

Ecological Risk Assessment of Inorganic and Organic Micropollutants in the Danube Catchment Area

A tiered risk assessment methodology for Danube sediment

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Voluntary activities: social environment & disabilities

Abstract:

An European and a Hungarian research project worked on the risk assessment of Danube sediment between 1997 and 2002.

A tiered risk assessment methodology has been developed for the characterisation of the risk of chemicals in the Danube sediment. The first tier, a qualitative risk assessment was applied for all organic and inorganic chemicals produced and used in the Danube catchment area. The selected Danube Sediment Priority (DSP) and High Priority (DSHP) chemicals were assessed in the second tier by a generic risk assessment methodology. The calculated Risk Quotient (RQ) characterise the risk of chemicals quantitatively and can be used for decision making. The third tier is the site specific quantitative risk assessment gives a more detailed picture on the risk for the site specific management of sediment pollution. Generic estimation of the concentration in Danube sediment was validated with site-specific measurements. Toxicity tests measure the sediment's adverse effects, together with the chemical analytical results characterise the toxicity buffering capacity and chemical time bomb fate of the sediments.

The sediment risk assessment methodology can be utilised in the sediment management practice, in planning a sediment monitoring-system, legislation, restrictions and remediation.

1. “Sediments and sentiments”

Sediments: 1. Suspended matter in surface waters, with large specific surface, functioning as an active surface for physico-chemical and biological processes and – amongst other – collecting sorbable contaminants; 2. rescuing the water phase from the harm of these pollutants; but 3. after piling up at sedimentation areas it represents a lower value habitat and 4. has long term potential for releasing the accumulated pollution into water and/or soil, 5. threatening the ecosystem and humans as a chemical time bomb.

Sentiments: 1. Scientist: sediments have high importance in aquatic structures, element cycles, many aquatic transport pathways ends up here. 2. Sentiments of human being: sediments’ time bomb fate endangers humans and human land uses, e.g. flooded areas. 3. Managers: continuous maintenance is necessary to keep river and lake bed quality, special waste-treatment and waste-utilising technologies are required for the management of dredged sediment. 4. Sentiments of the ecosystem: aquatic ecosystem has basic importance in global element cycles and in the keeping of ecological equilibrium, if they are injured/damaged, they cannot fulfil their task, which has serious consequences on all of the previous ones.

The risk of micropollutants in Danube sediment

The history of the production and use of chemicals and the fate of Danube sediment are strongly linked to each other. Every episode of the industrial development and decline of the 20th century has got imprinted into the historical layers of the river.

Sediments function as part of a highly adaptive and protective system of the global ecosystem, they lower the risk of chemicals in the water, preventing aquatic ecosystem. Fulfilling this function sediments are getting more and more damaged/deteriorated, representing tremendous secondary risk. To evaluate and characterise this risk scientists should answer many questions.

Which kind of and what quantity of risk are these? Appropriate quantitative risk assessment gives the correct answer.

Where is this risk accumulated? Sedimentation zones, natural sediment disposal areas, lakes and dead-arms of rivers are highly exposed.

How can we manage this risk? Firstly, we have to learn the nature and the fate of the different sediments, the interactions between sediments and pollutants, then we have to develop a complex tool for the long term solution by using eco-friendly sediment-management.

Research projects for the risk assessment of chemicals in Danube sediment

The results of two R&D projects will be summarised in this presentation. The risk of chemicals on Danube sediments was investigated between 1996 and 2001 with the participation of Budapest University of Technology and Economics (BUTE).

1. ECORISK: Ecological Risk Assessment of Pollution by Metals and Organic Micro-pollutants in the Danube catchment area (EU Phare, 101/91). Participants were Slovakia, Bulgaria, Czech Republic, Denmark and Hungary, and all the Danubian countries co-operated with country-specific information (Roncak et al, 1997).
2. ECOCHEMRISK: Ecological Risk Assessment of Heavy Metal Pollution in Danube Sediments: two Hungarian institutes: RISSAC (Research Institute for Soil Science and Agrochemistry) and BUTE (Gruiz et al, 1998).

The leading researchers of the two Danube sediment projects were: **Denmark:** Kristensen, P.; Pedersen, F.; Sören, B.; **Slovakia:** Roncak, P.; Murin, M; Borovickova, A.; Svobodová, Z.; **Hungary:** Murányi, A; Gruiz, K.; **Czech Republic:** Sucman, E.; **Bulgaria:** Machkova, M.; Ninov, P.; Velikov, B.

2. Risk Assessment framework: theoretical background

These two projects aimed at characterising and quantifying the risk of chemicals in the Danube sediment both at regional/catchment and local scale. Figure 1. shows the relation between environmental management and risk assessment.

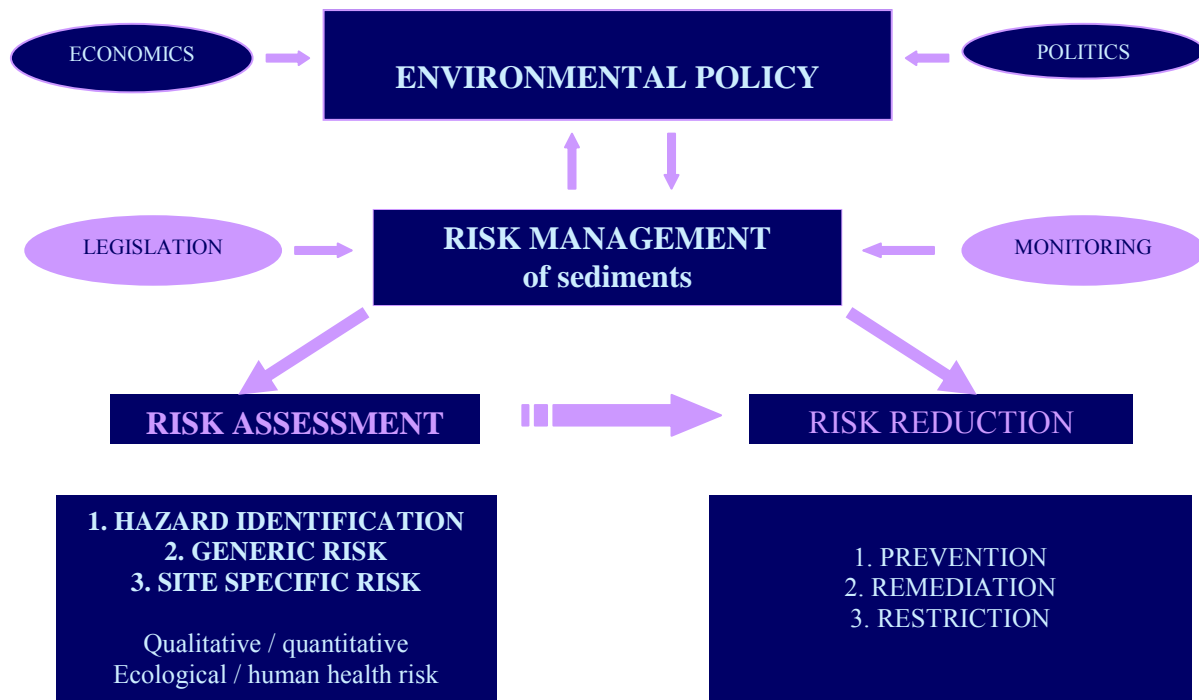


Figure 1. Relation between environmental management and risk assessment

Risk assessment of sediments is an important tool of environmental risk management. An optimal risk assessment procedure is a stepwise, iterative procedure, working on conservative basis. The tiered approach ensures cost-efficiency in risk assessment, because we can start with the few existing data, and exclude the negative cases after the first tier. Further data collection and detailed assessment is necessary only for the positive cases.

