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http://sarib.net/

INTRODUCTION

The Sava River (945 km) is the biggest tributary to the Danube River. The 95551 km^2 large catchment is extended over Slovenia, Croatia, Bosnia and Herzegovina and Serbia. In the development of the river basin management plan all countries are already collaborating under the International Commission for the Protection of the Danube River (ICPDR) guidance. Although the methodological bases for data collection have been reasonably unified, data on the ecological character of the river basin, inventory of pollution sources, dangerous substances, socio-economic parameters, cost and benefit implications are still lacking due to insufficient financing and recent warfare. Within the 6th FW EU project: Sava River Basin: Sustainable Use, Management and Protection of Resources (SARIB) specific tools based on combination of chemical analysis and biological effect methods are developed and validated for the estimation of the pollution of sediments and impact on aquatic biota. Geographical distribution of pollution is identified and historical trends defined. Integrated prediction model about the behaviour of hazardous chemical substances will be combined with the socio-economic prediction model to serve as a base for the elaboration of scenario, remediation measures and best practice techniques. For that purpose an expert data and information management system will be developed.

Pollution of sediments and water cycling processes

In order to assess the geographical distribution and historical trends in sediment contamination of the Sava River Basin, sediments were analysed in 20 selected sampling sites along the Sava River from its origin to its outfall into the Danube River. The extent of pollution was estimated by determination of the total element concentrations and by the identification of the most hazardous highly mobile element fractions and anthropogenic inputs of metals to sediments. For comparability of data to other river basins the sediment fraction < 63 μm was analysed. To asses the mobile metal fraction extraction in 0.11 mol L^{-1} acetic acid was performed, while anthropogenic inputs of elements were estimated on the basis of normalization data to aluminium concentration. According to the Water Framework Directive the following elements were investigated in sediments: cadmium, lead, nickel and mercury, as well as organotin compounds. Furthermore, copper, zinc, chromium and arsenic were also determined.
In addition, selected persistent organic pollutants (e.g. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides) were also determined in

sediments. The choice of pollutants followed the recommendations of the Water Framework Directive.
The geochemical dynamics of mineral weathering of the Sava watersheds using major elemental, stable isotope, and hydrogeochemical tracers was investigated in order to better understand hydrology, carbon and sulphur mass transport.

Availability and impact of pollutants on biota

Catchment sites for feral fish *European chub* (*Leuciscus cephalus*) selected at: 1) Otok Samoborski; 2) Sava in front of Jarun lake in Zagreb; 3) Oborovo; 4) Lukavec Posavski; 5) Jasenovac; 6) Košutarica. Two characteristic seasons selected to follow the impact of pollutants on the bioindicators, namely, spring and autumn, in two successive years, 2005 and 2006.

A database on health status of altogether 290 fish specimens exists. It includes bacteriological examination of gills, liver, spleen, kidney, ecto- and endoparasites, virusological examination and histological analysis of liver, kidney, spleen and intestine, including the bacteriological analysis of ambient water at the site of fish sampling.

Chronic exposure and effects of pollutants on *European chub* were assessed by the following biomarkers:

- metallothioneins (MT), as metal induced protein, in fish liver as detoxification organ related to metal exposure;
- metallothioneins (MT), as metal induced protein, in gills as a respiratory organ in direct contact with water and an important metal uptake route;
- cytosolic concentrations of metals that induce metallothionein synthesis (Zn, Cu, Cd) and additionally Fe and Mn;
- enzymatic activity EROD in fish liver inducible in response to organic pollutants PAHs, PCBs, dioxins and some pesticides;
- effect endpoints (AMES test) in fish liver;
- hydroxylated PAHs metabolites in fish bile.

