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Persistent chemical pollution in Romania: A threat to ecosystem and human health

A Swiss Romanian cooperative research programme on Environmental Science and Technology in Romania (ESTROM)

Editorial

Dear Reader

Changes in the Danube River Basin are significantly accelerating since the ICPDR was established in 1998. IAD as an observer has adopted its strategy and performance accordingly. Today these changes are evidenced by a new modern layout of the traditional DANUBE NEWS. I hope it will be well received, while we maintain the quality of popular scientific articles.

This issue is a special edition focusing on a specific scientific programme between Romania and Switzerland covering nine projects across the Danube Basin and the Danube Basin District in Romania. This interdisciplinary programme ESTROM was launched in April 2005 and completed in December 2007. The main goal was to foster cooperation between the two countries, to strengthen basic and applied scientific research in Romania and to implement public participation for promoting public awareness of environmental and water protection. The Figure shows the acronyms and geographical location of the projects. They encompass several Danube tributaries such as the Rivers Somes, Crisul Alb, Certej, Bahlui, Olt and Ialomita, as well as Danube Delta lakes and Lake Tasaul near Constanta. Soils, groundwater and drinking water quality are also addressed.

The general topic of the ESTROM Programme was pollution of waters with heavy metals and persistent chemicals, including pharmaceuticals, disinfection products, pesticides, PCBs and PAHs. Some projects treated also biological aspects of such contamination, eutrophication and human health. While pollution of the Danube River with nutrients has diminished since the 1990s, priority substances with toxic effects gain more and more of importance. Moreover, discharge affected by global warming and hydromorphology threatened by navigation, hydropower and flood protection are indispensable parts of a complex ecosystem. All these aspects are presented in the ESTROM Conference during 3-5 September 2008 in Bucharest (www.estrom.ch). Together they combine into the transboundary and "sustainable" river basin management that is necessary to implement the EU Water Framework Directive and "good ecological status".

We acknowledge all those people having actively supported the individual projects. This programme was financed by the Swiss National Science Foundation (SNSF), the Swiss Agency for Development and Cooperation (SDC) and the Romanian Ministry of Education, Research and Youth (MECT), while the Swiss Federal Institute of Aquatic Science and Technology (Eawag) provided substantial in kind contribution by delegating five project coordinators.

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ESTROM – History, perspectives and outlook

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The Swiss National Science Foundation (SNSF) and the Swiss Agency for Development and Cooperation (SDC) supported in a joint initiative since 1990 research collaboration between Switzerland and Eastern Europe in the so-called SCOPES programmes. The acronym SCOPES stands for Swiss Co-Operation between Eastern Europe and Switzerland. A bottom-up approach enabled researchers from Eastern Europe and Switzerland to collaborate on their scientific work in mutual partnerships. In 2003 SNSF and SDC decided to start as a pilot programme a managed research programme where proposals would be invited based on a given implementation plan. The successful National Research Programmes of SNSF served as a model for the new practice-oriented programme. Romania was selected as the partner country. The area of environmental research was chosen for this cooperative programme among several other Romanian proposals. Subsequently, an international steering committee decided to focus on applied research in the area of water pollution and to call the programme ESTROM meaning Environmental Science and Technology in ROMania.

The development of the ESTROM implementation plan was based on a schematic overview on the issues of "Water pollutants in the aquatic environment" (Figure 1). The major thrust of ESTROM was to include projects in the various environmental compartments and scientific topics from inputs of water pollutants via exposure analyses and risk assessments to mitigation measures.

A three-tiered approach led to the selection of the ESTROM projects based on 30 letters of intents, 15 project proposals and eventually 9 full research proposals. The ESTROM steering committee performed the evaluation and selection of the submitted proposals based on the assessments by external experts. The selection objectives were (a) high scientific and technological quality, (b) broad coverage of the programme area and (c) a reasonable geographical distribution among the universities and research centres in Romania. In addition, really new partnerships should be started, which was fulfilled by seven of the nine successful project applications.

The interdisciplinary ESTROM programme addressed questions such as the magnitude of exposure of the environment and of humans in Romania, the risks to human health and the measures to be taken for the protection of the environment and of humans (NEPOLL). From a broader perspective, ESTROM aimed to create a decision basis for industry and regulators on how to avoid the negative impact of today's environmental contaminants (PHARMSOMES, POPIASI, TASAUL). The nine ESTROM projects dealt with research issues on water pollutants with a strong focus on exposure analyses in wastewaters and natural waters including sediments and drinking water (WAQUA, ORSED). Some emphasis was put on human exposure, eco-toxic effects and socio-economic aspects (EIMAR). One project dealt with biogeochemical aspects including the emission of greenhouse gases (WASEDI). Another project aimed at an integrated water quality management (INWAQ). It occurred, however, that the finally selected nine projects did not include projects with a substantial emphasis on technology. The ESTROM investigations focused on environmental pollution by dangerous substances as defined by the EU Water Framework Directive (WFD), persistent organic pollutants, heavy metals, emerging contaminants (pharmaceuticals and biocides) and nutrients.

The successfully performed key elements of the ESTROM projects were:

– Development of reliable methods for qualitative and quantitative measurements of organic and inorganic water contaminants in aqueous and solid samples in aquatic systems, i.e. in wastewaters, ambient waters, drinking waters and sediments.

– Analytical determinations of organic and inorganic chemical contaminants in the aquatic environment in order to recognise and apportion inputs and occurrences of contaminants in municipal and industrial wastewaters, elucidate fate and behaviour in wastewater and drinking water treatment and assess residual amounts in ambient waters such as rivers, lakes and drinking water.

Particles and sediments in aquatic systems are primarily not considered as pollutants per se. However, due to their sorptive surfaces and their potential as sinks and archives they play a crucial role within a 'cycling of polluting substances'. Therefore, particles had to be considered, if conclusions are to be drawn on transport, distribution and deposition of pollutants, in order to assess their potential harm. As sediments serve often as a sink for dangerous substances, they may in turn become the source of secondary pollution after their deposition. Besides, sediments are useful archives for the recon¬struction of polluting events and widespread spatial distribution of polluting substances to assess measures of remediation.

The outcomes of the ESTROM programme will help the Romanian authorities to cope with activities of the European Union with respect to the implementation of the Water Framework Directive and derived measures regarding dangerous substances. The results of the ESTROM programme will be applied for improving the situation regarding water pollutants in Romania by recognising critical points of chronic or acute contaminations. An additional important objective was the progress in national and international networking among scientists, administrators and other stakeholders. Three ESTROM programme meetings and one international conference have contributed substantially to achieve this goal. There is a good chance that the Romanian ESTROM research groups will have improved oppor¬tunities to participate in future research projects of the European Union and other international or national projects.

Regarding the Swiss support for ESTROM follow-up projects it can be hoped that more funding will be made available for similar environmental research projects.

An important outcome of the ESTROM activities is the improvement of the involvement of Romanian scientists in international networks, which is exemplified by two cases:

(1) The Division of Chemistry and Environment of the association of the European Chemical and Molecular Sciences (EuCheMS) is organizing a biannual international conference for chemistry in the environment (ICCE). The ICCE 2009 to be held in Stockholm will probably include a special session on Eastern European and Romanian projects. It is suggested that the chemically oriented ESTROM projects should be presented at the ICCE 2009.

(2) An ESTROM laboratory will be the Romanian contact point of the proposed permanent European NORMAN-network, which will be established as a non-profit association of all interested stakeholders dealing with emerging substances. NORMAN is the acronym for network of reference laboratories, research centres and related organisations for monitoring of emerging envi-ronmental substances (www.norman-network.net). The focus of the NORMAN-network is on emerging environmental substances, which are not necessarily new chemicals, but may have often long been present in the environment, and whose presence and significance are only now being elucidated.

The fact that Romania is a member state of the European Union since 2007 will lead to many activities related to chemical, physical and biological aspects of the Water Framework Directive (WFD), for which the ESTROM scientists are now better prepared.

