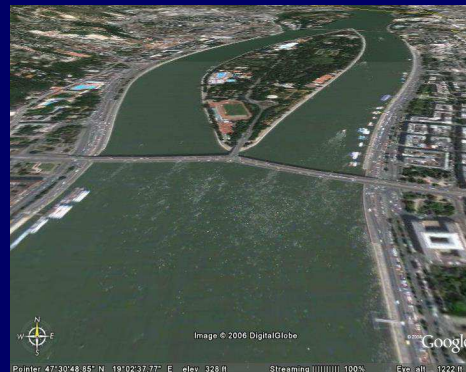


Katalin Gruiz

**Ecological Risk Assessment of
Inorganic and Organic Micropollutants
in the Danube Sediment**

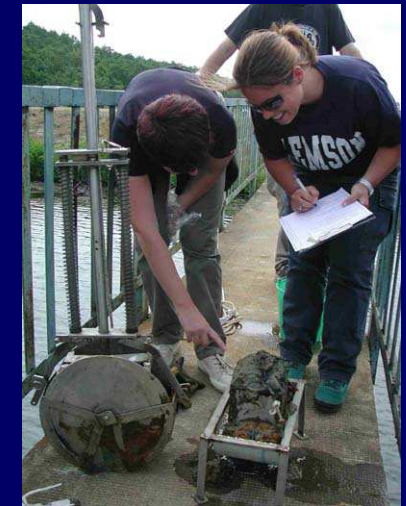


**Budapest University of Technology and Economics Department of Agricultural Chemical Technology
2006**

Gruiz, K. Risk Assessment of pollutants in Danube sediment

SEDIMENTS

1. **Suspended matter in surface waters, with large specific surface for physico-chemical and biological processes.**
- **2. Able to rescue the water phase from the harm of pollutants.**
- **3. After piling up at sedimentation areas it represents a low value habitat.**
- **4. Has long term potential for releasing the accumulated pollution into water and/or soil.**
- **5. Threatens the ecosystem and humans as a chemical time bomb.**

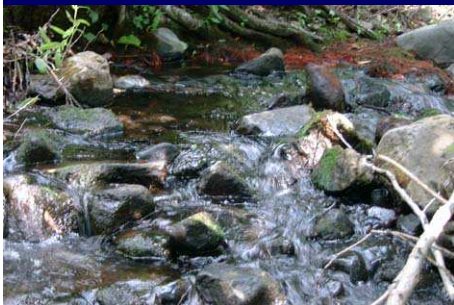


Gruiz, K. Risk Assessment of pollutants in Danube sediment

SENTIMENTS



- 1. Scientist: extremely high importance in aquatic structures, element cycles, transport pathways**
- 2. Human being: sediments' time bomb fate endangers humans and human land uses, e.g. flooded areas.**
- 3. Environmental 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. Ecosystem: the damaged aquatic ecosystem cannot fulfil its role in global element cycles and in the keeping of ecological equilibrium.**



INTRODUCTION

Aim

Introduction of the results of two former research projects on
Risk Based management of Danube sediment

Methodology and results

A 3-step tiered Risk Assessment methodology was developed and applied

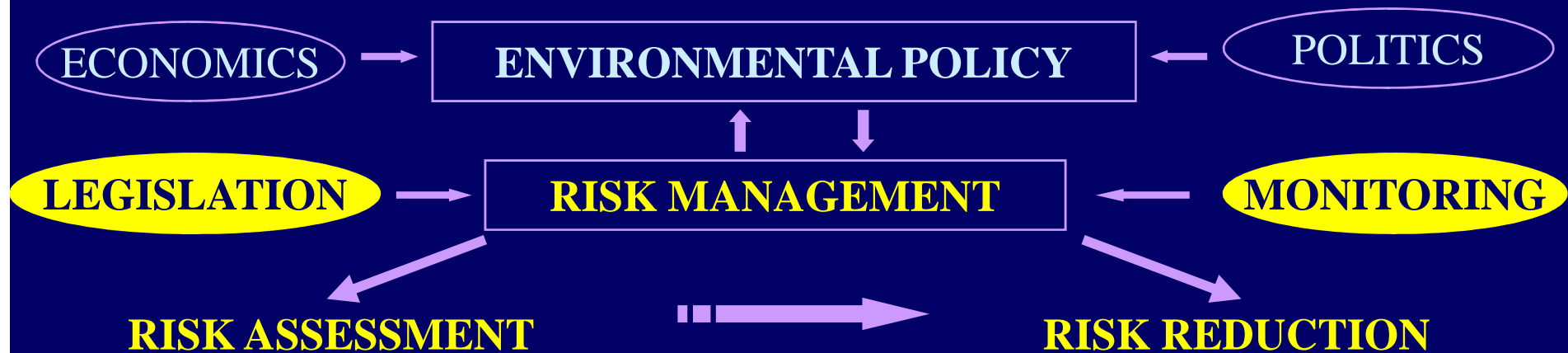
1. All chemicals produced and used in Danube catchment were collected
2. Tier 1.: Initial hazard assessment (qualitative RA): first ranking
3. Tier 2.: Hazard Assessment (Generic Qualitative RA): ranking by RQ
4. Tier 3.: Site specific Risk Assessment: local risk value
5. Evaluation, interpretation and use of data
6. Validation calculated risk with measured data.