Development and validation of specific tools

The use of potentiometric sensors, commercial and new ones, for determination of anionic and non-ionic surfactants in industrial effluents has been investigated. The determination was carried out on the modelled effluents formulations as well as on the real industrial effluents.
The potentriometric sensors served as end-point detector by potentiometric titration of low surfactant concentration levels (down to 10^{-5} mol dm^{-3} for anionic surfactants and 10^{-6} mol dm^{-3} for non-ionic surfactants). The results for anionic surfactants agree satisfactory with standard extraction-spectrophotometric MBAS method and are comparable with the results obtained using a commercially available surfactant electrode. Further investigation activities are directed toward increasing of the sensor sensitivity, extending of its linear response range, development of methods for surfactant pre-concentration in surface waters.

Integrated system for the management of the Sava River quality

The objective of the work was to determine the factors of: monitoring, controlling and application of bioremediation with the purpose of pollution prevention and environment protection. For this purpose different microbial cultures (individual, mixed) are used for application in processes of: a) biodegradation; b) nitrification; c) denitrification; d) phosphorous removal; and e) xenobiotic biodegradation. Each process is followed by determination of process factors.
Biodegradation of various wastewaters were confirmed in laboratory scale tests as discontinuous and continuous tests.

Data Base System

GIS platform concept and internet platform had been developed for the SARIB project in Sarajevo 2006. Thematic spatial data from The Sava River countries have been collected and put into GIS system. For the water quality data collected in the SARIB project relational data base has been developed. It is in the MS OFFICE ACCESS environment. The system has logical and spatial integrity and can be upgraded in any time needed with new codes or descriptors. The manual is produced.

Decision Support System

After the hot spots and major contaminants have been identified, a Decision Support System (DSS) is needed for the assessment and selection of applicable remediation technologies. DSS developed for the SARIB project:

- Enables environmental managers to identify and systematically compare information about innovative and conventional technologies to meet remediation goals
- Defines consistent, measurable indicators for key criteria that influence selection and deployment of technologies
- Provides documented, reproducible evaluation which can be updated as needed information becomes available
- Provides flexible, multicriteria optimization approach allowing tradeoffs among criteria on the basis of contaminant type and site-specific needs
- Helps focus dialogue between environmental managers and stakeholders, including regulators and policy makers

CONCLUSIONS – Pollution of sediments and water cycling processes

Among metals, Hg was found to be present in elevated concentrations in the sediments of the Sava River (concentrations in general ranged from 0.2 to 0.6 mg kg^{-1}). Results also indicated that the Sava River is moderately polluted with Cr and Ni in sampling site HE Moste in Slovenia (basin of the hydroelectric power plant) and in sampling sites in Croatia, BIH and

Serbia from Srbac up till Šabac. Normalization data to Al indicated the anthropogenic inputs of Cr and Ni in sediments. The origin of pollution with metals in sediments will be further investigated.
However, the data of the extraction in 0.11 mol L^{-1} acetic acid showed that the percentage of the easily soluble metal fraction of Cr and Ni were low (below 0.3% of total Cr and below 16% of total Ni, respectively). Analysis of the easily soluble concentrations of other elements were in general below 10%. Exceptions were Cd (30 – 50%) and Zn (5 – 40%). Despite high percentage of the easily soluble Cd content, these concentrations do not represent environmental hazard, since the total Cd concentrations were low.
Organotin analysis showed that the Sava River sediments are not polluted with butyltins, phenyltins or octyltins (the determined values were below LOD, in genral below 0.01 mg kg^{-1}) .
PAHs increases downstream Sava River and peaks around Brčko. Exceeded concentrations of persistent pesticide p,p-DDT were found in two locations (Galdovo: 2,562 ng g^{-1} and Košutarica (1,288 ng g^{-1}). Besides this chlorinated pesticide, HCB was determined in augmented values in two locations: Šabac (1,101 ng g^{-1}) and Beograd (90,823 ng g^{-1}), the later one was present in extremely high concentration. Analyses of PCBs showed no contamination of the Sava River sediments with these compounds.