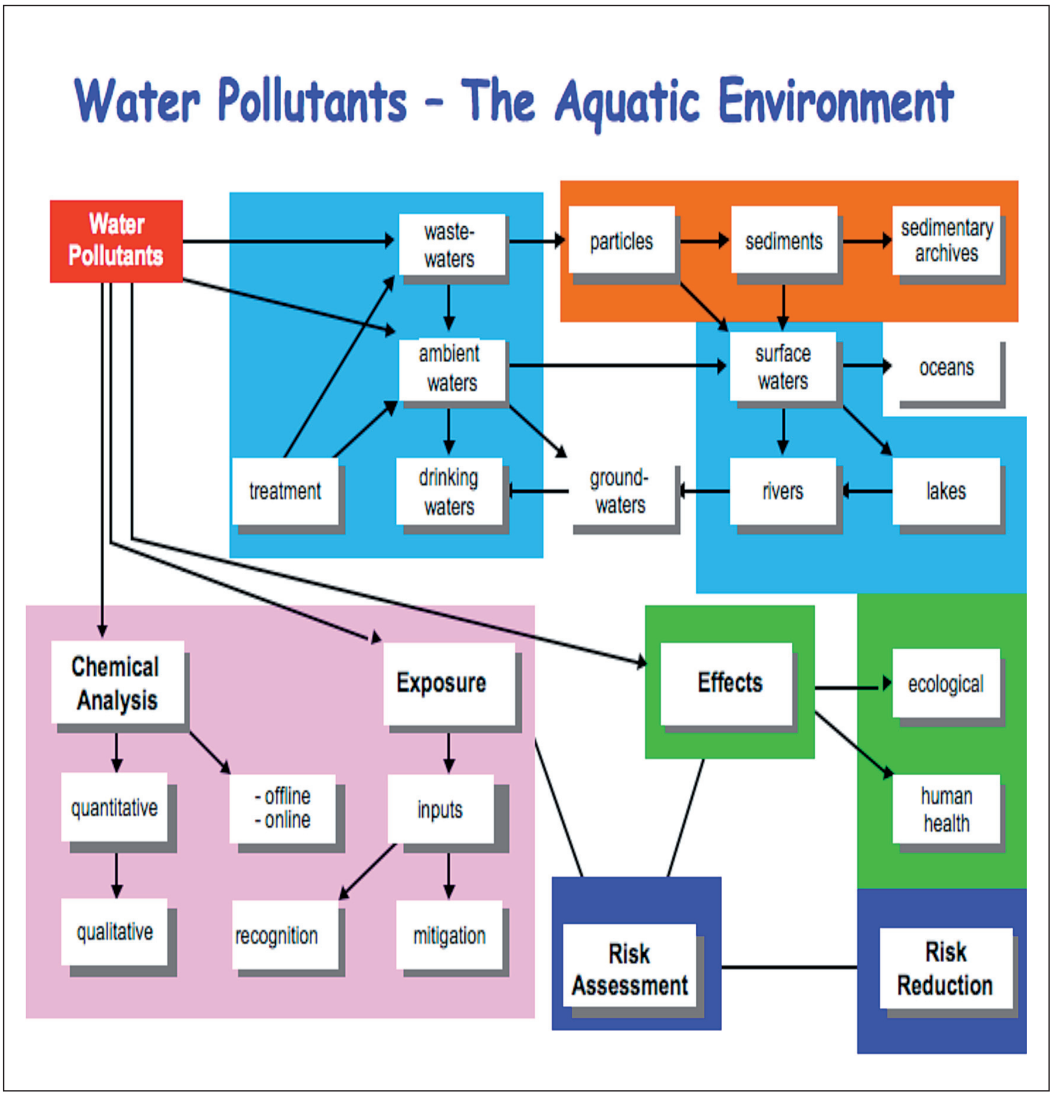

Figure 1. Water pollutants: from input sources via environmental fate and effects to risk assessment and risk reduction. Thorough analyses of exposures to chemical pollutants in wastewaters and assessments of associated risks to ecosystems and humans are aimed at reducing risk and mitigate measures with a strong emphasis on the reduction of inputs at the sources. The complexity of technical and natural aquatic systems with the many different compartments as well as characteristic system properties and dynamics must be considered. It is evident that problems of water pollutants must be tackled by an interdisciplinary approach

PHARMSOMES: Occurrence and behaviour of pharmaceuticals and musk fragrances in the Somes River before and after upgrading the municipal WWTP Cluj-Napoca

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The problem of micro-pollutants

Pharmaceutically active substances are a class of new, so called "emerging" contaminants, which has led to increasing concern about potential environmental risks. After excretion substantial amounts of unchanged pharmaceuticals and their metabolites are discharged into domestic wastewaters and if they are not removed during wastewater treatment, these substances will eventually reach ambient waters. Discharge of the effluents from wastewater treatment plants (WWTPs) into the receiving waters result in a further dilution of the pharmacological active substances which occur at concentrations up to the high ng/L range. The concentrations in surface waters are very much dependent on the contribution of the wastewater flow to the receiving water flow and therefore of the dilution of the wastewater that occurs.

Study area

The Somes River Basin is in the northwest of Romania (Figure 1). The Somes Mic originates south of Cluj-Napoca and merges at Dej with the Somes Mare to the Somes which flows into the Tiza in Hungary and later into the Danube. The Somes receives a variety of organic wastes from urban areas, factories and individual households and as well treated and nearly untreated wastewater effluents from several municipal WWTPs. The WWTP Cluj-Napoca is the largest WWTP in

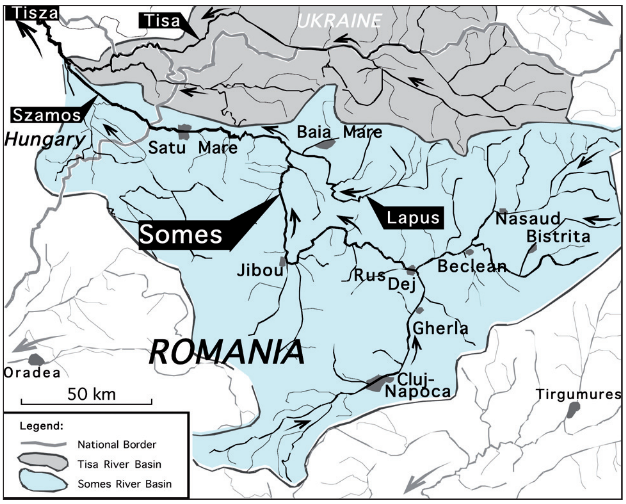

Figure1. Map of the Somes River Basin. For the shown results, river samples were collected at 3 sites: downstream of Cluj-Napoca, downstream of Gherla and upstream of Dej, after confluence of Somesul Mic with Somesul Mare

Transylvania and serves a residential population of around 350,000 inhabitants. In the years 1998-2003 the WWTP was upgraded and equipped for nutrient removal.

Sampling campaigns were conducted before (April 2003) and after (September 2006) the upgrade of the WWTP Cluj-Napoca.

Caffeine and carbamazepine as indicators for wastewater in surface water

The PPCPs (pharmaceuticals and personal care products) were selected on the basis of consumption at the regional scale, reported aquatic toxicity, and the suitability of the GC/MS method for the determination of the compounds at

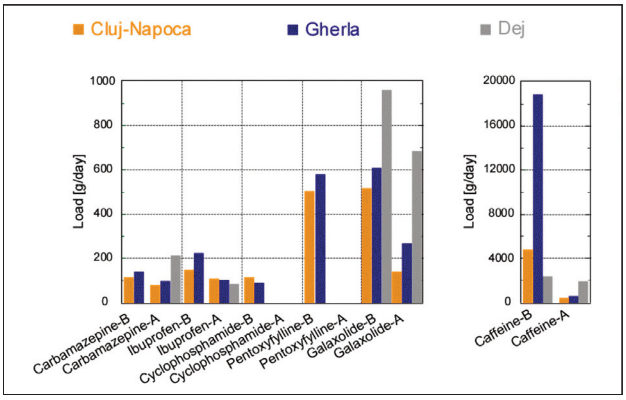

Figure 2. Loads of the studied compounds in the Somes River Basin before (B) and after (A) the upgrade of the WWTP Cluj-Napoca

trace levels: caffeine (stimulant), carbamazepine (antiepileptic), pentoxyfylline (anticoagulant), cyclophosphamide (cytostatic), ibuprofen (analgesic) and galaxolide (musk fragrance).

