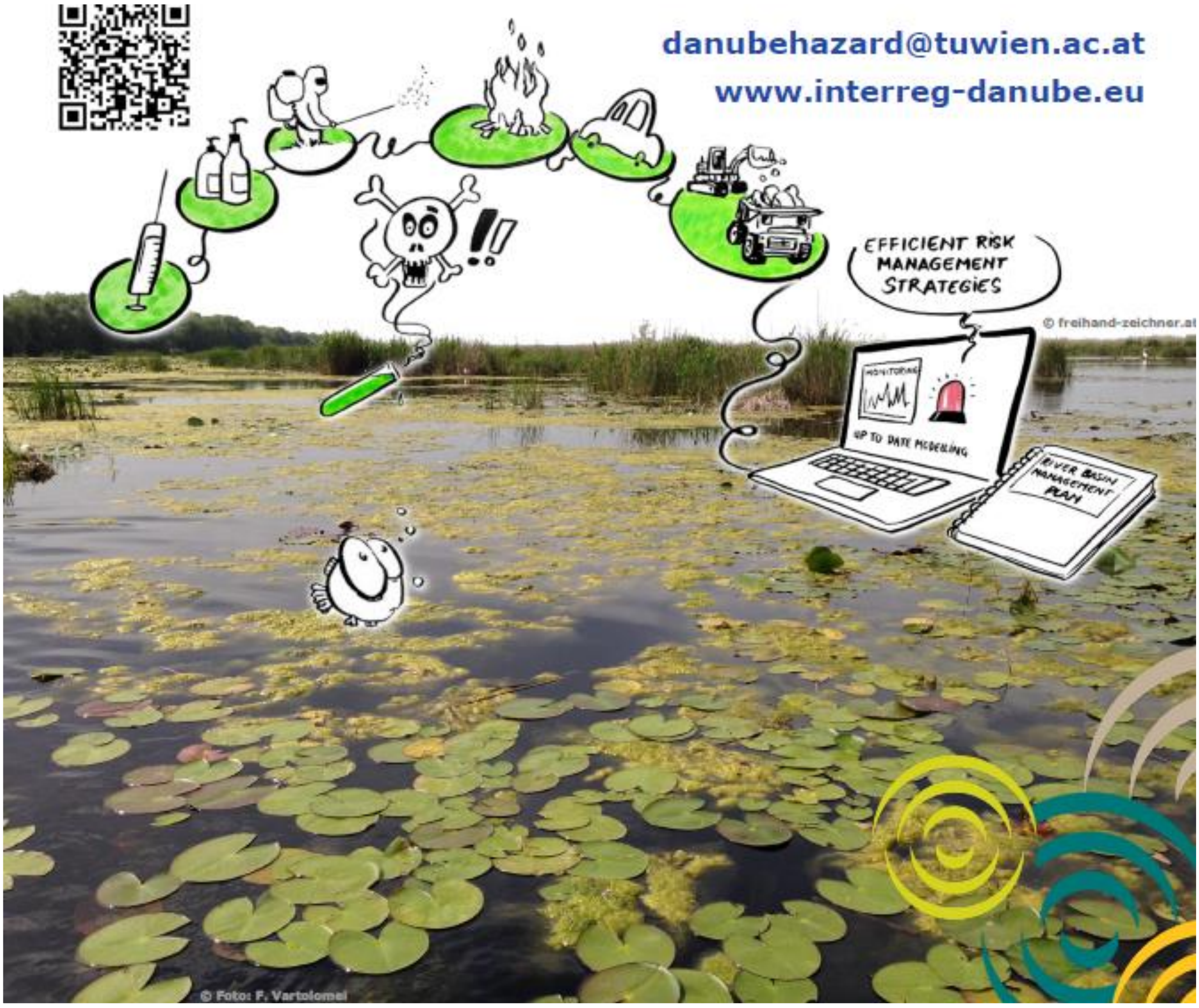
Project Danube Hazard m³c:
National/regional trainings on monitoring and inventorying of hazardous substances pollution



Output T4.2

TRAINING MATERIAL PACKAGE ON MONITORING AND INVENTORYING OF HAZARDOUS SUBSTANCES POLLUTION

October 2022

Project co-funded by European Union funds (ERDF, IPA, ENI) and National Funds of the participating countries

PROJECT TITLE: Tackling hazardous substances pollution in the Danube River Basin by Measuring, Modelling-based Management and Capacity building

ACRONYM: Danube Hazard m³c

DATE OF PREPARATION: 26.10.2022

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Executive summary

In the frame of Capacity Building work packages each project partner has organized one national training for stakeholders, dealing with monitoring and inventorying of hazardous substances pollution. ICPDR and CETI collaborated on the organization of a regional event for participants from Bosnia Herzegovina, Montenegro and Serbia.