Theoretical background

Risk of chemicals: scale of damage x probability of occurrence

- **Environmental Risk Assessment (ERA) methodologies: discursive, qualitative or quantitative risk assessment**
- **Kind of Generic ERA: calculates the quantity of risk with default (Danube) values**
- **Site Specific ERA: considers the characteristics of the site: environmental elements, contaminants, interactions, land uses, reg+local exposures, etc.**
- **Quantitative ERA: $RQ = PEC/PNEC$ and $HQ = ADD/TDI$**
- **Integrated Risk Model: unifies the transport- and the exposure model**
- **Aims of ERA:**
 - **to quantify risk**
 - **to define acceptable risk / environmental quality criteria**
 - **to compare risk to the acceptable risk,**
 - **to reduce risk to an acceptable level,**
 - **to determine site specific target value of remediation**

Environmental Risk Assessment: a tool for environmental management



1. HAZARD IDENTIFICATION

2. RISK ASSESSMENT

Generic / site specific

Qualitative / quantitative

Ecological / human health risk

1. PREVENTION

2. REMEDIATION

3. RESTRICTION

Management of contaminated sediment

Principles

To prevent further pollution

Precaution

Risk based management: RB priority setting, RB monitoring, RB remediation

Polluter should pay

Risk based decision making,

Scientific basis

Tiered risk assessment

Assessment of subsurface water and sediment: sampling, analyses, Triad approach

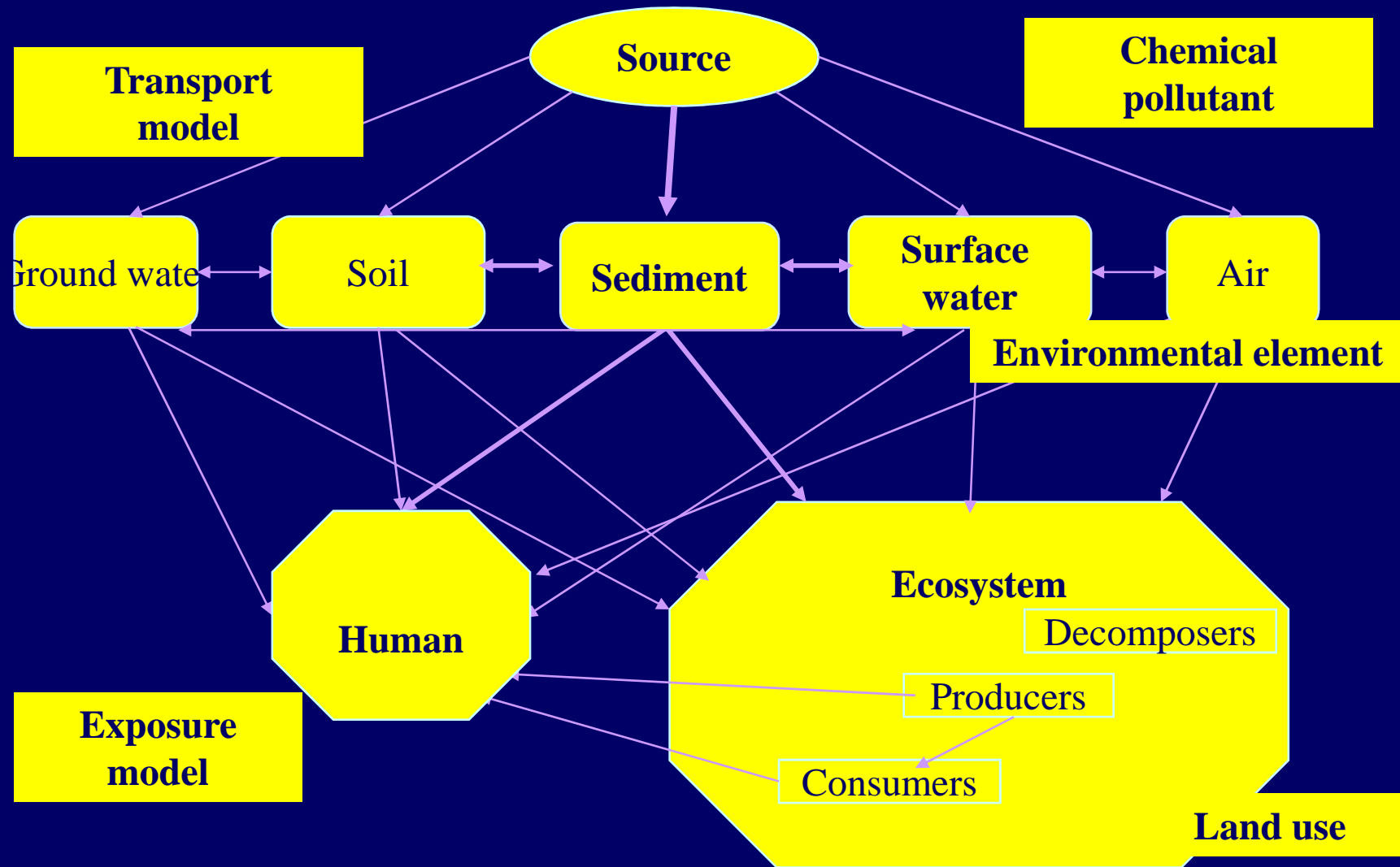
Exposure modeling

Qualitative and quantitative RA

Ecotoxicology and toxicology



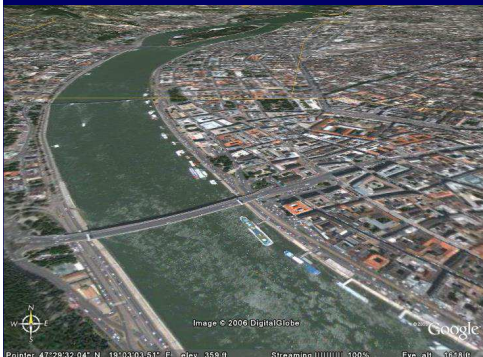
Integrated Risk Model



Tiered risk assessment of chemicals in Danube sediment

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

- 1. Initial hazard identification:** a qualitative risk assessment, aiming priority setting for those chemicals, which are produced and used in the Danube catchment.
- 2. Generic Risk Assessment or Hazard Assessment:** quantitative risk assessment, the result is an $RQ = PEC/PNEC$, the European default values were used in the calculations.
- 3. 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.