The concentrations in the Somes River varied from below 10 ng/L up to 10 µg/L. A substantial decrease of the exposure in the Somes River could be observed due to the upgrade of the municipal WWTP in Cluj-Napoca. The concentrations in the river stretch between Cluj-Napoca and Dej (Somes Mic) varied strongly: caffeine (230–9700 ng/L), carbamazepine (30–70 ng/L), galaxolide (10–310 ng/L), and ibuprofen (30–120 ng/L). Cyclophosphamide and pentoxyfylline could not be detected in the Somes River after the upgrade of the WWTP Cluj-Napoca. The concentrations and loads of caffeine decreased by one order of magnitude after the upgrade of the WWTP Cluj-Napoca whereas the levels of the persistent carbamazepine remained similar within expected temporal variations (Figure 2).

The relative contribution of treated and untreated wastewater in surface water may be assessed by measuring chemical indicators. Recalcitrant pharmaceuticals like carbamazepine are suitable as chemical markers for estimating the relative contribution of wastewater in surface water. Caffeine is efficiently eliminated in WWTPs and is therefore a suitable indicator for surface water pollution by raw sewage and barely treated wastewaters. During the second campaign the loads at Dej of the recalcitrant carbamazepine increased by a factor of 2 compared to the first sampling site. The concurrently increase of the caffeine load by a factor of nearly 5 refers to a discharge of untreated wastewater into the Somes. Because the increase of the load occurred after the confluence of the Somes Mic and the Somes Mare, this increase must be due to the discharge of untreated wastewater deriving from Bistrita, Nasaud and Beclean.

These data support the improvement of existing WWTPs and implementation of new ones where necessary in order to reduce the discharge of contaminants in the Somes Valley River Basin.

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WAQUA: Trihalomethane formation during disinfection in four water treatment plants of the Somes River Basin

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Trihalomethanes (THMs) are formed from the reaction of natural organic matter (NOM) present in all types of water, with chlorine used as a disinfectant in water treatment. THMs formed in the Cluj-Napoca distribution system were studied between July 2006 to March 2008 with gas chromatography with an electron capture detector (GC-ECD) using the headspace technique (HS). The Gilau water treatment plant (WTP) provides drinking water for the approximately 600,000 inhabitants of Cluj-Napoca, Gherla and several smaller villages downstream. Its principal water sources are the storage lakes Gilau and the Somesul Cald River. In the Gilau WTP, the disinfection process is based on the addition of chlorine gas. The chlorine gas is added manually to achieve a free chlorine residual at the exit of reservoir between 0.5 – 0.7 mg/L Cl_2 in the winter season and 0.7 – 0.9 mg/L Cl_2 in the summer season.

Chlorination of drinking water is not problematic

To identify factors that influence the THM formation, the chlorine decay and THM formation kinetics were followed in laboratory experiments every month during the study. Total chlorine, free chlorine and monochloramine were analyzed spectrophotometrically. Several factors affecting the formation of THMs were identified. The main factors having an influence on THM formation in the distribution system of Cluj-Napoca were the chlorine dose, presence of the natural organic matter (NOM) in water, reaction time, temperature/season (Figure 1) and the pH. The main THM identified was chloroform with a maximum concentration of 72 µg/L. Because of the low bromide concentration of the source water (5–7 µg/L), brominated THMs were always below 10 µg/L. Therefore, the current (150 µg/L) and future (80 µg/L) Romanian drinking water standard for total THM was never exceeded.

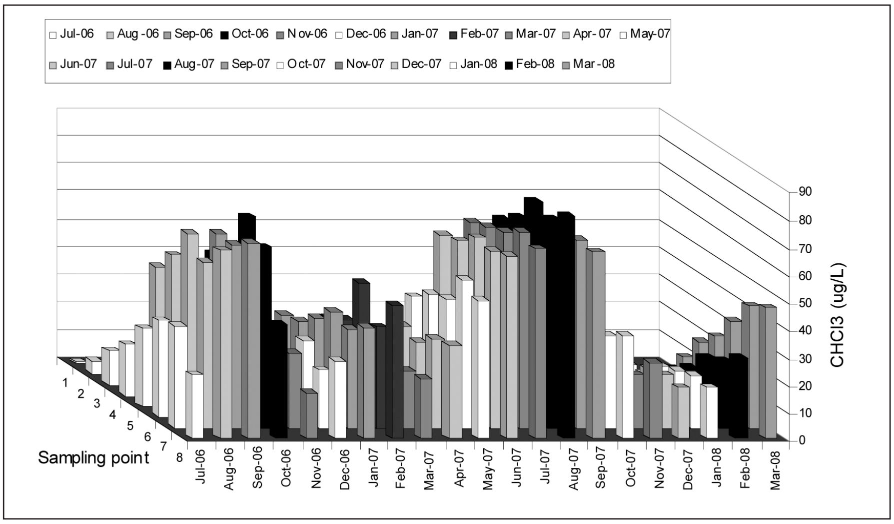

Figure 1. *$CHCl_3$ (µg/L) in different months during the study in all sampling points from the Gilau WTP and Cluj-Napoca distribution system*
1 – raw water/ 0 km
2 – filtrated water/ 1 km
3 – exit reservoir/ 5 km
4 – Sapca Verde/ 18 km
5 – Beer Factory/ 20 km
6 – Chemistry Faculty/ 22 km
7 – Environmental Faculty/ 26 km
8 – Institute of Public Health/ 31 km

EIMAR: Integrated Environmental and Socioeconomic Assessment of Impacts by Mining Activities in Western Carpathians, Romania

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Mining in Romania. In the region of the Apuseni Mountains, a part of the Western Carpathians in Romania, metal mining activities have a long-standing tradition since Roman time. Extracted ores have culminated in the 1950s and since 1996 decreased continuously until exploitation was abandoned lately. Mining industries created a clearly beneficial economic development. Nowadays, the region is confronted with the effects of mining closure and economic restoration. Mining activities also resulted in an apparent major acid mine drainage (AMD) combined with a persistent toxic heavy metal pollution in surface waters and sediments. This study investigated the impact of mining activities both from environmental and socio-economic perspectives and proposes integrated measures to mitigate mining problems.

Study sites and methods. The small Certej Basin covers an area of 78 km2. The larger basin, the Cris Alb Valley, has an area of 4200 km^2. Here, mining activities are concentrated in the upper basin. In this part and in the Certej Valley, mining was the main economic sector. Open pits and abandoned underground mines are producing concentrated acidic water that is discharged untreated into rivers. The solid waste of the mineral processing plants was deposited in several dumps and tailing dams, whereas the biggest impoundments contain several millions m3 of fine grained rock embodying the acidic water producing mineral pyrite. During several field campaigns, water was collected mainly from surface waters, dug-wells serving as drinking water resources, piezometers and impoundments, as well as solid samples from river sediments and the biggest tailing dams. Heavy metals, total and filtered fractions, major cations were analyzed by ICP-OES, heavy metals after enrichment. Major anions in waters were measured by IC, alkalinity and acidity were determined by titration. Tailings dam samples were characterized by XRD to obtain their mineralogical composition. Simultaneously in the Certej Basi the socio-economic team made several surveys and inquiries by questionnaires to evaluate people's perception to the river and drinking water quality.