The methodology for risk characterisation has included three steps (ECORISK, 1999):

1. Initial hazard identification
2. Generic Risk Assessment
3. Site specific Risk Assessment

The basic concept both for generic and site specific risk assessment is demonstrated by the integrated risk model, which helps to follow the transport of the pollutants from the source and the exposure of the receptors relevant to land uses.

The general scheme of the integrated conceptual model is shown on Figure 2. It integrates the transport and the exposure model. The general model shows all the transport and exposure routes by arrows. The site-specific quantitative model includes site specific pathways and the width of the arrows symbolise the pollutant flux.

The quantitative risk of the ecosystem is given by the Risk Quotient (RQ), which is the ratio of the Predicted Environmental Concentration (PEC) and the Predicted No Effect Concentration (PNEC) as shown at Figure 3. The calculation of the RQ value is a stepwise, iterative procedure, starting with a minimal data-set and using conservative (pessimistic) estimation. This enables the exclusion of the negative cases/substances/sites if highly justified.

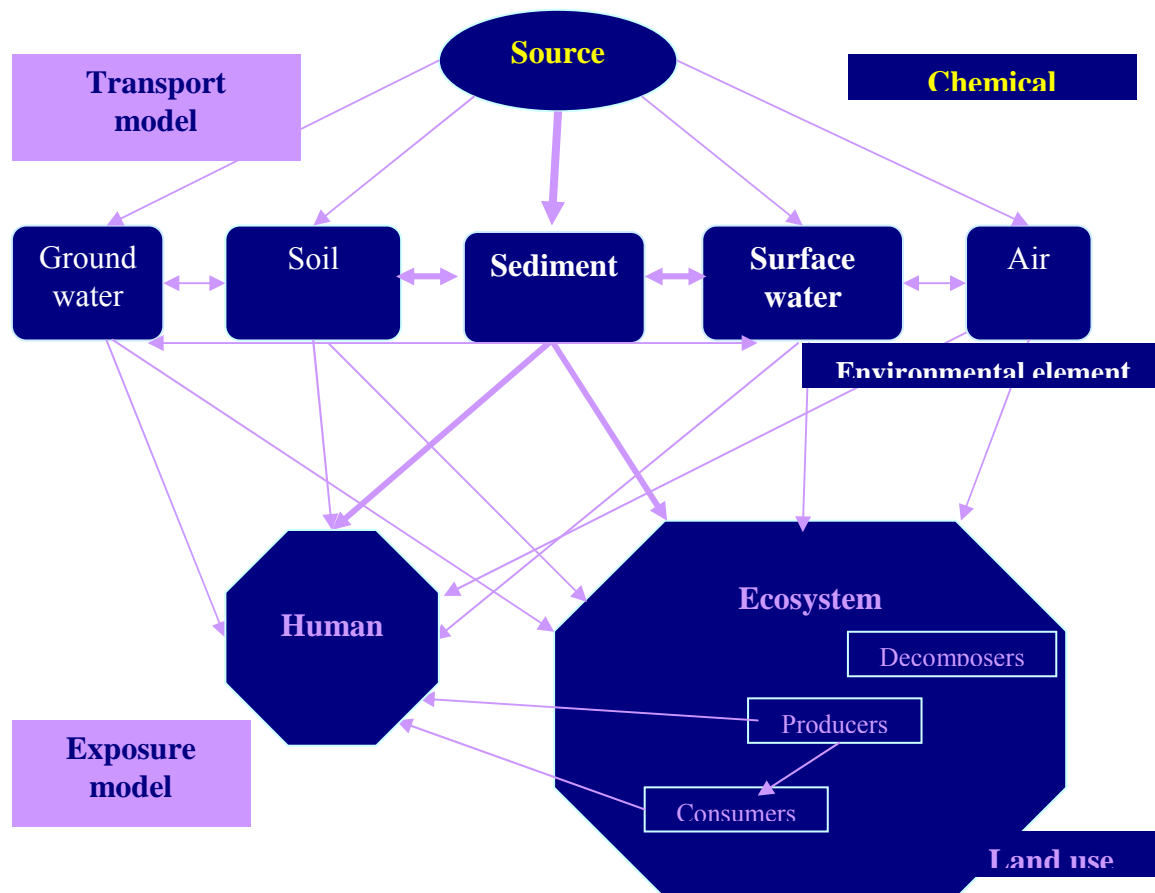


Figure 2. The integrated risk model

Similar to the RQ, which characterises the risk of the chemicals on the ecosystem, HQ, the human risk quotient is the ratio of the Average Daily Dose (ADD) calculated from PEC by the relevant exposure parameters and the Tolerable Daily Intake (TDI).

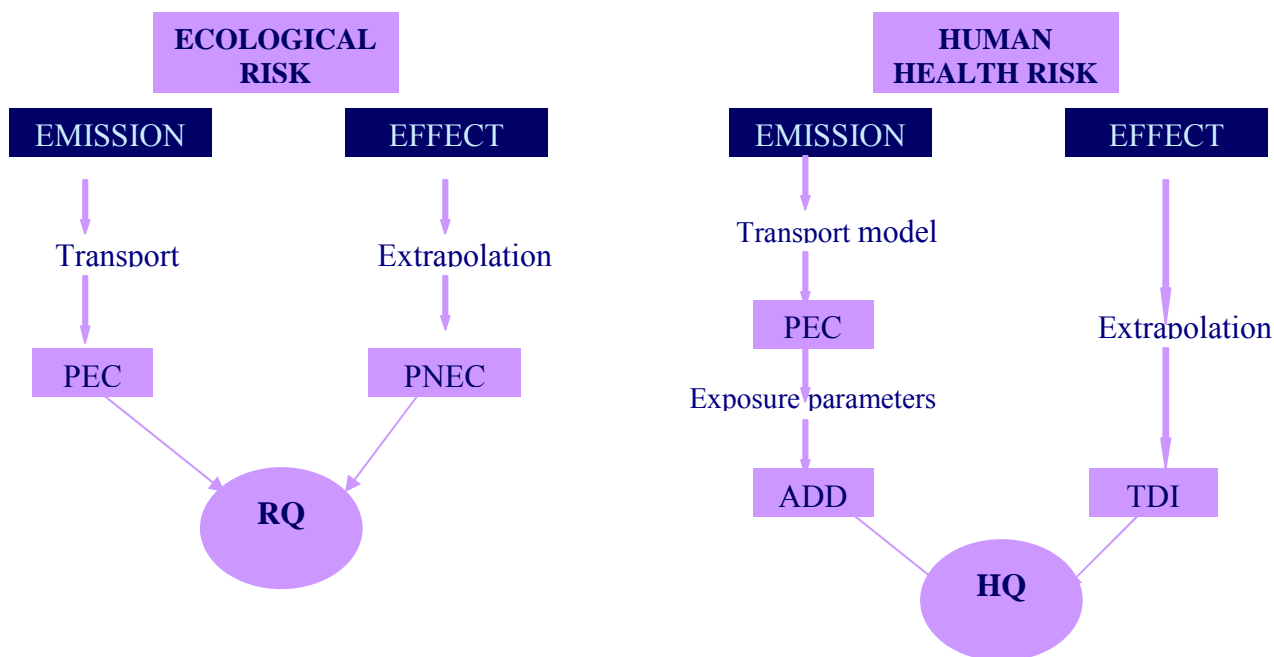


Figure 3. Quantitative characterisation of ecological and human health risk

3. Risk Assessment procedure for the Danube sediment

Initial hazard identification was a qualitative risk assessment, aiming priority setting for those chemicals, which are produced and used in the Danube catchment.