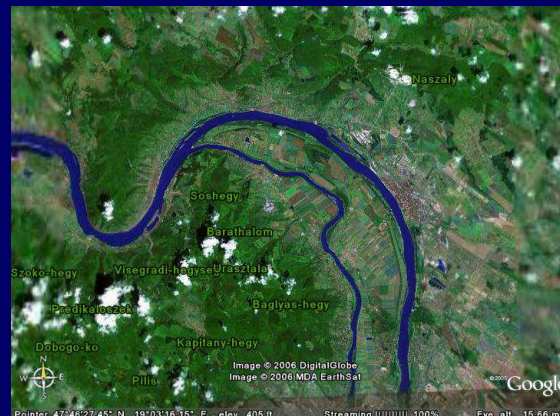
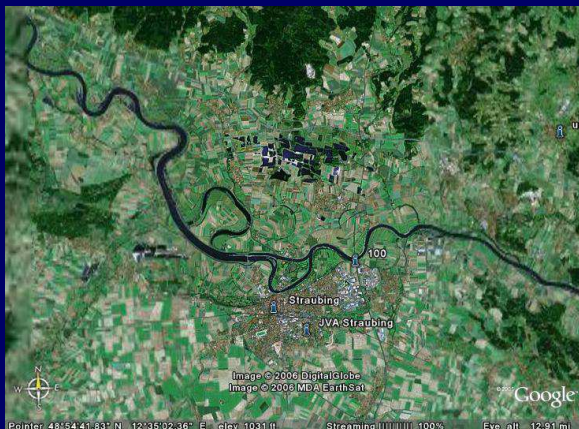


First tier of the risk assessment

Qualitative Environmental Risk Assessment and ranking of chemicals relevant to Danube sediment

CHARACTERISTICS OF QUALITATIVE ERA

- Also called initial hazard assessment and relative risk assessment
- Characterizes risk with points or marks or %
- It is useful for priority setting and ranking in case of many existing contaminants



First tier of the risk assessment

For initial hazard assessment and ranking of chemicals

Qualitative Environmental Risk Assessment

Suitable data: 1. production and use, 2. basic physico-chemical properties, 3. environmental nature and fate of the chemical substance, like K_{ow} , K_p : water solubility, degradability, 4. 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

TOXICITY

First tier of the risk assessment: selection of the most risky contaminants for sediment

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

Criteria: more than 10 % of the contaminant is bound to the SS (suspended solid)

For organics: cut off value: $\log K_{ow} > 4.5$

For inorganics: 1700 lit/kg.

2. **Degradability** biodegradation, hydrolyses and photo-degradation

a.) readily degradable: (EU-TGD): half-life time 15 days;

b.) not readily biodegradable: >15 days.

3. **Toxicity** risk of chemicals is dominantly due to their harmful effects, so that a cut-off value for toxicity was included already in the initial phase.

Cut-off values for organics:

1 mg/l – for chemicals 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.

Criteria setting for DSHPL and DSPL chemicals

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, for inorganics

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, for inorganics

7 days $<$ degradation half-life > 15 days

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

Results of the first tier: DSHP and DSP chemicals

| | First tier | Second tier | Third tier |
|------------------------------------|----------------|-------------|---|
| Danube Sediment High Priority List | 44 (-8 +10) | 46 | 26  |
| Danube Sediment Priority List | 102 | 80 | 20 |
| Non-Sediment Priority Chemicals | 421 | | |
| Waiting list | 134 | ? | ? |
| Total (CAS) | 701 | 126 | 46 |

Danube River convention: 40 chemicals.

23 of these did not get in our DSHPL or DSP list.

EU list (Dir. 76/464) of chemicals hazardous for aquatic env: 141 chemicals

Only 20 of these are included in our DSHPL or DSPL.

Sediment-specific priority list differs from the water-priority list!

Second and third tier: Quantitative Risk Assessment

- **Also called absolute risk assessment**
- **It characterizes the risk with real quantities**
- **Its result can be generic or site specific**
- **Its result is suitable for decision making**
- **The target value of remediation or other RR activity can be determined**
- **It can be used for preliminary or for detailed assessment**
- **It can be used for chemicals, activities or contaminated sites**
- **It works with a gradual iterative methodology: cost effective**
- **It works with worth case estimation: excludes the negative cases/contaminants during the procedure as soon as possible**
- **It is a conservative approach: overestimation of the risk and exclusion only of the safe negatives**

ECOLOGICAL RISK of substances

EMISSION (source)