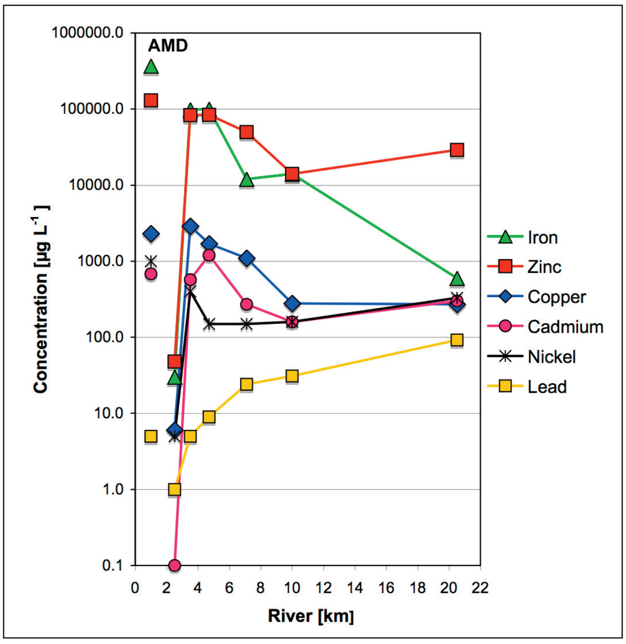

Figure 1. Concentration profile of heavy metals in Certej River. Contents at station 1 reflect background values and AMD represents the pollution source. Note the logarithmic scale in y-axis

Contaminated waters and sediments. Inputs of AMD only slightly increase the concentration of heavy metals and sulphate in the Cris Alb River as this water remains neutral, i.e., shows alkalinity. This contrasts strongly with the Certej Basin, where mining activities result in a strong heavy metal and sulphate pollution and the pH in the river drops to 3 (Zobrist et al. 2008). In both valleys, concentrations of pollutants decrease slightly downstream due to dilution by waters from tributaries. Metal concentrations measured at the most upstream stations and in the tributaries reflect background values in the range of the proposed environmental quality standards in the EU Water Framework Directive for dissolved heavy metals in rivers. Heavy metal concentrations in the polluted part of Cris Alb mostly match the old EU or Romanian river standards for the abstraction of drinking water. However, they are above the EU WFD quality standards. In Certej River, concentrations of pollutants exceed each quality standards by orders of magnitude.

Outflow of the big tailings dams, seeping waters, as well as the groundwater downstream of two tailing-dams exhibit the first sign of AMD, e.g., enhanced sulphate and calcium concentration. These waters still have a strong acid neutralizing capacity (alkalinity) and the pH is above 5.5. Pyrite was identified as the main sulphide mineral in the tailing dam that produces acidity and calcite represents the acid-neutralizing mineral. The acid-base accounting proved that the potential acid neutralizing capacity in the solid phases would not be sufficient to prevent the production of acidic water in the future.

Most dug-wells analysed deliver a drinking water that exhibits no sign of acid mine pollution although these wells were in distance from 10 to 30 m of the contaminated rivers. It seems that heavily polluted Certej River does not infiltrate significantly into groundwater. A minority of well waters show the first sign of mining pollution.

Money or water of good quality? The socio-economic study in the Certej Valley (Dogaru et al. 2008) showed that mining was perceived as a major source of income by 64% of the respondents. 20 % of the households in the main valley had redundant workers and over 45% of these households were partly or completely reliant on financial compensations as a result of mine closure. Unemployment was considered by the majority of the interviewed as the main cause of social problems in the area. The general educational profile of the people is vocational (secondary and apprentice schools) and theoretical (high school). Most professions were mine related. The estimation of the explanatory factors by logistic regression analysis revealed that education, household income, pollution condition in the last years and familiarity with environmental problems were the main predictors influencing peoples' opinion on the water quality in the main river. This model enabled to predict correctly 77% of the observations reported in the questionnaire, confirming that the river water was perceived as highly polluted by the local community. For the drinking water quality model three predictors were able to explain 66% of the observations. However, the model might not be able to consistently estimate whether people in the valley believe their drinking water to be polluted by mining.

Comparing the findings from the natural science and socio-economic approaches, we may conclude that the impact of mining on the Certej River water is high, while drinking water in wells is little affected. The perceptions of the respondents are to a large extent consistent with the measured results.

Conclusions. In terms of policy implications, it is well known that mining sites are subject to environmental protection measures, reconstruction actions and economic and social provisions, particularly after mines have been closed down. Our study, particularly the environmental perception analysis undertaken in the Certej Basin, shows the significant influence of such variables as education and familiarity with environmental problems in predicting local people's perception of water quality. The result has implications for specific regulatory actions (e.g., to rehabilitate a contaminated site). For example, as groups of higher educated people are more aware of environmental problems, they might be more willing to take part in environmental protection projects. In addition, people's knowledge and judgments of environmental risks in the areas they live in, are relevant inputs for planning environment reconstruction actions of degraded areas.

The results of this study can be used by various stakeholders, mainly the mining companies and local municipalities in order to integrate them in their post-mining measures, making them aware of the potential long-term impact of mining on the environment and human health.

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NEPOLL: Environmental pollution in the vicinity of an industrial area near Bucharest and the impact upon the health of people living in this area

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We investigated an industrial site near Bucharest, which is thought to be the major source of heavy metal deposition in the surroundings. The site stands as an example for many similar industrial activities in Romania. The industrial area is located 4 km south-east of Bucharest and about 2 km east of the nearest village (Pantelimon). The study site includes two plants recovering heavy metals such as lead from solid waste. There are two lakes in the neighbourhood. In a combined study the pollution of the environment was related to public health in the vicinity of this area.

Impact on the environment

Samples of water, soil and atmospheric depositions were taken between September 2005 and May 2007 at different locations in the study area. Heavy metal concentrations in water, soil and air were increased in the vicinity of the industrial area when compared to Bucharest (Figure 1). As expected, soil metal concentrations decreased with increasing distance from the industry This indicates the influence of the industrial activities on the deposition of heavy metals in

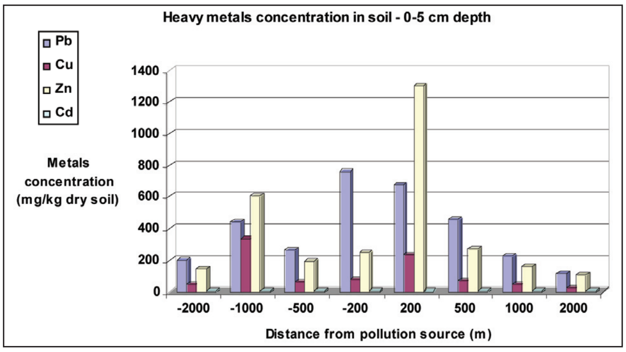

Figure 1: Heavy metal concentration in 0 – 5 cm soil depth dependent on distance from the industrial activities

the surrounding area. The highest heavy metal concentrations in soil profiles were found at a depth of 10-20 cm. In Pantelimon half of sampling locations showed lead concentrations above legal action limits for high-concern areas (100 mg Pb/kg dry soil); but also in the control samples in Bucharest half of the samples were above this limit. However, maximum values in Pantelimon are four times higher than in control samples of Bucharest. We found soluble lead concentrations in water above alert limits, and increased Zn concentrations in a lake and drinking water. For atmospheric deposition increasing distance to the industrial site resulted in a reduction of dust precipitation and heavy metal concentrations such as lead. The average dust deposit and the heavy metal values around the study area are higher than the reference sites in the middle of the city of Bucharest. The Swiss immission limits are exceeded manifold.

Impact on public health

Children

To evaluate effects of trace metal body burden on health and mental health of children, we performed in a first step trace element analysis in blood samples of 52 children from Pantelimon and 54 children from traffic deprived areas of the city of Bucharest.

Results indicate that both groups of children living in Pantelimon and in the city of Bucharest suffer from altered trace element concentrations (Table 1). In most cases values are above reference ranges given in the literature. Notably, the percentage of children with altered blood concentrations of trace elements is distinctly higher in the Pantelimon group for most elements. The same children groups were selected for behavioral analysis. Patterns of trace metal exposure were compared to performance in the Test of Attention Performance for Children (KiTAP). The KiTAP test battery provides a selection of four different tasks needed to achieve differentiated measurement of alertness, Go/Nogo, distractibility and flexibility. Generally speaking, children with higher lead levels make more errors in go/nogo, distractibility and flexibility (significant or borderline). These results are consistent with some earlier findings for lead. The lead-induced performance deficit may tentatively interpret as being indicative of subtle attention deficit induced by low-level childhood lead exposure. The results with parental education added to the model show that the lead-effect for errors is statistically even more pronounced, and it makes sense that the strongest lead-effect is for distractibility (the lead symptom of ADHS).

Adults

One study group from the resident population of Pantelimon village was chosen for the population aged 25-45 years old, both male and female. The control group having the same age and sex structure as the study group, comprises unexposed population not living in Pantelimon village. Blood samples were tested for lead, deltaaminolevulinic acid (DAL) values and free erythrocyte protoporphyrin (FEP).

