sediments (Woitke et al., 2003; ICPDR, 2009), Appendix 1. Previous study (Liška et al., 2008) provided information on dispersal of pollutants in water, sediment, suspended solids and aquatic biota along the Danube, however comprehensive study on contamination and related processes in riparian area was not done for the navigable stretch (about 2400 km). The eight trace elements, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn, were selected for analysis during JDS1-JDS3 because they are on the current List of Priority Substances for the Danube River Basin, as agreed by the ICPDR (https://www.icpdr.org/main/issues/hazardous-substances). In this respect, the main objectives

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