Generic risk assessment was a quantitative assessment, the result was given in the form of $RQ = PEC/PNEC$, the European default values were used in the calculations.

Site specific risk assessment used the PEC/PNEC approach too, but instead of default values the site specific measured concentrations and environmental parameters were used.

3.1. Initial hazard identification and priority setting

Suitable data are: 1. production and use, 2. Basic physico-chemical properties, mainly those, which characterise the environmental nature and fate of the chemical, like K_{ow} = octanol-water partition coefficient; K_p : solid-liquid partition (distribution) coefficient; water solubility, degradability. 3. Biological/ecotoxicological properties, like biodegradability, toxicity, bioaccumulation.

To find the most risky chemicals in the Danube catchment, three properties were taken into account: *partition, degradability* and *toxicity*.

3.2. Generic Risk Assessment

After having the ranking list of initial hazard assessment for the priority substances, a generic RA has been done: The $RQ_{generic}$ was calculated for each pollutant expected in the Danube-sediment based on generic exposure assessment (PEC) and effect assessment (PNEC).

Exposure assessment: After data collection the PEC was calculated by using the European default parameters (EU-TGD, 1996). Data for the exposure model: produced/used volume of the chemical substance, potential release during production and use, average water-flow in the Danube, suspended matter content in the Danube and average sedimentation rate.

The whole life-cycle of the chemical substance was taken into consideration, both statistical and measured data were used. The transport and environmental fate of the chemical was characterised in details. Main importance has the degradability (stability, persistence) of the chemical compound, degradation pathways and breakdown/transformation products, mainly if they are suspected to be persistent and toxic.

In case of a *generic risk assessment*, transport and fate models predict the behaviour of the contaminant under standard conditions, e.g. under the European default environmental parameters.

Effect assessment's result is the Predicted no Effect Concentration on the ecosystem (PNEC), which was created from toxicity data of aquatic/benthic test-organism or from any other effect based sediment quality criteria (SQC). The PNEC may be based on measured or calculated values. Minimum three single species from three different trophic levels should be tested and the data used for extrapolation to the whole benthic-ecosystem.

Default values: generic risk assessment works with default values. We created Danube specific default values or used the European recommendation EU-TGD (1996).

Generic risk values are quantitative risk values ($RQ_{generic}$) used for more precise priority setting, for the quantitative characterisation of the risk of chemicals on the Danube sediment and for decision making on the necessity of risk reduction. As a result, we created a "red list" of chemicals, relevant for the Danube sediment.

3.3. Site specific risk assessment

Site specific risk assessment uses site specific environmental parameters, – like flow rate, sedimentation rate, suspended matter – and the results of parallel physico-chemical and ecotoxicity data. Published sediment toxicity data were also collected and used to create PNEC values. Further details, like bioaccumulation, food-chain effects, secondary poisoning were taken into consideration. If no sediment data were available, water-data were used to estimate sediment-data on the basis of K_{ow} or K_d/K_p , partition between sediment phases (Gruiz et al 1997; 1998; 1999).

The main source of the methodological problems was the lack of measured and historical data, like production and use, the lack and the low quality (not standardised, not comparable) of monitoring data. At that time there was no water directive, due to different legal background in the EU countries, different strategies were used to ensure the quality of Danube water and sediment.

In spite of the above mentioned difficulties the following results were achieved: 1. Danube sediment specific-integrated methodology for priority setting, risk assessment and decision support. 2. “High priority” and “priority” list of chemicals representing hazard on the Danube sediment according to the initial qualitative hazard assessment. 2. Priority list based on quantitative risk values as a result of generic risk assessment; 3. Site specific risk values of some target chemicals at selected sedimentation areas.

4. Results

4.1. Danube-specific priority list of sediment-specific microcontaminants

Three properties partition, – degradability and toxicity – were taken into account to find the most risky organic and inorganic chemicals by the initial hazard assessment (ECORISK, 1999)

1. Partition between solid and liquid phase, which determines the sorption of the chemicals on the sediment particles.

For organics: $K_d = C_s/C_w = f_{oc} \times K_{oc}$

C_s : concentration of the sorbed contaminant on sediment particles; C_w : dissolved concentration in the equilibrium water phase (pore water); f_{oc} : organic matter; K_{oc} : distribution coefficient between particulate organic carbon and water. K_{oc} can be calculated from the K_{ow} (octanol-water partition coefficient). By a conservative estimation $K_{oc} = K_{ow}$ (always smaller).

Mass balance: $M_{total} = SS \times C_s + W \times C_w = (SS \times f_{oc} \times K_{ow} + W) \times C_w$

SS = suspended matter, which for the Danube is: 25–32 mg/l (SK), 38 mg/l (HU), 67 mg/l (SK).

Organic content: $f_{oc} = 44\text{--}50\%$, from this the carbon content is 40%, equal with 18–20 % of SS.

We calculated with 67 mg/litre.

Cut off value: $\log K_{ow} \geq 4.5$. It means that more than 10 % of the contaminant is bound to the SS. The partition is: $9 \times SS \times C_s = W \times C_w$

For inorganics: $K_p = C_s/C_w$ Binding capacity, like clay content of the sediment influences the K_p value.

Cut off criteria: more, that 10 % of the contaminant is bound to SS:

$W / (9 \times SS) = 1/9 \times 67 \times 10^{-6} = 1700 \text{ lit/kg}$.

If no data on sorption are available, we can use water solubility data. Cut-off value in water is determined by the solubility: 1 mg/litre.

2. Degradability: biodegradation, hydrolyses and photo-degradation was included. For initial RA an arbitrary cut-off value has been selected: a.) readily degradable: (EU-TGD): half-life

time of 15 days; b.) not readily biodegradable: >15 days. If no data on biodegradability are available we can calculate it directly from the chemical structure with QSAR.

3. Toxicity: risk of chemicals is dominantly due to their harmful effects, so that a cut-off value for toxicity was included in the initial phase. Toxicity data for sediment are rare, so aquatic toxicity data were also used instead.

Cut-off values for organics 1 mg/l for chemical with $\log K_{ow} < 4.5$ and $M_w = 200$
10–20 mg/l for chemicals with $\log K_{ow} = 3$ and $M_w = 200$.

Cut-off values for inorganics 1 mg/l.