These series of trainings in national languages had the objective of effective reaching to the national target groups in respective countries.

For the training course the project partners developed jointly a learning package that covered the following five topics:

- Topic 1. Hazardous substances aspects of water quality monitoring and inventorying of pollution sources and pathways
- Topic 2. Monitoring of the hazardous substances
- Topic 3. Technical aspects of HSs sampling and measuring
- Topic 4. Contribution of the results of our DHm3c monitoring to the inventory of hazardous substance pollution
- Topic 5. Modelling of Hazardous Substances

All materials were translated into national languages and their content was adapted to specific territorial needs so that the national training courses suited best the current state-of-art in the partner countries and provided high added value for the participating audience.

The trainings took place in:

- Austria,Vienna, 31st May – 1st June 2022
- Bulgaria, Ribaritsa, 23-24th June 2022
- Croatia, Zagreb, 2-3rd June 2022
- Hungary, Balatonszárszó, 1-2nd June 2022
- Moldova-Colibita, Romania, 7-8 July 2022
- Romania-Colibita, 7-8 July 2022
- Slovenia-Ljubljana, 21-22 May 2022
- Slovakia- Bratislava, 12-13th September 2022
- and for the regional course, in Podgorica, Montenegro for Bosnia Herzegovina, Montenegro, Serbia with support of ICPDR, 8th and 9th of June 2022.

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The main purposes of the monitoring and inventorying of HS pollution training course were to:

- improve knowledge and skills of experts working in the field of river basin management;
- improve knowledge on established and innovative smart monitoring strategies for the effective assessment of concentrations and loads through different emissions pathways and in rivers, as well as for assessment of the chemical status of water bodies;
- enhance the understanding of the concepts, approaches and methodologies to develop harmonized inventories for HS emissions, according with the requirements of the Water Framework Directive (WFD), including relevance for HS modelling;
- provide educational outcomes and improve relevant skills and competences in the Danube Region, since they focus on learning outcomes which are relevant for employability and innovation, i.e. with relevance for HS modelling.

Agenda of event

Danube Hazard m³c

Tackling hazardous substances pollution in the Danube River Basin by Measuring, Modelling-based Management and Capacity building

National training on Monitoring and inventorying of HS pollution

2022

Agenda

Day 1		
09:00	**10:00**	**Welcome and opening the training course**
10:00	**10:45**	**Hazardous substances aspects of water quality monitoring and inventorying of pollution sources and pathways**
10:45	**11:15**	**Questions and answers**
11:15	**11:30**	**Coffee break**
11:30	**12:15**	**Monitoring of the hazardous substances**
12:15	**12:45**	**Questions and answers**
12:45	**14:00**	**Lunch break**
14:00	**14:45**	**Technical aspects of HSs sampling and measuring**
14:45	**15:15**	**Questions and answers**
15:15	**16:00**	**Conclusions and end of the Day 1**
Day 2		
09:30	**10:15**	**Contribution of the results of our DHm3c monitoring to the inventory of hazardous substance pollution**
10:15	**10:45**	**Questions and answers**
10:45	**11:00**	**Coffee break**
11:00	**11:45**	**Modeling of hazardous substances**
11:45	**12:15**	**Questions and answers**
12:15	**13:00**	**Conclusions and feedback of the participants**
		End of the Training course

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WP T4 - Capacity building
National training course on Monitoring and inventorying of HS pollution