We can observe differences, changing trends on natural (climate, precipitation, bedrock, soils, vegetation) and direct anthropogenic (land-use, industry, population, water and waste water management, agriculture) influences moving along the lower Sava until its confluence. The first results indicate that lower Sava watershed is not influenced only by weathering processes, but also by other effects mainly human activities which are reflected in the Ca^{2+}/Mg^{2+} ratio and $\delta^{13}C_{DIC}$ values. Further, biological and biochemical processes are probably more dominating than in the upper flow of the Sava driven by transport and transformation processes. Higher concentrations of NO_3^- ions are observed in Croatia reaching up to 7.39 mg/l which could indicate the influence of agricultural activities, while the highest concentrations of SO_4^{2-}, Na^+ and Cl^- ions were determined in the Bosna River the main tributary of the Sava River. Bosna seems to be the most polluted tributary of the Sava River. Therefore, more analysis will be performed on this river including the $\delta^{34}S_{SO4}$ measurements in order to determine the possible source of sulfate pollution.

CONCLUSIONS - Availability and impact of pollutants on biota

Database contains predominantly juvenile, 2 and 3 years old *European chub* specimens. Biological assessment of metal availability based on cytosolic metal concentrations in chub gills indicates to the elevated cytosolic Cd concentrations at Oborovo location. The same trend exists for metallothionein (MT) level and gills mass. In the gill cytosol, concentrations of Zn, Cu and Mn are kept at the defined level, irrespective of metal concentration in the ambient water. On the contrary, in the gill cytosol, concentrations of Fe and Cd are not regulated and reflect the available ambient concentrations of those metals.

In Sava River water total dissolved metal concentrations (filtered and acidified) were determined in order to define background concentrations of priority pollutants according to the Water Framework Directive and to compare with the environmental quality standards (EQS) for inland surface waters. For Cd, Pb and Ni the concentrations are significantly lower than the annual average EQS. Passive samplers for time-integrated metal accumulation (Diffusive Gradient in Thin films=DGT) were deployed in order to define bioavailable concentration of pollutants (Cd, Pb, Ni, Co, Cr(III), Cu, Zn, Fe, Mn). Deployment occurred over the extended period in autumn 2005 and spring 2006. Bioavailable metal concentrations estimated with passive samplers indicate that the majority of studied metals in the Sava River water are less than 50% of the total dissolved metal concentrations, which is the consequence of the significant contribution of inert organic complexes and metals bound to colloids.

EROD activity in *European chub* liver follows the pollution level, increasing down to Jasenovac.

Chemical analysis of organic pollutants was performed on 14 muscle and 13 liver composite samples, which represent an average concentration for all fish specimens caught at a give location. Total PCBs, sum of 7 PCBs and total DDTs were determined and expressed on wet tissue mass and respectively on extractable organic matter (EOM). EOM in *European chub* muscle amounts 0.4 to 3.2% while in liver 2.4 to 19.7%. According to Croatian Official Journal 16(2005) the maximal allowed partition of a sum of 7 PCBs in edible part of fish like muscle, amounts to 2 mg/kg. In 3 campaigns the range of a sum of 7PCBs is 3 to 20 μg/kg in *European chub* muscle. It indicates to low level of PCBs in edible part of *European chub* from Sava River.

In addition, unsubstituted polycyclic aromatic hydrocarbons (PAHs) in muscle and liver of *European chub* were determined in the same composite samples like the PCBs. Predominant were phenanthrene, fluoranthene and pyrene out of 16 analyzed PAHs compounds. Analysis of hydroxylated metabolites of polycyclic aromatic hydrocarbons (OH-PAHs) in individual *European chub* bile is in good agreement with the distribution of unsubstituted PAHs. This primarily applies to the fact that phenanthrene and pyrene are predominant parent PAHs in both muscle and liver tissue. Hydroxylated PAH bile metabolites indicate to the recent exposure of individual fish specimens to PAHs. Most prominent individual metabolites were: 1-OH phenanthrene, 1-OH pyrene and 3-OH benzo(a)pyrene. Low concentrations in fish bile specimens from Otok Samoborski to Oborovo are uniform, while significant increase is observed at the locations Lukavec Posavski and Jasenovac, expecially related to the field campaign in September 2005.