4. Selection procedure: different criteria setting was applied to select the chemicals for the “Danube Sediment High Priority List” and the “Danube Sediment Priority List”.

Criteria for “**High Priority List**”:

$\log K_{ow} > 4.5$ for organics; $K_d > 1700$ l/kg, $S_w < 1$ mg/l

Degradation half-life: >15 days

Acute toxicity for aquatic species: < 1 mg/l.

Criteria for “**Priority List**”:

$3 < \log K_{ow} < 4.5$ for organics; $100 < K_d < 1700$ l/kg,

7 days < degradation half-life > 15 days

1 mg/l < acute toxicity for aquatic species: < 100 mg/l.

Data collection, characteristics of the substances from databases with environmental aspect: CHEMBANK, IRIS, Richardson (1993), etc. Data requirement: K_{ow} , K_d , solubility in water, degradability, acute toxicity. The relevant substances were included from: Bavaria, Austria, Czech Republic, Slovakia, Hungary, Romania, Bulgaria, Moldova, Ukraine. Important: we started from national-level data, from the most relevant data-set.

Result: 701 substances were collected and put on the gross list identified by their CAS number (Chemical Abstract Registration Number).

| | Initial | Revised | RQ |
|--|--|---------|------|
| DSHPL: Danube Sediment High Priority List: | 44 (-8, +10) | 46 | + 20 |
| DSPL: Danube Sediment Priority List: | 102 | | |
| Non-Sediment Priority Chemicals List: | 421 | | |
| Waiting list: | 134 (not enough data in the first phase) | | |
| Total | 701 | | |

After the initial phase 36 chemicals were on the waiting list, waiting for more data collection and evaluation. After the first revision 8 were excluded from DSHPL, but an other 10 were added, so the final number of the DSHP chemicals is 46. After the quantitative assessment 20 of the chemicals on DSPL were placed on DSHPL.

Comparing these numbers with other priority lists: Danube River convention includes 40 chemicals: 23 of these did not get in our DSHPL or DSPL list.

The EU list (Dir. 76/464) of chemicals hazardous for aquatic environment includes 141 chemicals. Only 20 of these are included in our DSHPL or DSPL.

Differences prove, that the sediment-specific priority list differs from the water-priority list!

4.2. Generic risk assessment: quantitative risk of Danube Sediment Priority chemicals

Exposure (PEC) and effect (PNEC) assessment has been done, and $RQ_{generic}$ was calculated as a ratio of PEC and PNEC.

Exposure assessment required the collection of data on the production and use (whole life cycle!) of chemicals from all European Danubian countries. For the exposure assessment the emission to the surface waters was estimated in the Danube catchment area. For the estimation

of the concentration in the sediment, the emission was modified according to the environmental fate characteristics (partition, degradation). Methodology based on EU-TGD (1996).

Exposure assessment for generic risk assessment requires the following data:

T = tonnage: produced and used tonnage in the catchment area; production volumes (EU list), import and export statistics, use of chemicals by public (fuel, household chemicals, etc.), industry and ministry data;

f_w: fraction of tonnage released into river water: the release from production and use has been estimated on the basis of EU-TGD (1996), according to use-patterns:

| | |
|--|----------------------------|
| Use in closed system | f _{water} 0.01 |
| Use resulting in inclusion into matrix | 0.1 |
| Non-dispersive use | 0.2 |
| Dispersive use | 1.0 |

Fate of chemicals after emission is considered by the following parameters:

Dilution was calculated with the Q = average annual flow of Danube: 2044 m³/sec.

Degradation rate by a rough estimation: f_{degr water}: 0.1 for readily degradable chemicals; 0.5: for inherently degradable and 1.0 for persistent chemicals.

From the first order biodegradation rate constant the half-life times are the following: 15 days for the readily degradable chemicals; 50–150 for inherently degradable ones and infinite for persistent chemicals.

Sorption is characterised by the K_d for inorganic and the K_p for organic compounds.

Calculation of the concentration in the sediment: $PEC_{\text{sediment}} = K_p \times PEC_{\text{water}}$;

$K_{p \text{ susp}} = f_{oc} \times K_{oc}$; $PEC_{\text{water}} = \text{Tonnage} \times f_{\text{water}} \times f_{\text{degr}} / Q$

Effect assessment was done by the estimation of the PNEC value from ecotoxicity data or by using effect based sediment quality criteria, SQC (VROM, 1993–94).

Two different models/approaches were applied:

1. Estimation from water toxicity data using the partition coefficient: $SQC = K_d \times WQC$.
2. Extrapolation from the results of acute and chronic laboratory bioassay using the results of minimum of three toxicity tests of testorganisms from 3 different trophic levels by the method of factorial extrapolation.

The data collected for generic risk assessment were summarised for each Danube-relevant priority chemical. One of these chemicals, the trifluralin, a pesticide, is shown in the sheet of Table 1.

The results of the generic risk assessment can be seen in Table 2. The quantitative risk assessment was carried out on those chemicals which were put on the DSHP or DSP list prepared by the initial qualitative risk assessment. The result of the generic risk assessment is shown in Table 2. and Table 3: the quantitative risk quotient. $RQ = PEC / PNEC$ of the “High Priority” and “Priority” chemicals which potentially pollute the Danube sediment.

Table 1. **ECORISK (1999) data sheet for risk assessment of chemicals in Danube sediment)**

| Substance: Trifluralin | | CAS No.:1582-09-8 | |
|--|------------------|--|----------------|
| Use pattern (EU-TGD) Industrial category: (0-16) | | Use category: (No. 0-54): pesticide | |
| Tonnage (tons/year) | | Release factors | |
| <i>Production:</i> | | F _{water} [-]: | |
| HU: 184 (1993) | HU: 114 (1996) | 0,02 (production) | |
| <i>Use:</i> | | 0,02 (formulation) | |
| BG: 30 (1996) | Cz: 31 (1996) | 0.1 (use) | |
| Mo: 62 (1996) | HU: 254 (1996) | 0,06 (STP) | |
| AUS: 12 (1996) | BRD: 16 (1996) | | |
| Physico-chemical properties | | | |
| Molar weight [g/mol]: 335,3 | | Water solubility [mg/l]: 0,2 | |
| Vapour pressure [Pa]: 0,10 | | log P _{ow} [-]: 4,8–5,3 | |
| Henry's law constant [-]: | | Sorption coeff., K _d [l/kg]: 57,0–126,0 | |
| Henry's law const. [Pa·m ³ /mol]: 144,1 | | (type of solid - pH, %OC) (OC varied between 0,5 and 2) | |
| Fate related properties | | | |
| Biodegradability: Inherently biodegradable | | Biodeg. half-life [days]: 57,0–126,0 | |
| BCF [-]: 1060,0–6000,0 | | Anaerobic half-life [days]: - | |
| | | Hydrolysis half-life [days]: - | |
| Toxicity to pelagic organisms | | | |
| Organism | Effect parameter | Concentration range [mg/l] | No. of species |
| Algae | EC50 | 2,5– | 1 |
| Crustacean | LC50 | 0,05–12,0 | 9 |
| Crustacean | NOEC | 0,004– | 1 |
| Fish | LC50 | 0,010–1,0 | 6 |
| Fish | LOEC | 0,005 | 2 |
| Fish | NOEC | 0,001 | 2 |
| Water Quality Criteria / PNEC _{aquatic} [mg/l]: 0,0001 | | | |
| Toxicity to sediment organisms | | | |
| Organism | Effect parameter | Concentration range [mg/kg] | No of species |
| Insect | EC50 (96 hr) | 3,0– | 1 |
| Crustacean | EC50 | 0,6– | 1 |
| Other | EC50 (96 hr) | 0,6– | 1 |
| Sediment Quality Criteria / PNEC _{sediment} [mg/kg]: not realistic to estimate from measured data | | | |
| PNEC _{sediment} [mg/kg]: from water WQC using K _d partition coefficient: 0,1–0,2 | | | |
| Generic risk assessment | | | |
| Fdeg _{water} [-]: 0,5 | | Foc [-]: 0,2 | |
| Koc [l/kg]: 6 500,0–13 400,0 | | | |
| PEC _{regional} _{water} [mg/l]: 0,0003 | | PEC _{regional} _{sediment} [mg/kg]: 0,4–0,8 | |
| Risk characterization (RQ) [-]: 1,4–3,2 | | | |
| References: | | | |
| Lyman W., W.F.Reehl and D.H.Rosenblatt: Handbook of Chem. Property Estimation Methods, McGraw-Hill Book Co. 1982 | | | |
| The Pesticide Manual, Ed. C. Tomlin, Tenth Edition, Bath Press, Bath, 1995 | | | |
| Verschuieren K.: Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Co., N. Y. 1983 | | | |
| Danish Ministry of Energy Environmenat, Order No. 921/1996 | | | |