Transport model

PEC

EFFECT

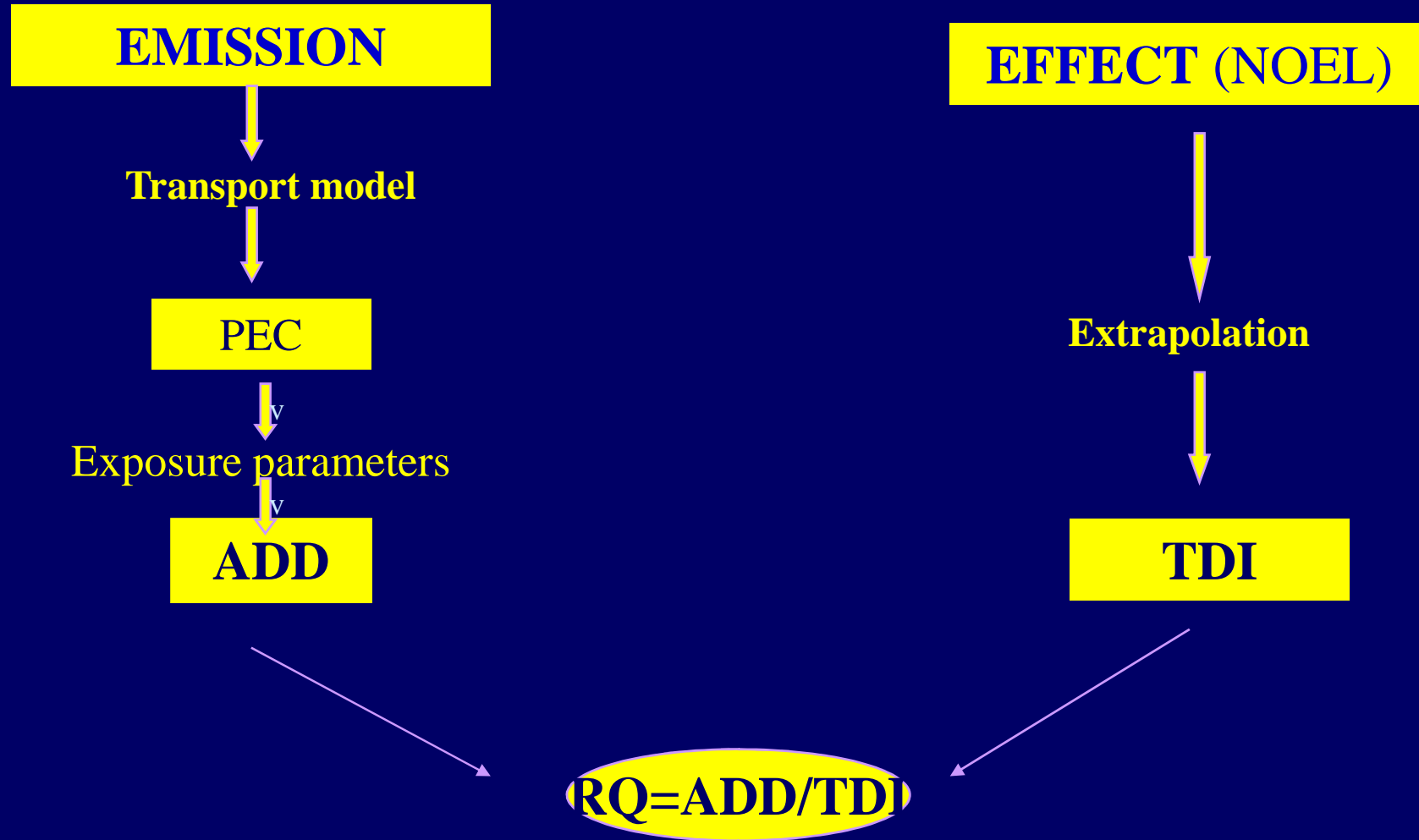
Extrapolation

PNEC

$$RQ = PEC/PNEC$$

Technical guidance document for environmental risk assessment of new and existing substances, Brussels, 1996: it supports the orders of EC 1488/94 and EEC 793/33