In the study group 34 out of 38 subjects, totalling 89.5%, had higher than normal blood lead (BLL) values, in the control group 19 out of 28 subjects (67.9%) showed higher than

Table 1: Percentage, numbers and sex of children living in the industrial area of Pantelimon or in the City of Bucharest with trace element concentrations in blood above reference ranges or Rf-values (Pb and Hg)

Region	PANTELIMON		Total Pantelimon		BUCHAREST		Total Bucharest	
	Girls	Boys	All	%	Girls	Boys	All	%
Trace ELEMENTS								
Al	26	26	52	100.0	20	21	41	100.0
Be	15	20	35	67.3	-	-	-	-
Co	4	4	8	15.4	-1	-	1	2.5
Ga	26	26	52	100.0	20	21	41	100.0
Hg (Rf-value)	12	11	23	44.2	6	7	13	31.7
Li	13	16	29	55.8	2	4	6	14.6
Mn	17	8	25	48.1	12	14	26	63.4
Pb	11	9	20	38.5	-2	4	6	14.6
Sb	5	8	13	25.0	-	1	1	2.5
Se	5	5	10	19.2	6	3	9	22.0
Sr	5	4	9	17.4	-	-	-	-
Zn below norm.	15	15	30	57.7	11	10	21	51.2
Zr	4	7	11	21.2	-	-	-	-

normal BLL values. We found statistically significant ($p<0.001$) contrasting frequencies of the subjects with DAL > 5 mg/L in the study group and the control group. The FEP values were compared with the value ≤ 80 µg/100 mL, considered to be normal in the general population. In the study group 23 out of 38 subjects (60.5%) had increased FEP values, in the control group 1 out of 28 subjects (3.6 %).

The main results show significant changes in the biotoxicological aspects of Pantelimon residents.

Conclusions

Mainly in sensible places such as populated areas further measures have to be taken to avoid health risks for people living in this area. The measures already taken to reduce emissions from the industrial site will help to avoid further increases in heavy metal concentrations. Medical measures should be evaluated for children and adults with increased heavy metal concentrations in blood and specific symptoms.

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POPIASI: Chemical, biological and ecotoxicological assessment of pollution with pesticides and POPs in Bahlui River, Romania

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Degradation of aquatic systems cannot be understood only through chemical measures of priority pollutants, because they provide no information on the biological-ecological effects. The Water Framework Directive of the European Commission recommends that monitoring and management should be carried out with integrated, chemical and biological approaches (WFD 2000). The present study is one of the first having such an interdisciplinary approach and thus independent of the national water authorities (Administratia Nationala 'Apele Romane'). The objective was to establish for the study area a body of baseline information for future studies of the kind. This was done by using a limited number of methods from each type of approach as described by Neamtu et al. (2008).

In Romania, as epitomised by our study area (north-eas-tern Romania, close to the city of Iasi, 320,000 inhabitants), very scarce information is available upon persistent organic pollutants (POPs) and their effects. From what is known, it is very unlikely that the standards of the European Union are systematically met. The study area is impacted by both agricultural and industrial activity. The river, a tributary to the Prut River, 104 km long, average annual flow of 2.8 m^3s^{-1}, falls into the WFD river intercalibration type R-E2: medium-sized lowlands, altitude <200 m, mixed geology dominated by sand and silt. Concentrations of nitrate (NO_3-N) measured by us (April 2007) varied in the City of Iasi between 4.6 and 8.5 mg/L.

Water quality decreased from river springs to river mouths. Pollutant concentrations reported herein (Table 1) are lower or similar than those reported by earlier studies (RIZA 2000; Dragan et al. 2006). No national pollution thresholds were exceeded. Ratios of individual PAH compounds suggest that PAHs originated mainly from the combustion of fossil fuels. The calculated values of the Saprobic Index and of the Diatoms' Index correspond to moderate pollution. Species richness in phytoplankton displayed no clear pattern. Water

Table 1: Pesticide and POP concentrations, biological indices and toxicity in Bahlui River (2006)

Parameter measured	Values found	Interpretation
PCB (sediment)	3.0 – 26 ng/g dw	Below admitted thresholds
HCHs (sediment)	0.4 – 3 ng/g dw	Below admitted thresholds
DDTs (sediment)	0.2 – 18 ng/g dw	Below admitted thresholds
PAHs (sediment)	6.0 – 155 ng/g dw	Below admitted thresholds
Saprobity Index (phytoplankton)	1.99 – 2.70	Moderate organic load (β-α-mesosaprobic)
Diatoms Index (phytoplankton)	3.48 – 3.14	Moderate pollution
Species Richness (phytoplankton)	28 – 50 species	Within known limits for such rivers
River water acute toxicity *(Daphnia magna)*	EC_{10} > 100 % of samples	No detectable toxicity (invertebrates)
Sewage water acute toxicity *(Daphnia magna)*	EC_{50} = 28 % of samples	High toxicity (invertebrates)
River water acute toxicity *(Pseudokirchneriella subcapitata)*	EC_{50} = 91 % of samples	Low toxicity (green algae)
Sewage water acute toxicity *(Pseudokirchneriella subcapitata)*	EC_{50} = 16 % of samples	High toxicity (green algae)

toxicity testing indicates low toxicity of river with two notable exceptions at domestic wastewater treatment discharges and at an old open-air deposit of domestic waste.

All in all, river water quality is better than expected. This is probably due to the collapse of agricultural and industrial activity after the fall of communism in 1989. Of course, further studies will be carried out to confirm and refine these results, in compliance with the Water Framework Directive. This study, instead, appeals for increased attention, because economic activities are alertly increasing in the area. We recommend pursuing precisely this type of multidisciplinary investigations: chemical, ecotoxicological and ecological. The final aim should be to elucidate the interactions between pollution, producers and consumers in aquatic ecosystems, and the effects on human health.

We recommend to extend the here-presented approach to a larger number of pollutants and ecological indices and batteries of standardized ecotoxicological tests. The chosen methods should take into account the recommendations and needs issued from an inter-calibration exercise. When river pollution is low, ecotoxicological testing should target hotspots of pollution. We also suggest that cheaper approaches should be preferred because these (1) will be more applicable locally and (2) will disclose resources for in-depth investigations. We expect several levels of impact of such studies in the examined area: local, national, EU countries, and EU neighbourhoods (Ukraine and Republic of Moldova), via the platform provided by the International Commission for the Protection of the Danube River (ICPDR).

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ORSED: Bioavailability of mercury and toxicity of sediments from the Olt River reservoirs (Romania)

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Introduction

Mercury (Hg) is a ubiquitous and hazardous contaminant, which easily accumulates in organisms. In aquatic environments, mainly at the sediment water interface, the organic form, methyl mercury, is synthesized by bacteria. This form shows a strong biomagnification, i.e. its concentration increases by orders of magnitude through the aquatic food chain from the phytoplankton to the top predatory fishes and birds. The most common transfer path to humans is the consumption of contaminated fish. A severe Hg poisoning may damage the central nervous system. Hg releases from chlor-alkali plants are known as one of the most important point sources of Hg pollution in the aquatic environment. Although the chlor-alkali industry recently uses an alternative Hg-free technology, the heritage from the past releases is still a considerable problem in the concerned areas.

The principal goal of this study, carried out between 2006 and 2007 in the framework of the ESTROM program, was to asses the current status of mercury pollution in the Babeni reservoir, one of the numerous reservoirs of the Olt River, the largest and the longest Romanian tributary of the Danube. The reservoir is located downstream of the industrial channel evacuating the Rm Valcea industrial platform wastes to the river. Mercury contamination originates from a chlor-alkali plant, which discharged an unknown quantity of this metal between 1968 and 1999, but apparently does not use the Hg-based technology anymore. A survey by GeoEcomar (unpublished) in 1996 revealed a high Hg pollution in the Babeni reservoir. However, nothing is known about the relevance and bioavailability to organisms.

In August 2006, 74 surface sediment samples were taken mainly from the Babeni, but also from the Govora and Valcea reservoirs. Several long cores were sampled in the Babeni and Valcea reservoirs and three of them were examined in detail. Total Hg was measured in sediments and in benthic organisms *(Chironomus* and Oligochaetes) using an AMA 254 mercury analyzer. Further, biotests were performed with laboratory organisms *(Chironumus riparius)* to evaluate the bioavailability and toxicity of Hg in surface and buried sediments from the Babeni reservoir, the most polluted reservoir of the Olt River.