Table 2. Risk Quotient of the Danube Sediment High Priority Chemicals

| DSHP chemical's name | RQ | DSHP chemical's name | RQ |
|------------------------------|---------|--|------------|
| Methoxichlor | 343–724 | Fluoranthene | 0,36 |
| DHTDMAC (cationic detergent) | 55 | Bromopropylate | 0,1–0,3 |
| Bis (2-ethylhexil) phthalate | 33 | Dicofol | 0,1–0,2 |
| Cypermethrin | 28 | Zinc | 0,16 |
| Dibutylphthalate | 25 | Bis (2-ethylhexil) adipate | 0,1 |
| Pendimethalin | 1,6–3,2 | Lead | 0,05 |
| Trifluralin | 1,4–3,2 | Pencycuron | 0,05 |
| Propargite | 0,5–2,5 | DDT (dichlorodiphenyltrichloroethane) | <0,05 |
| Cyhalotrin | 2,3 | Dieldrin | <0,05 |
| HCH isomers | 0,5–1,5 | Ethalfuralin | 0,01–0,03 |
| N-Phenyl-2-naphtylamin | 1,7 | Aldrin | 0,001–0,03 |
| Oxifluorphen | 0,1–1,4 | Pyridate | 0,007 |
| Cadmium | 1,3 | Heptachlor | <0,005 |
| Endrin | 1,2 | Heptachlor-epoxid | <0,004 |
| MDI | 1,0 | Pentachlorophenol | <0,001 |
| Copper | 0,9 | Benzo(a)piren | no data |
| Mercury | 0,8 | DDD (dichlorodiphenyldichloroethane) | no data |
| PCB | <0,75 | DDE (dichlorodiphenyldichloroethylene) | no data |
| Nickel | 0,65 | Hexachlorobenzene | no data |
| Benfluralin | 0,64 | | |

We can see from Table 2. that some of the substances on the initial DSHP list have high quantitative risk, others negligible. The main reason of the differences between initial and quantitative generic risk assessment is, that the latter considers the volume of production and use.

Interpretation of the RQ values: <0,001: negligible risk 0,001–0,1: low risk
 0,1–1,0: slight risk 1–10: high risk >10: very high risk

Table 3. Risk Quotient of the Danube Sediment Priority Chemicals

| DSP chemical's name | RQ | DSP chemical's name | RQ |
|--|----------|---------------------------|-----------|
| NPEO (anionic detergent) | 219 | | |
| Fenarimol | 9,9–78,3 | HCH isomers | 0,5–1,5 |
| Bifenoxy | 0,5–30 | Fenvalerate | 1,0 |
| Kerosene | 0,16–16 | PCB | <0,75 |
| N-izopropyl-N'-phenyl-p-phenylenediamine | 8,8 | Alachlor | 0,1 |
| Metolachlor | 5,0 | 1-Methylnaphtalen | no data |
| Ethylbenzene | 4,9 | 2,3,4,6-Tetrachlorophenol | no data |
| N-cyclohexyl-2-benzothiazole-sulfen | 4,8 | 2,6-Dibromo-4-nitrophenol | no data |
| Endosulfan | 4,0–4,5 | Acenaphthene | no data |
| Diflubenzuron | 3,3 | PAHs | no data e |
| Lindane (gamma HCH) | <3 | | |

After the generic risk assessment we have got 25 chemicals, which have high or very high risk on Danube sediment and a further 15 substances, which have slight risk. We have got some risky chemicals on our waiting list, which have not been evaluated yet.

4.3. Site specific risk assessment of chemicals at sedimentation sites of river Danube

Some of the most risky chemicals were analysed from sediment samples taken from sedimentation zones of the Danube river catchment. One sampling site was in Slovakia, close to Zilina, at Hricov Reservoir, the other in Hungary, South from Budapest, a baylet used for fishing in the Ráckeve-Soroksár Danube Arm (RSD).

Sediment samples were tested by an integrated methodology: the physico-chemical analyses were complemented with ecotoxicity testing. The evaluation of the results makes possible a risk related interpretation. Ecotoxicity results integrate in their result the interactions between chemicals (synergism, antagonism), between contaminant and sediment matrix (mobility, availability, bioavailability) and the biota and the contaminant : effects of biodegradation, biotransformation, bioaccumulation, food chain effects (Ahlf and Wild-Metzko, 1991; Calow, 1993; Gruiz and Vodicska, 1993; Gruiz et al, 2001).

The ten sampling sites at Hricov reservoir and the 5 at RSD Danube Arm were tested by 8 different toxicity tests for pore water and whole sediment. Toxicity testing indicates analytically not measurable chemicals by their adverse effects, or those, which were not included into the analytical programme. Ecotoxicity testing gives additional information about mobility and availability of the chemicals.