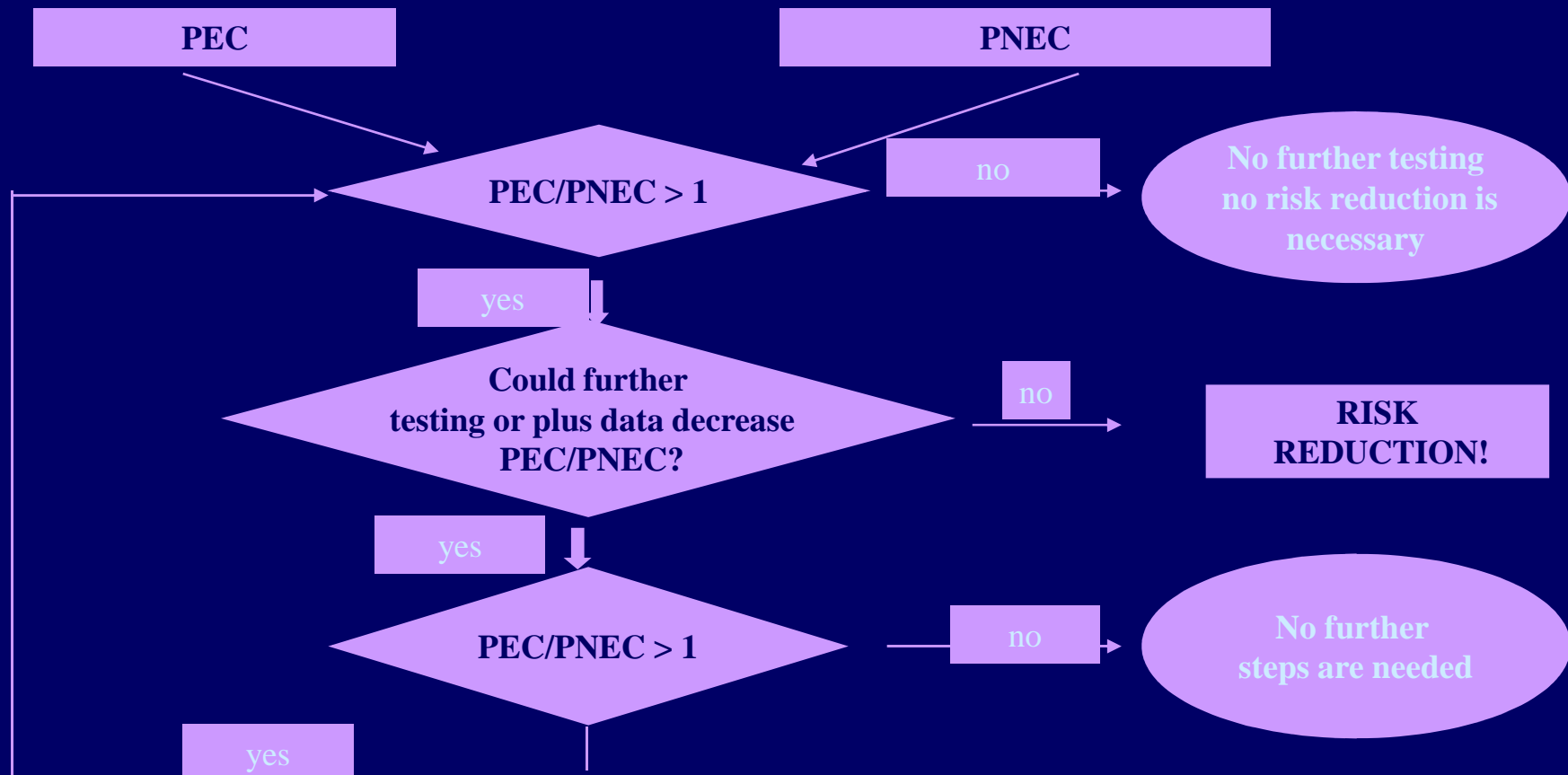
HUMAN HEALTH RISK of substances



Quantitative environmental risk assessment of substances

Characteristics:

- gradual procedure (cost effective),
- iterative
- it uses worst case estimation (pessimistic model)
- it works also in case of lack of data (exclusion)



Second tier: Generic Risk Assessment

The quantity of risk of Danube Sediment Priority chemicals: 126 substances

1. Exposure (PEC) with European default values
2. Effect (PNEC) assessment
3. RQ was calculated as a ratio of PEC and PNEC



Second tier: generic risk assessment

1. Exposure assessment (PEC) requires the following data

T = tonnage: produced and used tonnage in the catchment area;

f_{water} = 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: 0.01

use resulting in inclusion into matrix: 0.1

non-dispersive use: 0.2

dispersive use: 1.0

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

Degradation rate: $f_{\text{degrwater}}$: 0.1 for readily degradable chemicals (hlt: 15 days)
0.5 for inherently degradable (hlt: 50-150 days)
1.0 for persistent chemicals (hlt: infinite)

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

Concentration in the sediment: $PEC_{\text{sediment}} = K_p \times PEC_{\text{water}}$;

$$K_p = f_{oc} \times K_{oc};$$

$$PEC_{\text{water}} = \text{Tonnage} \times f_{\text{water}} \times f_{\text{degr}}/Q$$

Second tier: generic risk assessment

2. Effect assessment

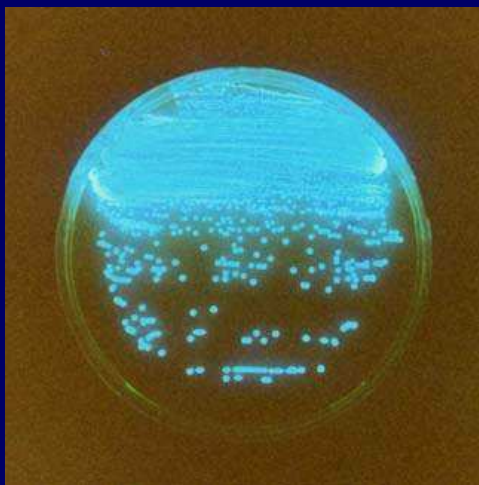
estimation of the **PNEC** value from ecotoxicity data or by using effect based sediment quality criteria, **SQC**

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 from the results of minimum of three toxicity tests of testorganisms from 3 different trophic levels by the method of factorial extrapolation.



| 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 | Ethylfluralin | 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 yet |
| Mercury | 0,8 | DDD (dichlorodiphenyldichloroethane) | no data yet |
| PCB | <0,75 | DDE (dichlorodipenyldichloroethylene) | no data yet |
| Nickel | 0,65 | Hexachlorobenzene | no data yet |
| Benfluralin | 0,64 | | |

| 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 |
| Bifenox | 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 yet |
| Ethylbenzene | 4,9 | 2,3,4,6-Tetrachlorophenol | no data yet |
| N-cyclohexyl-2-benzothiazole-sulfen | 4,8 | 2,6-Dibromo-4-nitrophenol | no data yet |
| Endosulfan | 4,0–4,5 | Acenaphthene | no data yet |
| Diflubenzuron | 3,3 | PAHs | no data yet |
| Lindane (gamma HCH) | <3 | | |

Site Specific ERA

PEC estimation and its refined assessment (for all environmental phases)