CONCLUSIONS - Development and validation of specific tools

The potentriometric sensors developed served as end-point detector by potentiometric titration of low surfactant concentration levels (down to 10^{-5} mol dm^{-3} for anionic surfactants and 10^{-6} mol dm^{-3} for non-ionic surfactants). The results for anionic surfactants agree satisfactory with standard extraction-spectrophotometric MBAS method and are comparable with the results obtained using a commercially available surfactant electrode. Further investigation activities

are directed toward increasing of the sensor sensitivity, extending of its linear response range, development of methods for surfactant pre-concentration in surface waters.

CONCLUSIONS - Integrated system for the management of the Sava River quality

Granulated mixed microbial cultures are prepared as suspensions (industrial cultures) and used in biodegradation of targeted compounds and biodegradation of compounds in wastewater different origin: domestic wastewater, industrial wastewater (dairy, brewery, vegetable oil), refinery wastewater and wastewater from chemical industry (pesticides).

CONCLUSIONS - Data base

Thematic spatial data from The Sava River countries have been collected and put into GIS system in the following way: (1) topographic map obtained (scale 1:500.000) for georeferencing data (control, base for input of hydrography, scanning, 118 dpi raster (5 maps), raster input into Lambert conformal Conical projection; test: vectorised data in Cartesic projection Gauss Krüger 5 zone (SLOVENIA) has been put into Lambert Conformal Conical projection). (2) all available vectorised data in different projections have been put into Lambert Conformal Conical projection), tools used: Autodesk Map; (3) thematic layers rpoduced: administrative borders, The Sava river catchment areas, The Sava River, The Sava River tributaries, The Danube River (part), measurement points (chem. anal.), fish sampling points, meteorological stations, hydrological stations, CORINE (land cover), simplified raster data; (4) obtained data: 750 files in ESRI shape, Autodesk drawings, tables, text documents, scanned pictures (text, tables, other data). The work for GIS has been further done in ArcGIS (ArcView) and MS Office (Word & Excel) environment. In the step 1, the methodology (legends, layers, other) has been defined, then (Step 2) data sorting, cleaning of drawings (layers, data, double values) and export from Autodesk drawings to ESRI shape data merging, data digitizing have been performed; then export to raster images (step 3) followed.

For the water quality data collected in the SARIB project relational data base has been developed. It is in the MS OFFICE ACCESS environment. The system has logical and spatial integrity and can be upgraded in any time needed with new codes or descriptors. The manuel is produced.

CONCLUSIONS – Decision Support System

The Decision Support System (DSS) for SARIB Project is an Internet/Intranet application aimed at helping decision-makers (investors, technologists, policy makers, environmentalists and other stakeholders) to make the best choice among alternative remediation technologies,

simultaneously taking into account numerous sustainability indicators (environmental, technological, economic, social, regulatory, etc.).

DSS is used to perform Multi-Criteria Analysis (MCA) having a set of chosen remediation technologies and a set of chosen contaminants and criteria. For each hot spot problem, a decision-maker can create a session, where the actual remediation technologies, contaminants and criteria of interest can be chosen and Multi-Criteria Analysis for the selected technologies, contaminants and criteria can be performed.

Within DSS contaminants are categorized into the following groups: explosives, fuels, halogenated SVOCs, nonhalogenated SVOCs, halogenated VOCs, nonhalogenated VOCs, heavy metals, inorganics and radionuclides.

The selection criteria include: clean-up time required, data needs, development status, minimum achievable concentration, overall cost, public acceptability, reliability and maintenance, residuals produced, safety and stand alone character.

The remediation technology repository contains 37 groundwater treatment (air emissions/off gas treatment, biological treatment, containment, physical/chemical treatment) and 37 soil remediation technologies (biological treatment, physical/chemical treatment, thermal treatment).