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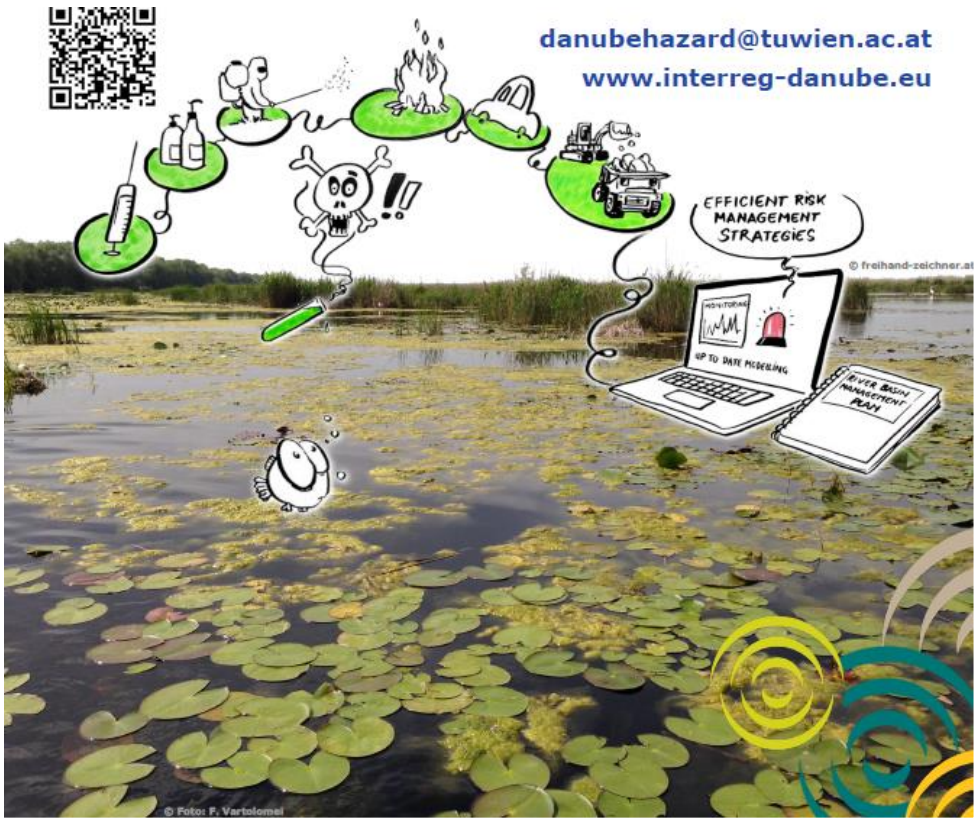

TECHNISCHE UNIVERSITÄT WIEN

Institute of Chemistry

BULGARIAN WATER ASSOCIATION

Center for Eco-Toxicological Research

ICPDR IKSD
International Commission for the Protection of the Danube River
Internationale Kommission zum Schutz der Donau

FKITMCMXIX

umweltbundesamt
ENVIRONMENT AGENCY AUSTRIA

ADMINISTRAȚIA NAȚIONALĂ APELE ROMÂNE

Jožef Stefan Institute, Ljubljana, Slovenia

MŰEGYETEM 1782

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The main purposes of the monitoring and inventorying of HS pollution training course are:

- improve knowledge and skills of experts working in the field of river basin management;
- improve knowledge on established and innovative smart monitoring strategies for the effective assessment of concentrations and loads through different emissions pathways and in rivers, as well as for assessment of the chemical status of water bodies;
- enhancing the understanding of the concepts, approaches and methodologies to develop harmonised inventories for HS emissions, according with the requirements of the Water Framework Directive (WFD), including relevance for HS modelling;
- improvement of educational outcomes and relevant skills and competences in the Danube Region, since they focus on learning outcomes which are relevant for employability and innovation, i.e. with relevance for HS modelling.