- 1. Maximal measured concentration (in the contamination source)**
- 2. Site specific transport model, which considers emission and decrease of the concentration between source and receptor**
- 3. Application refined transport model considering partition and biodegradation**
- 4. Special needs, eg. food chain effects: bioconcentration, biomagnification**

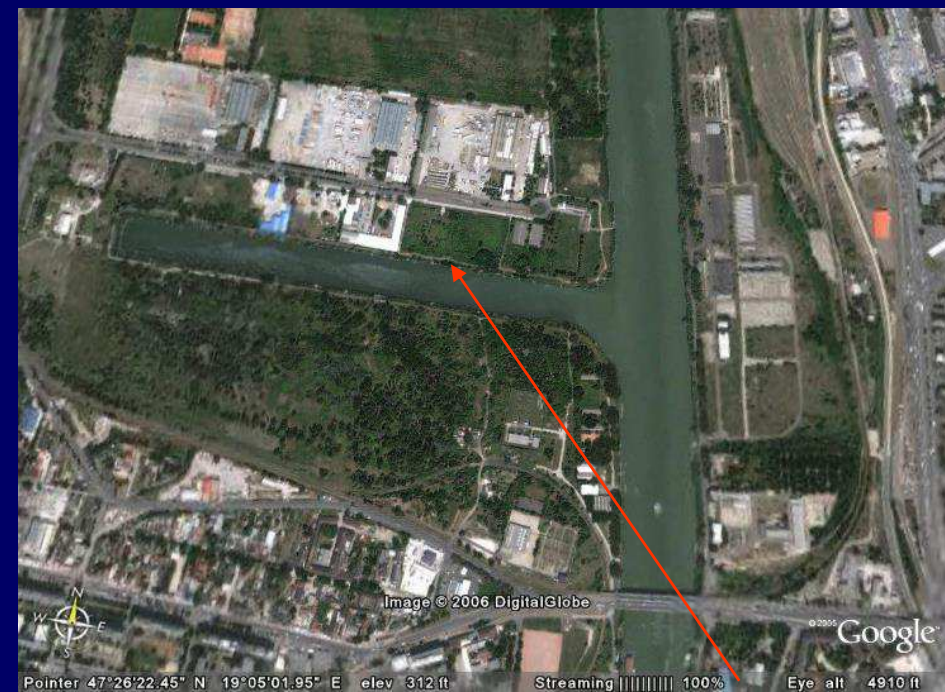
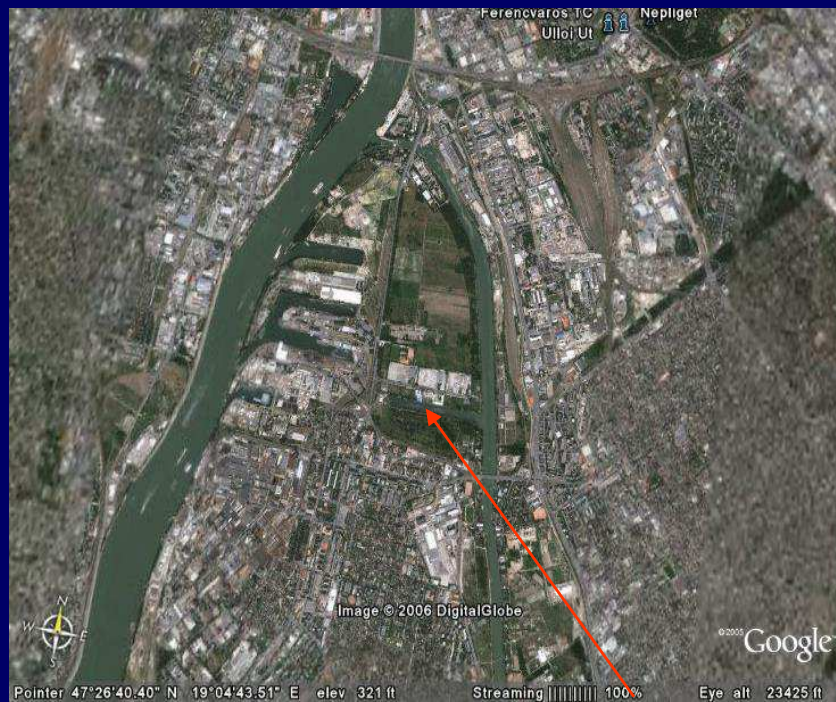
PNEC estimation and it refined assessment

- 1. Application of generic PNEC, eg. limit values, or EQC for most sensitive land use**
- 2. Considering site specific land uses and habits**
- 3. Direct ecotoxicity and toxicity testing: measuring site specific PNEC with indigenous ecosystem-memebers.**

Site Specific Risk Assessment

Selected sites:

1. HRICOV-reservoir/Slovakia and
2. RSD Danube-branch/Hungary



| Name of the pollutant | Hricov/ Sk µg/kg | RSD / Bp µg/kg | PNEC µg/kg | RQ _{local} | RQ _{reg} |
|------------------------------|---------------------|-------------------|---------------|---------------------|-------------------|
| 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 |

| Name of the pollutant | Hricov Sk µg/kg | RSD Bp µg/kg | PNEC µg/kg | RQ_{local} | RQ_{reg} |
|------------------------------|----------------------------|-------------------------|-----------------------|---------------------------|-------------------------|
| 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 | 0,15–0,3 | <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 | 71–34 | 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 | 1,2–0,3 | 1,7 |
| Pendimethalin | 199 | 178 | 300 | 0,7–0,6 | 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 |

Evaluation and interpretation of the results of RQ regional (generic) and RQ local

Evaluation: if $RQ > 1$, refined RA and RR is necessary

- RQ generic > 1 : regional level action at Danube catchment scale
- RQ local > 1 : local restriction or remediation

Comparative evaluation of regional and local RQ:

- RQ regional agrees with RQ local: chemicals with widespread use in the whole Danube catchment.
- RQ regional differs from RQ local: locally different production and use
 - RQ regional $<$ RQ local: local production and/or use
 - RQ regional $>$ RQ local: missing local production and use

If facts do not support/confirm these results repeat the assessment with more precise input data. Additional testing of sediment samples is also recommended!