Table 1 Concentration of mercury (µg/g dry weight) in organisms collected in the field, in laboratory-raised organisms and in associated sediments

Reservoir	[Hg] in sediment	*Chironomus*	Oligochaetes	Lab *Chironomus**
Valcea	0.09	0.13	0.05	0.14
Babeni 1	2.90	2.14	0.92	1.10
Babeni 2	1.44	not found	2.84	1.25

**values obtained in laboratory microcosm experiments with raised Chironomus riparius*

Results and discussion

Current and historical pollution

In surface sediments from the three reservoirs (Valcea, Govora and Babeni), the highest Hg concentrations (21 µg/g) were recorded in the sediments deposited in the river near the industrial discharge, upstream of the Babeni reservoir. In the Babeni reservoir, the Hg concentration in samples collected close to the dam was around 4 µg/g. The Valcea reservoir sediments provided a local background level, with low concentrations in the range 0.01 - 0.05 µg/g. Higher but still comparatively low concentrations were found in the Govora reservoir (0.02-0.20 µg/g). Sediment cores from the Babeni reservoir showed Hg peaks in deep sediments with extremely high concentrations of Total Hg, reaching 30 and 44 µg/g at 88.5 and 111.5 cm depth, respectively. These sediment layers are ^{137}Cs-dated at about 1987. However, concentrations up to 8 µg/g were also measured in much younger sediments (12.5 cm depth).

Hg concentrations in organisms

The concentration of metals in organisms sampled in situ should represent the concentration in equilibrium with sediments. Benthic organisms were sampled in the Valcea reservoir (one site) and in the Babeni reservoir. In the latter two sampling points were assessed: one located close to the industrial wastewater input (Babeni 2) and the other located close to the dam (Babeni 1, Table 1). Internal concentrations found in *Chironomus* were in the same range as those measured in the host sediments. However, the internal concentrations in the Oligochaetes do not necessarily reflect the sediment concentrations: in Babeni sediments, a higher Oligochaetes concentration was found in Babeni 2, which is less contaminated than Babeni 1 (Table 1). In addition, the accumulated concentrations are high as compared to those measured by Vidal and Horne (2003) for Oligochaetes (0.6 µg/g d.w. in Oligochaetes and 3.6 µg/g d.w. in sediments).The Oligochaetes internal concentrations of Hg do not reflect the concentrations in sediments, suggesting that methyl mercury rather than total Hg is important in the bioaccumulation process.

Laboratory tests

Toxicity and bioaccumulation tests were carried out to asses the pollution effects on biota and to evaluate the potential hazards to food chain and human health. Toxicity tests were performed with *Chironomus riparius* in microcosms with sediments from the Valcea, Babeni 1 and Babeni 2 sites during 7-day exposure, using growth rate (length) and mortality as indicators. A significantly higher toxicity was observed in Babeni 2 sediments as compared to the Valcea sediments (control). This possibly explains the absence of local Chironomidae at site Babeni 2 (Table 1), whereas they were present at site Babeni 1. However, the toxicity tests integrate the effect of the various pollutants present in the sediments and thus the toxic effects cannot be attributed only to mercury.

Bioaccumulation factors of mercury (concentration in the organism over the concentration the sediment) calculated for each site after 10-day exposure were higher in Babeni 2 (0.87) than in Babeni 1(0.37).

Conclusions and recommendation

This study provides evidence of a severe mercury contamination of surface sediments in the Babeni reservoir. Concentrations of one to two orders of magnitudes higher than the local background concentration were measured. The historical record from sediment cores testifies an extremely high contamination in the late 1980s, suggesting a severe and chronic exposure of the local population Bioaccumulation tests reveal clearly the availability of Hg to the benthic organisms. Although the concentrations in recent sediments are lower than in the past, the whole area is probably contaminated beyond an acceptable level. These results call for a comprehensive assessment of the current impact on biota, especially the concentrations in fishes, which are not monitored. Mercury level in hair and, if necessary, in blood should be monitored. The fate of Hg in the reservoirs downstream of Babeni needs also to be investigated.

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INWAQ: Development of an integrated water quality management system, with application to the Ialomita River Basin

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Any action aiming at improving water quality in a broad sense (pollution alleviation or remediation, ecosystem preservation, drinking water improvement, etc.) to be effective has to be thought and designed at the scale of a river basin, taking the water system as a whole into account, and giving special attention both to the spatial and causal relationships among its components. Being able to handle, maintain and provide (with respect to stakeholder involvement) a large and complex set of multiform information is a very crucial aspect of these necessarily integrated approaches to resource management. Due to the importance of the spatial dimension of this information, geographical information systems (GIS) are privileged tools to address water quality management issues. The objective of the INWAQ project was to develop a GIS platform devoted to water quality management and addressing the specific Romanian context of water management (administrative setup, on-going projects, EU Water Framework Directive, etc.). The starting point was in fact a pre-existing system that is currently used in a regional water administration in Switzerland, a system that could also be improved thanks to this applied research project.

In setting up or adapting a GIS system, one has to follow a set of well defined steps in order to make sure that the effective needs of end-users will be met and that the provided system will really make a difference in their daily practice: the first and very important step is the assessment of needs (on the basis of a careful analysis of the various activities and missions of the water administration and other relevant stakeholders in water management related issues). On that basis, a conceptual data model (CDM) can be developed. This complex model is then engineered into a physical database (i.e. a set of interlinked tables with the relevant fields in a database management software). The database has then to be fed with data, which can be a very time-consuming process showing that the set up of such a system has to be thought and planned in the longer term. Finally specific additional functionalities (i.e. functionalities not provided by classical commercial GIS software), also identified during the assessment of needs, are developed. This methodological approach has been applied with the central board of the national water administration of Romania (ANAR) and its local branch on the Ialomita River Basin, which was used as a test field.

The results obtained from this action-research project consist in a set of tangible elements, among which (i) a conceptual data model adapted to the Romanian specialities regarding water resources management (needs, data availability, etc.), (ii) a related spatial relational database (objects and attributes in tables, links, etc.) that can be used to store the data collected, among others, by the water administration, and later on exploited with geographical information systems, (iii) a toolbar (in the specific GIS environment used at ANAR) offering the requested data processing and visualising functionalities. This material will be disseminated among all river basin authorities in Romania on behalf of the national water administration (ANAR). The envisaged further developments, to address more precisely water quantity issues, show that this project was successful in providing an appropriate input to improve water quality in Romania on the longer term.

Less tangible, the main lessons learned in this sort of technology transfer process could be summarized by the need for flexibility, which is paradoxically not the main quality one would promote to be successful in proposing a bilateral research project. The fact is that due to the novelty of the

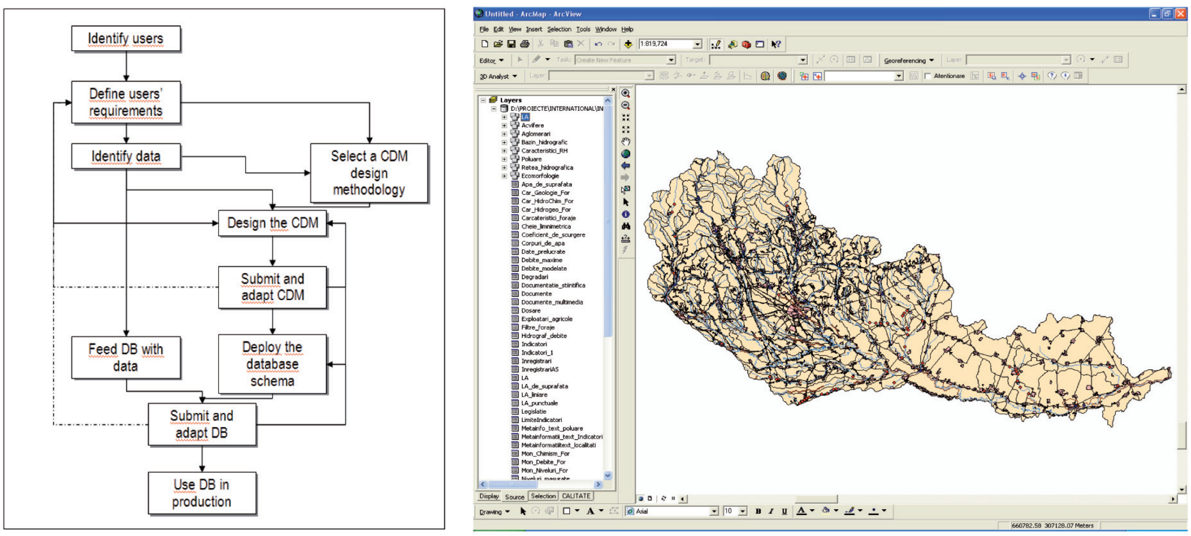

Figure 1: Database development steps and screenshot of the GIS platform for the Ialomita River Basin

methodology and the lack of local experience in developing such systems, along with the absence of an existing water related database management system (which is an important brick upon which a GIS system has to be built upon), the project shifted slightly away from its original objectives (developing elaborated new functionalities, such as for example a link to the modeling of pollutant fluxes at the river basin scale) to spend much of the effort on consolidating the bases of the whole process. Flexibility, with respect to the original plans, was very necessary since it allowed to adjust to the real day-to-day needs of the end-users, ensuring thus that the developed tools will really be used.