Table 4. RQ values of generic and local risk assessment for the Danube sediment

| Name of the pollutant | Hricov Slovakia µg/kg | RSD Budapest µg/kg | PNEC or SQC µg/kg | RQ _{local} | RQ _{generic} |
|------------------------------|--------------------------|-----------------------|----------------------|---------------------|-----------------------|
| Bifenox | 30 | | 20 | 15 | 0,5–30 |
| Br-propylate | 11 | | 400 | 0,027 | 0,1–0,3 |
| Cyhalotrin | | 153 | 30 | 5,1 | 2,3 |
| Cypermethrin | 361 | | 8 | 45 | 27,6 |
| Bis (2-ethylhexyl) adipate | 300 | | 60 000 | 0,005 | 0,1 |
| Bis (2-Ethylhexyl) phthalate | 1580 | 1439 | 30 000 | 0,05 | 33 |
| Alfa-HCH | 1,34 | 1,15 | 2 | 0,6 | 0,1–1,5* |
| Beta-HCH | 115 | | 2 | 55 | 0,1–1,5* |
| Gamma-HCH | 1,38 | 0,93 | 2 | 0,6 | 0,1–1,5* |
| Delta-HCH | | 0,15 | 2 | 0,075 | 0,1–1,5* |
| 2,6-Dibromo-4-nitrophenol | | 3491 | 400 | 8,7 | no data |
| Dibutyl-phthalate | 879 | 1108 | 120 | 7,3–9,2 | 25 |
| Diphenyl-amin | 1180 | 1122 | 400 | 2,9–2,8 | 0,25 |
| Endosulfan | 43 | 76 | 2 | 21–38 | 4,0–4,5 |
| Fenarimol | 121 | | 80 | 1,5 | 9,9–78,3 |
| Fenvalerate | 1858 | 4060 | 9 | 206–451 | 1,0 |
| Heptachlor | 75 | 160 | 500 | 0,15–0,32 | <0,005 |
| Heptachlor-epoxid | | 266 | 500 | 0,53 | <0,004 |
| Hexachlorobenzene | 530 | 257 | 50 | 10,6–5,1 | no data |
| Methoxychlor | 70,6 | 34,2 | 1 | 70,6–34,2 | 343–724 |
| Metolachlor | | 215,6 | 6 | 36 | 5 |
| Nonylphenol | | 48,8 | 100 | 0,49 | no data |
| NPEO | no data | no data | 100 | | 219 |
| N-Phenyl-2-naphthylamine | 556 | 165 | 480 | 1,16–0,3 | 1,7 |
| Pendimethalin | 199 | 178 | 300 | 0,66–0,59 | 1,6–3,2 |
| Propargite | 83 | | 200 | 0,4 | 0,5–2,5 |
| 2,3,4,6-Tetrachlorophenol | 102 | 88 | 4000 | 0,02 | no data |
| Total PAH | 2990 | 455 | 40 | 75–11,4 | no data |
| Total PCB | 313 | 726 | 20 | 15,6–36 | <0,75 |

* generic risk was calculated for total HCH

Table 4. shows the chemical-analytical results of some priority chemicals in Hricov- and in RSD-sediment, the assessed RQ_{generic} and the RQ_{local} calculated from measured data.

We selected and put into the table the highest measured data of 10 samples from Hricov Reservoir and 5 of RSD Danube-arm for creating RQ_{local}. In some cases local and generic risk values agree well, mainly for those chemicals, which have widespread use in the Danube

catchment. Differences between generic and site specific RQ highlights locally different production and use patterns. In some cases the generic risk is lower, than the site specific, due to local production or use. If generic risk is much higher, than the site specific one, and the lack of local production and use does not confirm this difference, it is worth to control the generic risk value and repeat the assessment with more precise input data. In this case additional testing of sediment samples is also recommended for the validation of the generic RQ value.

4.4. Assessment of toxic metals from Danube sediment along the river

A detailed site specific assessment was made for toxic metals in Danube sediment. Some data are shown below to demonstrate the importance of monitoring and risk assessment of sediments.

Table 5. Monitoring data of copper in Danube water and sediment (1995)

| Sampling site Danube river km | C _{Cu water} (µg/l) | C _{Cu sediment} (mg/l) | K _{sed/waterCu} (l/g) |
|----------------------------------|---------------------------------|------------------------------------|-----------------------------------|
| 1848.4 | 22.5 | 22.9 | 1.0 |
| 1806.2 | 23.4 | 2.5 | 1.0 |
| 1802.0 | 24.6 | 39.0 | 1.6 |
| 1761.0 | 27.9 | 50.0 | 1.8 |
| 1717.0 | 24.6 | 21.9 | 0.9 |
| 1707.0 | 4.2 | 43.0 | 10.2 |
| 1659.0 | 2.9 | 47.0 | 16.2 |
| 1560.0 | 2.0 | no data | |
| 1479.0 | 2.1 | no data | |

Copper as an example draws our attention to the partition of metals between water and sediment, and on the fact that there is no equilibrium between water and sediment concentrations.

Copper (similar to not shown toxic metals, like Cd, Cr, Ni, Pb, Zn) shows high concentration from the entering (to Hungary) down to Esztergom (cca. 1700 river km) but downstream Visegrád the metal content decreases significantly. In spite of the high metal concentration of the water, the sediment is below the Holland MPC value or the very strict Canadian TEL values. It means, that the sediment has lower heavy metal concentration than the theoretical equilibrium (which could be calculated by a $K_p = 50$ lit/g, as recommended by WQDB). It clearly indicates, that there is no equilibrium between Danube water and sediment and the toxic metal binding capacity of the sediment is not saturated. It can be seen from the growing metal concentration in the sediment parallel to the decreasing concentration in the water.

The high “toxicity buffering” capacity of the Danube sediment ensures the relatively good quality of the water. But on long term, the Danube sediment will be saturated and functioning as a chemical time bomb (Gruiz et al, 2000).

Seventeen sedimentation areas were identified, mainly upstream Budapest, between 1811 and 1586 river km and the metal contents of sediment samples were determined by HF digestion (total metal content) and BCR sequential extraction (mobile fractions). The concentrations were measured by ICP-AES. Ecotoxicity was measured by three bacterial and one plant bioassay. Chemical and ecotoxicological results are studied and evaluated together.

In Table 6. the basic sediment characteristics are summarised, like humus and clay content.

Table 7. contains the toxic metal data: instead of the total metal content, the difference of the measured and the limit value was calculated, showing the risky excess.

In Table 8. the results of sequential extraction are summarised. Sediments differ from each other in the distribution of the acidic, reducible and oxidisable fractions (Ure et al, 1993).

In Table 9. we compare the chemical analytical results and ecotoxicity data of the sediments.

Table 6. Basic sediment characteristics along the river Danube

| River | Site location | River km | CaCO ₃ | humus | Mechanical composition | | |
|-------------------|------------------------|-------------|-------------------|-------|------------------------|------|------|
| | | | | | Sand | Silt | Clay |
| | | | % | % | % | % | % |
| Danube | Szap | 1811 | 20.5 | 2.4 | 22.8 | 66.1 | 11.0 |
| Danube | Medve right | 1802 | 14.5 | 0.2 | 92.0 | 5.6 | 2.5 |
| Moson Danube Arm | Vének left 2 km | 1794 | 6.5 | 3.2 | 39.0 | 42.8 | 18.2 |
| Moson Danube Arm | Vének right 2 km | 1794 | 11.0 | 1.3 | 79.0 | 14.9 | 6.1 |
| Conco creek | Ács 2 km | 1777 | 23.0 | 3.5 | 48.6 | 36.1 | 15.3 |
| Danube | Upstream Komárom | 1770 | 16.0 | 0.7 | 85.5 | 10.2 | 4.4 |
| Danube | Downstr. Komárom | 1761 | 14.0 | 2.0 | 74.1 | 18.2 | 7.7 |
| Átalér creek | Mouth 1.5 km | 1750 | 16.5 | 1.5 | 84.0 | 10.3 | 5.7 |
| Kenyérmezei creek | Mouth 1 km | 1722 | 19.0 | 4.2 | 23.2 | 55.3 | 21.5 |
| Danube | Esztergom | 1716 | 23.5 | 4.3 | 42. | 45.2 | 12.9 |
| Danube | Basaharc | 1707 | 21.5 | 3.3 | 46.0 | 44.3 | 10.0 |
| Danube | Visegrád | 1694 | 16.5 | 2.2 | 52.5 | 38.5 | 9.1 |
| Danube | Pünkösdfürdő | 1658 | 19.5 | 2.2 | 72.7 | 22.4 | 5.0 |
| Danube | M0 Bridge left | 1632 | 17.5 | 1.5 | 78.1 | 15.7 | 6.2 |
| Danube | M0 Bridge right | 1632 | 21.5 | 2.2 | 65.5 | 27.4 | 7.1 |
| RSD Danube Arm | Gubacsi Bridge 53.9 km | 1586 | 22.0 | 1.0 | 96.3 | 2.8 | 0.8 |
| RSD Danube Arm | VITUKI 57.3 km | 1586 | 17.7 | 0.8 | 42.5 | 46.0 | 11.5 |