Inorganic micropollutants in HU-Danube sediment

Copper content of Danube water and sediment

| Danube km | $C_{Cu\ water}$ (ppb) | $C_{Cu\ sediment}$ (ppm) | K_{swCu} (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 | |

Similar trends are shown by other toxic metals!!

| River | Site location | River km | CaCO ₃ % | humu s % | Mechanical composition (%) | | |
|-----------------|-------------------------|-------------|------------------------|----------------|-------------------------------|------|------|
| | | | | | Sand | Silt | Clay |
| Danube | Szap | 1811 | 20.5 | 2.4 | 22.8 | 66.1 | 11.0 |
| Danube | Medve right | 180 | 14.5 | 0.2 | 92.0 | 5.6 | 2.5 |
| Moson Arm | Vének left 2 | 179 | 6.5 | 3.2 | 39.0 | 42.8 | 18.2 |
| Moson Arm | Vének right | 179 | 11.0 | 1.3 | 79.0 | 14.9 | 6.1 |
| Conco creek | Ács 2 km | 177 | 23.0 | 3.5 | 48.6 | 36.1 | 15.3 |
| Danube | Upstr. | 177 | 16.0 | 0.7 | 85.5 | 10.2 | 4.4 |
| Danube | Komárom | 176 | 14.0 | 2.0 | 74.1 | 18.2 | 7.7 |
| Átalér creek | Komárom Mouth 1.5 km | 175 | 16.5 | 1.5 | 84.0 | 10.3 | 5.7 |
| Kenyérmezei | Mouth 1 km | 172 | 19.0 | 4.2 | 23.2 | 55.3 | 21.5 |
| Danube | Esztergom | 171 | 23.5 | 4.3 | 42.0 | 45.2 | 12.9 |
| Danube | Basaharc | 170 | 21.5 | 3.3 | 46.0 | 44.3 | 10.0 |
| Danube | Visegrád | 169 | 16.5 | 2.2 | 52.5 | 38.5 | 9.1 |
| Danube | Pünkösdfürdő | 165 | 19.5 | 2.2 | 72.7 | 22.4 | 5.0 |
| Danube | M0 Bridge left | 163 | 17.5 | 1.5 | 78.1 | 15.7 | 6.2 |
| Danube | M0 Bridge right | 163 | 21.5 | 2.2 | 65.5 | 27.4 | 7.1 |
| Soroksár | 53.9 km | 168 | 22.0 | 1.0 | 96.3 | 2.8 | 0.8 |
| Arm Soroksár | VITUKI 57.3 | 158 | 17.7 | 0.8 | 42.5 | 46.0 | 11.5 |

| River | Site location | River km | Excess heavy metals in sediment (ppm) | | | | | | | |
|--------------|------------------------|-------------|---------------------------------------|------|-------|--------|-------|--------|--------|-----|
| | | | Cd | Co | Cr | Cu | Ni | Pb | Zn | TEL |
| Danube | Szap | 1811 | - | 3.80 | -4.33 | 13.71 | 17.85 | -34.81 | 21.99 | 57 |
| Danube | Medve right | 1802 | 0.19 | 1.17 | - | -15.87 | -2.39 | 3.63 | -5.65 | 5 |
| Moson Arm | Moson Vének left 2 km | *1794 | 0.27 | 3.11 | 33.92 | 3.76 | 5.59 | -47.79 | 31.71 | 44 |
| Moson Arm | Moson Vének right 2 km | *1794 | 0.09 | 2.22 | 21.85 | -10.50 | -2.60 | -44.01 | -6.58 | 2 |
| Conco creek | Ács 2 km | *1777 | - | - | 31.97 | -12.57 | - | -57.35 | -44.26 | - |
| Danube | Upstream Komárom | 1770 | 0.41 | 5.03 | 53.37 | -13.90 | 10.03 | -44.75 | -12.18 | 1.5 |
| Danube | Downstr. Komárom | 1761 | 0.29 | - | 32.93 | -10.55 | -2.61 | -37.07 | 3.91 | 4 |
| Átalér creek | Átalér Mouth 1.5 km | *1750 | 0.25 | 0.50 | 35.43 | -12.34 | -8.70 | -36.75 | 3.54 | 3.5 |
| Kenyérmezei | Km. Creek mouth 1 km | *1722 | 0.25 | 0.24 | 32.89 | - | 8.28 | -44.53 | 40.69 | 215 |
| Danube | Esztergom | 1716 | - | 1.49 | 30.67 | 4 | 1.45 | -21.07 | 49.67 | 52 |
| Danube | Basaharc | 1707 | 0.29 | 2.68 | 27.78 | -3.25 | 3.65 | -46.89 | 37.71 | 44 |
| Danube | Visegrád | 1694 | 0.27 | 2.76 | 25.23 | -4.80 | 2.22 | -43.95 | 26.53 | 31 |
| Danube | Pünkösdfürdő | 1658 | 0.33 | 3.70 | 27.67 | -7.52 | 2.74 | -41.09 | 29.16 | 36 |
| Danube | M0 Bridge left | 1632 | 0.22 | 2.33 | 29.03 | 2.13 | 0.72 | -33.69 | 57.37 | 63 |
| Danube | M0 Bridge right | 1632 | 0.16 | 2.21 | 24.79 | 3.70 | 2.74 | -27.87 | 52.80 | 62 |
| Soroksár Arm | RSD Gubacsi Br. 53.9km | *1586 | 0.10 | - | 27.11 | 3.20 | 1.61 | 175.19 | 15.25 | 203 |
| Soroksár Arm | RSD VITUKI 57.3 km | *1586 | - | 2.84 | 10.94 | 36.07 | 17.52 | 8.40 | 201.0 | 277 |
| | Target values for HM | | 0.18 | 20 | 100 | 36 | 35 | 85 | 140 | |