WASEDI: Water and sediment dynamics affecting nutrient cycles and greenhouse gas emissions in the Danube Delta

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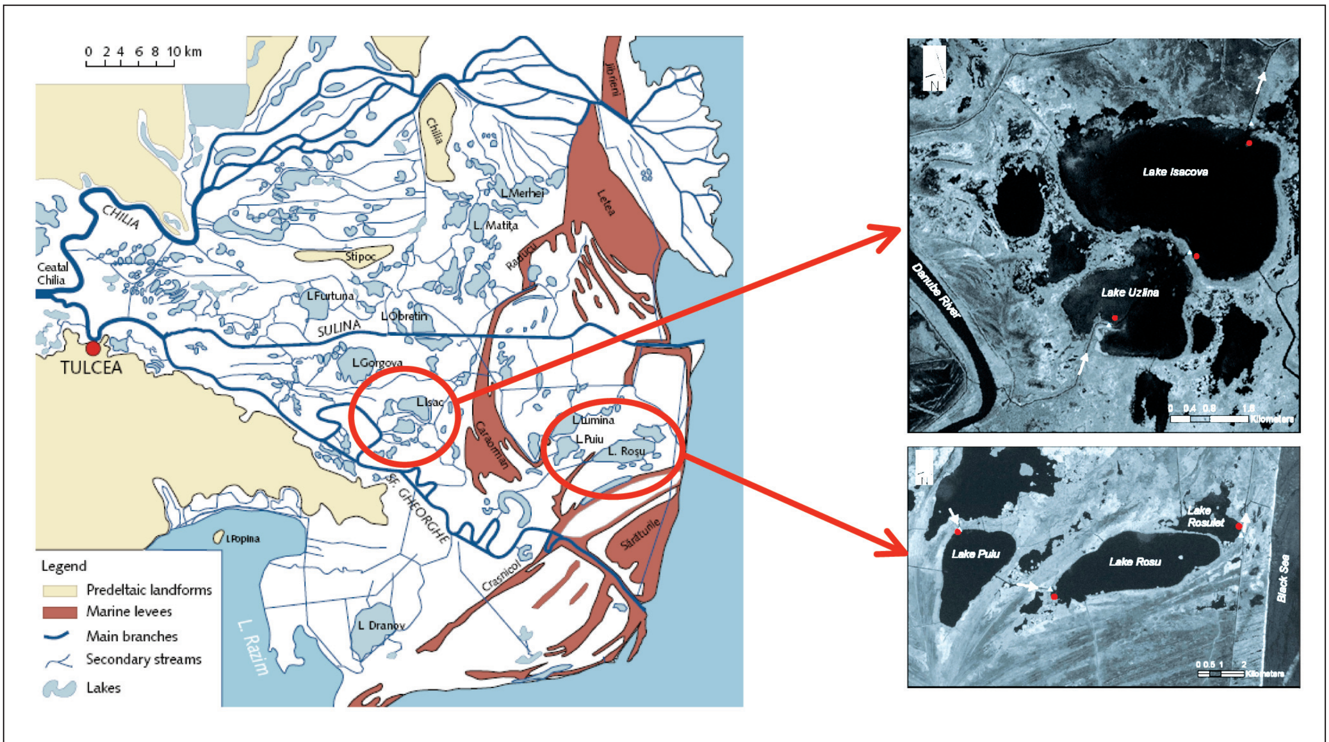
In view of global warming research into sources and sinks of greenhouse gases is of great importance. The many lakes and wetlands in the Danube Delta provide key study sites as the hydrological regime of the Danube River significantly influences the water level and hence the limnological behavior of these lakes.

The study was conducted in two different chains of flow-through lakes between the Sulina and Sf. Gheorghe Branch of the Danube River during high and low water levels in spring and late summer (Figure 1). Transsects from close to river lakes to distant lakes, i.e., from Uzlina to Isacova Lake and from Puiu to Rosu and Rosulet Lake, showed decreasing nitrogen (N) loads and increasing soluble phosphorus (P) fractions. Biochemical drivers along these lake chains where N and P are taken up by plankton to increase biomass production are mainly reedbeds in the connecting channels with bacterial N and P recycling and sedimentation. While nutrients are eliminated with distance from the Danube main channel the organic fraction (total organic carbon = TOC) is increasing and through biological transformation bioavailability is reduced. An increasing TOC/Total N ratio in organic matter with distance from the Danube indicates a shift from fluvial to terrestrial material.

Sediment pore water core profiles demonstrated the key role of sulfates in the sediment-water interface. There is a strong link between sulfate supply in sediments and methane concentrations and fluxes. Sulfate reducers and methanogens showed similar depth profiles. RNA-Analysis proved for the first time the presence of anaerobic methane oxidizers in freshwater sediments.

Figure 1: *Map of the Danube Delta showing the lakes studied*



Finally, nutrient budgets were linked with trace gas emissions of carbon dioxide (CO_2), methane (CH_4) and laughing-gas (N_2O). The gas concentrations were measured by a special Online-System just above lake surface, hence providing emission maps of the lakes investigated (Figure 2).

The greenhouse gas emissions changed gradually with increasing distance from the Danube main channel. In fall 2005 when the Danube River featured low flow CO_2 emissions increased while CH_4 and N_2O decreased. However, in May 2006, when the Danube River discharge and the load of organic material were high, CO_2 and CH_4 emissions decreased while N_2O increased. In addition to the lake's distance from the main river also the lake's shape and morphometry affect greenhouse gas emissions. For example, methane is rather oxidized in deep lakes while it is removed into the atmosphere in the form of gas bubbles rising from the sediments of shallow lakes. Methane is an even more effective greenhouse gas than carbon dioxide and is released into the atmosphere mainly in spring (high water discharge and organic load). Carbon dioxide emission is most prominent in lakes close to the main river, where most of the organic material is deposited and reduced by bacteria.

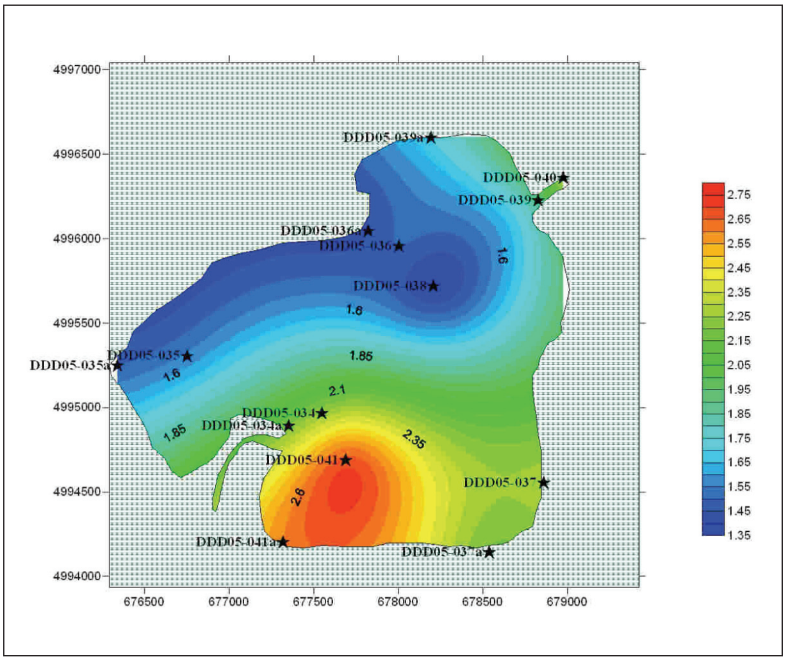


Figure 2: Uzlina Lake: Total trace gas emission in function of distance from the main Danube channel (red = high emission and close to the Danube; blue = low emission and remote from the Danube)

The results of the project WASEDI could be "dynamite": We now know that wetlands are rather sources than sinks of carbon. If such wetlands in the northern hemisphere increase in size due to melting of permafrost in Siberia or Canada the global scale is definitively reached.