Organic and mineral composition of the sediments differs markedly. The contaminant concentration is in correlation with the basic sediment composition: sandy sediments do not adsorb big amount of pollutants, but the clayey and silty sediments bind considerable amount of toxic metals. Sediments with high humus-content, like Vének, Kenyérmezei creek inflow or Esztergom have high organic pollutant concentration (not shown here).

The pollution is not in correlation with the local source (emission) but with the sediment's organo-mineral composition; it explains that the processes of binding of pollutants to suspended matter and the sedimentation of this material are not closely associated with each other.

Table 7. Toxic metal excess(total – limit value) in Danube sediments along the river

| River | Site location | River km | Excess heavy metal contents (ppm) | | | | | | | Σ + |
|--------------|-----------------|-------------|-----------------------------------|-------|--------|--------|--------|--------|--------|------------|
| | | | Cd | Co | Cr | Cu | Ni | Pb | Zn | |
| Danube | Szap | 1811 | -0.19 | 3.8 | -4.33 | 13.71 | 17.85 | -34.81 | 21.99 | 57 |
| Danube | Medve right | 1802 | -0.27 | 1.17 | -33.92 | -15.87 | -2.39 | 3.63 | -5.65 | 5 |
| Moson D. Arm | Vének left 2 km | 1794 | 0.09 | 3.11 | -21.85 | 3.76 | 5.59 | -47.79 | 31.71 | 44 |
| Moson D. Arm | Vének right 2km | 1794 | 0.32 | 2.22 | -31.97 | -10.50 | -2.60 | -44.01 | -6.58 | 2 |
| Conco creek | Ács 2 km | 1777 | -0.41 | -5.03 | -53.37 | -12.57 | -10.03 | -57.35 | -44.26 | (-) |
| Danube | Upstr. Komárom | 1770 | -0.29 | 1.53 | -32.93 | -13.90 | -3.21 | -44.75 | -12.18 | 1.5 |
| Danube | Dwnstr. Komárom | 1761 | -0.25 | -0.50 | -35.43 | -10.55 | -2.61 | -37.07 | 3.91 | 4 |
| Átalér creek | Mouth 1.5 km | 1750 | -0.25 | -0.24 | -32.89 | -12.34 | -8.70 | -36.75 | 3.54 | 3.5 |
| Kenyérmezei | Mouth 1km | 1722 | 3.18 | -1.49 | -30.67 | 162.74 | 8.28 | -44.53 | 40.69 | 215 |
| Danube | Esztergom | 1716 | -0.29 | 1.20 | -27.78 | -3.36 | 1.45 | -21.07 | 49.67 | 52 |
| Danube | Basaharc | 1707 | -0.27 | 2.68 | -25.23 | -3.25 | 3.65 | -46.89 | 37.71 | 44 |
| Danube | Visegrád | 1694 | -0.33 | 2.76 | -27.67 | -4.80 | 2.22 | -43.95 | 26.53 | 31 |
| Danube | Pünkösdfürdő | 1658 | -0.22 | 3.70 | -29.03 | -7.52 | 2.74 | -41.09 | 29.16 | 36 |
| Danube | M0 Bridge left | 1632 | -0.16 | 2.33 | -24.79 | 2.13 | 0.72 | -33.69 | 57.37 | 63 |
| Danube | M0 Bridge right | 1632 | -0.10 | 2.21 | -27.11 | 3.70 | 2.74 | -27.87 | 52.80 | 62 |
| RSD Danube | Gubacsi Bridge | 1586 | 0.20 | -2.84 | 12.43 | -3.20 | -1.61 | 175.19 | 15.25 | 203 |

| | | | | | | | | | | |
|------------|----------------|------|-------|------|-------|-------|-------|------|-------|------------|
| RSD Danube | VITUKI 57.3 km | 1586 | -0.18 | 4.24 | 10.94 | 36.07 | 17.52 | 8.40 | 200.6 | 278 |
|------------|----------------|------|-------|------|-------|-------|-------|------|-------|------------|

Table 8. **The BCR Sequential Extraction of Cr, Cu, Ni, Pb from Danube sediments**

| River | Site location | River km | BCR fractions – Sum of Cr+Cu+Ni+Pb [ppm oven dry sediment] | | | |
|--------------|------------------|----------|---|--------------|----------------|----------|
| | | | I. acidic | II.reducible | III.oxidisable | Sum of 3 |
| Danube | Szap | 1811 | 8 | 4 | 41 | 53 |
| Danube | Medve right | 1802 | 12 | 29 | 15 | 56 |
| Moson D Arm | Vének left 2 km | 1794 | 11 | 19 | 25 | 55 |
| Moson D Arm | Vének right 2 km | 1794 | - | - | - | - |
| Conco creek | Ács 2 km | 1777 | 8 | 4 | 20 | 32 |
| Danube | Upstr. Komárom | 1770 | - | - | - | - |
| Danube | Downstr. Komárom | 1761 | 8 | 17 | 18 | 43 |
| Átalér creek | Mouth, 1.5 km | 1750 | - | - | - | - |
| Kenyérmezei | Mouth 1km | 1722 | 24 | 10 | 172 | 206 |
| Danube | Esztergom | 1716 | 10 | 4 | 59 | 73 |
| Danube | Basaharc | 1707 | 10 | 5 | 36 | 51 |
| Danube | Visegrád | 1694 | 9 | 5 | 28 | 42 |
| Danube | Pünkösdfürdő | 1658 | 8 | 4 | 26 | 38 |
| Danube | M0 Bridge left | 1632 | 9 | 6 | 36 | 51 |
| Danube | M0 Bridge right | 1632 | 7 | 5 | 40 | 52 |
| RSD D. Arm | Gubacsi Bridge | 1586 | 39 | 136 | 271 | 446 |
| RSD D. Arm | VITUKI, 57.3 km | 1586 | 17 | 5 | 136 | 158 |