Ecotoxicity testing: the proper tool for ERA

Problems of testing of sediment samples

- mixture of contaminants: synergism, antagonism
- interactions between contaminants, matrix and biota
- medium: extract, pore water, whole sample
- biotransformation: effect of products
- biodegradation
- availability: physico-chemical and biological availability differs
- analytical programme includes only part of the really occurring chemicals
- biotic and abiotic composition of the environmental sample influence the results

Ecotoxicity testing gives solution for some of the problems

- integrates interactions between toxicants
- integrates interactions between toxicant and matrix
- measures bioavailable ratio of the contamination
- measures chemically not measurable toxicants by their effect
- measures effects of chemicals not included into the analytical programme

| River | Site location | River km | Ecotoxicity testing | | | | |
|--------------|------------------|-------------|---------------------|-----------------|----------------|------------------------|------------------|
| | | | <i>B. subtilis</i> | <i>A. agile</i> | <i>S. alba</i> | <i>Vibrio fischeri</i> | |
| | | | | | | EC ₂₀ | EC ₅₀ |
| Danube | Szap | 1811 | - | + | - | <1 | 50 |
| Danube | Medve right | 1802 | - | + | - | 34 | >50 |
| Danube Arm | Vének left 2 km | 1794 | - | + | - | 5.5 | 28 |
| Danube Arm | Vének right 2 km | 1794 | - | +/- | - | 28 | >50 |
| Conco creek | Ács 2 km | 1777 | - | +/- | - | 50 | >50 |
| Danube | Upstr Komárom | 1770 | - | +/- | - | 26 | >50 |
| Danube | DwnstrKomárom | 1761 | - | +/- | - | 20 | >50 |
| Átalér creek | Mouth 1.5 km | 1750 | - | + | - | 50 | >50 |
| Keny. creek | Mouth 1 km | 1722 | - | + | - | <1 | 1.9 |
| Danube | Esztergom | 1716 | - | + | - | 1.5 | 50 |
| Danube | Basaharc | 1707 | - | +/- | - | 1.8 | 50 |
| Danube | Visegrád | 1694 | - | + | - | 22 | 35 |
| Danube | Pünkösdfürdő | 1658 | - | + | - | 50 | >50 |
| Danube | M0 Bridge left | 1632 | - | + | - | 16 | 50 |
| Danube | M0 Bridge right | 1632 | - | + | - | 7.0 | 48 |
| RSD | Gubacsi Bridge | 1586 | - | + | - | 2.1 | 9.2 |
| RSD | VITUKI 57.3 km | 1586 | - | + | - | 2.7 | 12.3 |

| River | Site location | River km | Comparison of chemical and ecotoxicity data | | |
|-------------------|------------------------|----------|---|------------------|------------|
| | | | Sum of Δ TEL | Clay in sediment | Toxicity |
| | | | ppm HM | % | g sediment |
| Danube | Szap | 1811 | 57 | 11 | 25 |
| Danube | Medve right | 1802 | 5 | 2.5 | >42 |
| Moson Danube Arm | Vének left 2 km | 1794 | 44 | 18 | 15 |
| Moson Danube Arm | Vének right 2 km | 1794 | 2 | 6 | >39 |
| Conco creek | Ács 2 km | 1777 | 0 | 15 | >50 |
| Danube | Upstream Komárom | 1770 | 1.5 | 4 | >38 |
| Danube | Downstream Komárom | 1761 | 4 | 8 | 35 |
| Átalér creek | Mouth 1.5 km | 1750 | 3.5 | 6 | >50 |
| Kenyérmezei creek | 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 | Gubacsi Bridge 53.9 km | 1586 | 203 | 1 | 5.5 |
| RSD | VITUKI 57.3 km | 1586 | 277 | 12 | 7.5 |

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 |

Metal content of sediments (ppm), mussels (deviation from the control) and the calculated BCF

| 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 $C_{\text{sample}} - C_{\text{control}}$ (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 |
| $C_{\text{sample}} - C_{\text{control}} / C_{\text{sediment}}$ (-) | | | | | | | |
| 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 | (-) | (-) | (-) |

Conclusions

1. Tiered Risk Assessment of pollutants in Danube sediment is the proper tool for **RANKING & PRIORITY SETTING** of chemicals
2. For regional scale risk management: **GENERIC ERA**
3. For local risk management: **SITE SPECIFIC ERA**
4. Risk of chemicals on sediments differs from their risk on water!!
5. For decision making a Quantitative ERA is needed
RISK BASED monitoring and **RISK REDUCTION**
6. Harmonised analytical tools and toxicity testing is necessary
7. Databases with environmental parameters and data on the effect, fate and nature of chemicals' polluting sediment