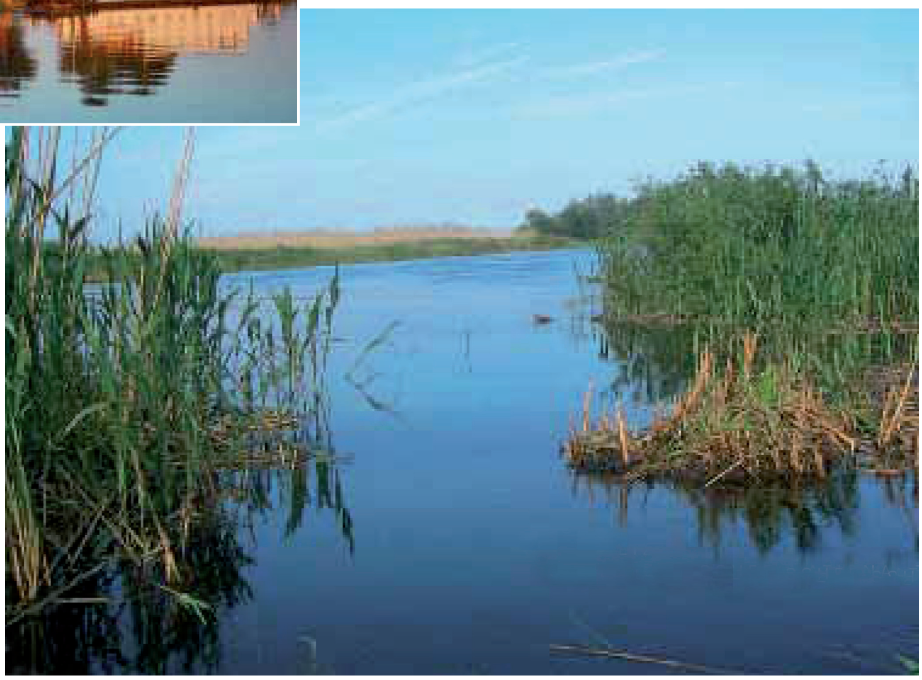


Figure 3: The Danube Delta provides beautiful landscapes that attract many tourists eager to view the wonderful flora and fauna (mosquitos included!). Visiting scientists combine hard work and enjoyment

TASAUL: Assessment of anthropogenic impacts on Tasaul Lake Romania, and ecosystem rehabilitation

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Coastal Tasaul Lake (area 23.35 km^2, max. depth 4 m) near Constanta on the Romanian Black Sea is an important ecosystem changed in the 1990s by a complex man-made canal system from an open saline lagoon into a freshwater system which is threatened by various polluters and fishing overexploitation. In 1994–1995 a drastic decline in fish-catch from 180 to 50 t was observed that continued to 5 t until 2000. This may be attributed, apart from over-fishing by man, to a lack of scientifically based management, reduced fish reproduction due to unfavorable conditions (e.g., high turbidity, small food source), and internal and external nutrient loading (eutrophication).

Tasaul Lake, monitored from May 2005 to June 2007, showed the typical features of a shallow, turbulent and eutrophic lake (Alexandrov 2008). Frequent wind prevented stratification and oxygen depletion near lake bottom, and induced sediment resuspension and turbidity. Mean phosphate and nitrate concentrations (17 resp. 370 µg/L) varied spatially and seasonally. Primary production (80–2712 mg $C_{ass}/m^2.h$), algal biomass (mean 38 mg/L) and chlorophyll a (mean 164 µg/L) were high. Phytoplankton (69 species) was dominated by Cyanophytes (67–94%) forming frequent blooms. Secchi depth often was <1m. Zooplankton (35 species) was dominated by rotifers with low diversity and productivity. There was a lack of Cladocerans. The total number of bacteria was $5 \cdot 10^3 – 1.6 \cdot 10^6$ per mL, and two stations with anthropogenic influence showed increased bacteria concentrations including pathogenic forms. The low benthos abundance (39 mg/m^2, no Mysids and Amphipods) can be explained by anoxic sediments providing unsuitable habitat for bottom fauna.

Table 1: Selection of chemical data from Tasaul Lake, water and sediments (2005–2007). Persistent contaminants showed significant temporal and spatial variation but no severe pollution as mostly below national and international threshold values in water and in sediments. However, some chronic pollution was evident

Contaminant	Concentration in water Mean Range	Concentration in sediments Mean Range
Copper (Cu)	12.6 (3.1–48.3) µg/L	34.5 (18.6–57.4) µg/g
Cadmium (Cd)	0.27 (0.02–1.3) µg/L	1.95 (0.6–3.4) µg/g
Lead (Pb)	0.73 (0.05–4.5) µg/L	73.9 (26.9–126) µg/g
Nickel (Ni)	5.4 (0.4–24.1) µg/L	65.0 (10.7–92.1) µg/g
Chromium (Cr)	2.6 (1.3–4.3) µg/L	–
total (15) PAH's	380 µg/L	700 ng/g
total (9) pesticides	1790 ng/L	250 ng/g a

Fish stock in Lake Tasaul was assessed in 2005 for two out of eight species *(Carassius gibelio* [giebel carp] and *Rutilus rutilus* [roach]) from a total of 581 specimens investigated. FAO related methods were applied by using "age-structured" models based on population parameters such as length frequency diagrams and length-weight relationships. Biomass in 2005 was 23.6 tons for giebel carp and 34.2 tons for roach. Since the fishing mortality coefficient was greater than the natural mortality coefficient, fishery is claimed not to be sustainable (i.e., over-exploitation). The maximum sustainable yield would be, according to the model based on standard fish catch of 10 tons/year, 10.9 tons/year for giebel carp and 12.2 tons/year for roach (Alexandrov et al. 2008).

Casimcea River, the main tributary of Tasaul Lake with a large catchment, discharged much suspended solids and anthropogenic nutrient input: runoff, erosion and leaching from fertilized agricultural areas and wastewater from cities/villages and industry. Peak concentrations were 0.54 mg/L total phosphorus (TP) and 15.7 mg/L total nitrogen (TN) which represents quality class III-IV (high to extensive pollution). A load estimate yielded 3 tons TP/year and 660 tons TN/year. Three smaller tributaries contributed less than 10% of the total nutrient load.

Contamination of Tasaul Lake was mostly below threshold values, see Table 1 (heavy metals [Cu, Cd, Pb, Ni] in water <0.02 mg/L and sediment <0.08 mg/g; 15 poly-aromatic hydrocarbons 700 ng/g; 9 organochlorine pesticides 1790 ng/l in water and 250 ng/g in sediments). Hence, pollution with toxic substances was less than expected, but potentially may cause sub-lethal effect on biota, fish in particular.

The results were disseminated to end-users and schools in a public event during April 2007. Our recommendations (Alexandrov & Bloesch 2008) towards a more sustainable fishery management in Lake Tasaul are (1) to reduce nutrient input of Casimcea River by fighting point sources and possibly diminish algal blooms; (2) to monitor and quantify yearly restocking of fish (fishing effort/input) and perform detailed statistics about net catches, angling and poaching (fishing/output). A potential conflict of interests may be the predation of fish by cormorants and pelicans. Since Tasaul Lake is an important bird area according to Birdlife International, the interaction of birds and fish will need further attention.

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Hydrological catchment of the River Danube

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