Table 9. **Comparison of the chemical and the ecotoxicity data of Danube sediment**

| River | Site location | River km | Comparison of chemical and ecotoxicity data | | |
|----------------|----------------------|----------|---|-------------------|--|
| | | | Sum of excess metal mg/kg | Clay content % | Toxicity: average of EC20 and EC50 g sediment |
| Danube | Szap | 1811 | 57 | 11 | 25 |
| Danube | Medve right | 1802 | 5 | 2.5 | >42 |
| Moson D. Arm | Vének left 2 km | 1794 | 44 | 18 | 15 (+ org.) |
| Moson D. Arm | Vének right 2 km | 1794 | 2 | 6 | >39 |
| Conco creek | Ács 2 km | 1777 | 0 | 15 | >50 |
| Danube | Upstr. Komárom | 1770 | 1.5 | 4 | >38 |
| Danube | Downstr. Komárom | 1761 | 4 | 8 | 35 |
| Átalér creek | Mouth 1.5 km | 1750 | 3.5 | 6 | >50 |
| Kenyérmezei | Mouth 1km | 1722 | 215 | 21 | 1.5 |
| Danube | Esztergom | 1716 | 52 | 13 | 26 |
| Danube | Basaharc | 1707 | 44 | 10 | 26 |
| Danube | Visegrád | 1694 | 31 | 9 | 28 |
| Danube | Pünkösdfürdő | 1658 | 36 | 5 | >50 |
| Danube | M0 Bridge left | 1632 | 63 | 6 | 33 |
| Danube | M0 Bridge right | 1632 | 62 | 7 | 27 |
| RSD Danube Arm | Gubacsi Bridge, 53,9 | 1586 | 203 | 1 | 5.5 |
| RSD Danube Arm | VITUKI, 57.3km | 1586 | 277 | 12 | 7.5 |

Metal-contaminated sediments have got high toxicity. High clay content binds toxicant strongly, so bioavailability and toxicity is relatively lower, than indicated by the chemical analytical results. If toxicity is high, but the toxic metal content measured by chemical analyses is low, the toxic effect derives from non-metallic compounds. The Danube sediment samples from downstream Komárom were analysed for organic pollutants, and the results have shown high PAH and PCB content (100xSQC).

Metals in the sediment are not only toxic, but they can get into the food chain by bioaccumulation. The bioconcentration factor (BCF) gives the ratio of the toxic chemical in the organism and the environmental element, showing the uptake and the rate of concentration.

$$BCF_{\text{plant}} = C_{\text{plant}} / C_{\text{soil}}$$

$$BCF_{\text{mussel}} = C_{\text{mussel}} / C_{\text{sediment}}$$

Table 10. **Mussels for the testing of bioaccumulation of toxic metals**

| Date of placing mussels out | Site | River km | Flow rate m/s | Depth m | Mussel piece |
|-----------------------------|-----------------------------|----------|---------------|---------|--------------|
| 12. 09. 1996 | Vének, Danube | 1794 | 0.2 | 2.2 | 16 |
| 12. 09. 1996 | Vének, Mosoni Danube 2km | 1794 | 0.2 | 2.1 | 16 |
| 12. 09. 1996 | Mouth of Kenyérmezei Creek | 1722 | 0.4 | 1.7 | 15 |
| 12. 09. 1996 | Mouth of Soroksári Dan. Arm | 1586 | 0.2 | 2.0 | 15 |
| 11. 09. 1996 | Ráckeve-Soroksár Arm | 19 | 0.05 | 2.3 | 16 |
| 11. 09. 1966 | Dunaföldvár | 1560 | 0.05 | 2.1 | 16 |

Table 11. **Average heavy metal content of the recollected mussels (mg/kg)**

| Sample | Cd | Co | Cr | Cu | Ni | Pb | Zn |
|------------------------|------------|-----|------|------|------|-----|------------|
| Vének Danube, October | 1.3 | 1.3 | 1.4 | 11.0 | 13.8 | 4.7 | 495 |
| Vének Danube, November | 1.2 | 1.0 | 0.8 | 13.1 | 11.2 | 4.7 | 382 |
| Vének Mosoni, October | 1.6 | 1.3 | 0.8 | 20.0 | 10.9 | 7.4 | 706 |
| Vének Mosoni, November | 0.3 | 2.3 | 0.4 | 13.0 | 10.0 | 1.5 | 484 |
| Ráckeve, October | 0.4 | 0.5 | 0.3 | 9.0 | 8.6 | 2.2 | 291 |
| Ráckeve, November | 1.7 | 0.7 | 1.2 | 15.2 | 1.0 | 7.2 | 405 |
| Soroksár Arm, October | 1.3 | 0.7 | 0.4 | 11.8 | 8.8 | 3.1 | 231 |
| Dunaföldvár, October | 1.9 | 1.0 | 0.3 | 9.3 | 11.3 | 4.4 | 707 |
| Control | 0.6 | 0.7 | 0.14 | 8.4 | 10.2 | 3.9 | 476 |

Table 12. **Metal content of sediments (ppm), mussels (deviation from the control) and the calculated BCF [(C_{sample} - C_{control}) / C_{sediment}]**

| Sediment samples (mg/kg) | Cd | Co | Cr | Cu | Ni | Pb | Zn |
|--|------------|------|------------|-------------|-------------|------------|--------------|
| Vének, Danube | 0.16 | 7.1 | 21.0 | 0.7 | 10.1 | 56.3 | 51.9 |
| Vének, Mosoni Arm | 0.52 | 18.9 | 64.6 | 31.6 | 33.8 | 23.6 | 141.1 |
| Soroksári Arm, VITUKI | 0.32 | 15.8 | 83.9 | 58.4 | 39.0 | 70.6 | 286.2 |
| Mussels C _{sample} - C _{control} (mg/kg) | | | | | | | |
| Vének Danube, October | 0.7 | 0.6 | 1.3 | 2.6 | 3.6 | 0.8 | 19 |
| Vének Danube, November | 0.6 | 0.3 | 0.7 | 4.7 | 1.0 | 0.8 | less |
| Vének Mosoni, October | 1.0 | 0.6 | 0.7 | 11.6 | 0.7 | 3.5 | 230 |
| Vének Mosoni, November | less | 1.6 | 0.3 | 4.6 | 0.2 | less | 8.0 |
| Soroksár Arm, VITUKI, October | 0.7 | 0.0 | 0.3 | 3.4 | less | less | less |
| C _{sample} - C _{control} / C _{sediment} (-) | | | | | | | |
| Vének Danube, October | 4.4 | 0.08 | 0.06 | 3.7 | 0.36 | 0.01 | 0.3 |
| Vének Danube, November | 3.8 | 0.05 | 0.03 | 6.7 | 0.1 | 0.01 | (-) |
| Vének Mosoni, October | 1.9 | 0.03 | 0.01 | 0.4 | 0.02 | 0.15 | 1.6 |
| Vének Mosoni, November | (-) | 0.08 | 0.004 | 0.1 | 0.006 | (-) | 0.05 |
| Soroksár Arm, VITUKI, October | 2.2 | 0.00 | 0.003 | 0.06 | (-) | (-) | (-) |

The bioaccumulation strongly correlates with the mobility of the contaminants. Active biomonitoring ensures a well controlled population to test both the toxic effect and the bioaccumulation of the pollutants in sediment-living mussel species and the ecological risk of pollutants in sediments.

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