AGENDA

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Topic 1. Hazardous substances aspects of water quality monitoring and inventorying of pollution sources and pathways

Topic 2. Monitoring of the hazardous substances

Topic 3. Technical aspects of HSs sampling and measuring

Topic 4. Contribution of the results of our DHm3c monitoring to the inventory of hazardous substance pollution

Topic 5. Modeling of Hazardous Substances

Topic 1: Hazardous substances aspects of water quality monitoring and inventorying of pollution sources and pathways

a. Danube Hazard m3c - objectives and scope of the project

b. Definitions (hazardous substances, sources, pathways etc.)

c. Legal requirements of water quality and emission regulations (EU Directives and national regulations including the approaches presented in the EU Guidance documents)

d. Role of monitoring and the main pathways in the context of hazardous substance management, including correlation with the modelling aspects

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Topic 1
a. The main objectives of the Project

The **durable and effective transnational control and reduction** of hazardous substances water pollution in DRB

Improving baseline knowledge on the status quo of HS water pollution and on the relevance of different emission pathways

Effective and harmonized management of HS water pollution in the DRB, based on the prioritization of measures at transnational level and on the simultaneous consideration of specific territorial needs

Long-lasting competent **management, control and reduction** of HS water pollution across scales in the DRB through enhanced institutional expertise, skills and instruments

The main results of the project:
the improved knowledge and joint understanding of HS pollution of water bodies in the DRB and the coordinated prioritization of HS transboundary management measures

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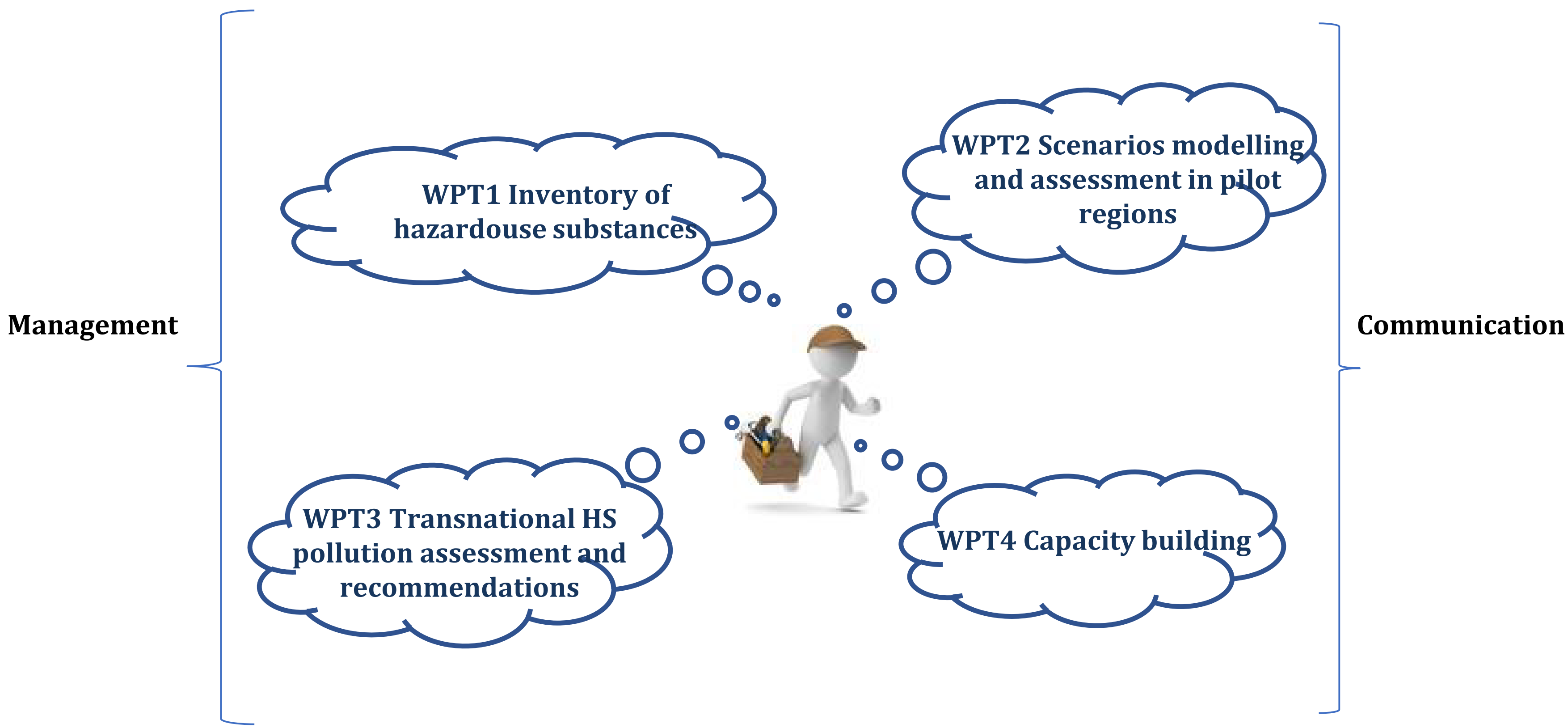
Topic 1
a. Objectives and scope of the project

The main project activities



Topic 1 a. Objectives and goals of the project

A.T1 – Inventoring of hazardous substances

OT1.1 Inventory of concentration of hazardous substances in the DRB
OT1.2 Measurement concept for the monitoring of HS river pollution

A.T2 – Scenarios modelling and assessment in pilot regions

OT2.1 Harmonized MORE model adapted to specific territorial characteristics within DRB
OT2.2 Report on improved system understanding as basis for adapted transnational emission modelling at DRB scale
OT2.3 Management plan development process at wateshed level for HS pollution based on emission modelling in 7 pilot regions

A.T3 Transnational HS pollution assessment and recommendations

OT3.1 Technical guidance manual on HS management for stakeholders
OT3.2 Upgrade version of the Solution model adapted to territorial needs for transnational modeling of HS emissions in the DRB
OT3.3 Policy guidance document

A.T4.4 International workshop on management of HS pollution – (07.2021-12.2022)

OT4.1 (9) National/regional trainings on monitoring and inventorying of HS pollution;
OT4.2 – learning documents (EN and national languages)
OT4.3 (3) transnational trainings on modelling and scenario evaluation;
OT4.4 – learning documents (EN)
OT4.5 Technical guidance manual on HS management
OT4.6 International workshop

Topic 1
a. Inventoring of HS - Tasks and objectives

Provide a solid database on HS concentration levels in surface waters, and in pathways of emissions into surface waters within the DRB

Collection of existing data and setup of the database

Demonstrate the innovative measurement concept at a pilot level

Targeted measurement of HS in 7 selected pilot regions

Provide input as source for input variables into emission modelling and for the validation of river models

Statistical analysis of the inventory of hazardous substances

Topic 1
b. Definitions – 1

The main objectives of the Water Framework Directive 2000/60/EC (WFD) establishing a framework for Community action in the field of water policy (WFD):

- achieving of the good status (ecological and chemical) of the surface water bodies (SWBs)
- to prevent deterioration of the good status of all SWBs
- to prevent or limit the input of pollutants into groundwater bodies (GWB) and to prevent the deterioration of the status of all GWBs

Good chemical status of the SWBs is the chemical status achieved by a body of surface water in which concentrations of pollutants do not exceed the environmental quality standards (EQSs) established in Annex I of the EQS Directive (2008/105/EC, as amended by Directive 2013/39/UE);

Environmental quality standards - the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceed in order to protect human health and the environment.

Topic 1
b. Definitions – 2

Hazardous substances (HS) – substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or group of substances which give rise to an equivalent level of concern;

Priority substances (PS) **-** are those which present a significant risk to or via the aquatic environment, identified in accordance with art. 16(2) of the WFD and listed in Annex 1 of the Directive 2013/39/UE;

Pollutant – any substances liable to cause pollution;

Sources - all processes and activities that are likely to contribute to the input of pollutants into the environment (any type of diffuse or point sources: industries, agricultural, transports, human agglomeration).

Topic 1
b. Definitions – 3

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Art. 5 of the Environmental Quality Standards Directive establish an inventory of emissions, discharges and losses of all PSs and other pollutants

Discharges, emissions and losses – refer to all inputs coming from point and diffuse sources and which coming from land and sea based sources or airborne transport

Point source - a single localized point of discharge of wastewater containing one or more pollutants (i.e. waste water treatment plants, farms etc.)

Diffuse sources - the many smaller or scattered sources from which pollutants may be released to land, air or water (i.e. from urban area, agriculture, industry - mining etc.)

Pathways are the means or routes by which specific substances can migrate or are transported from their various sources to the aquatic environment (i.e. atmosferic depositions, surface waters, stormwaters, waste water treatment plants, soil).

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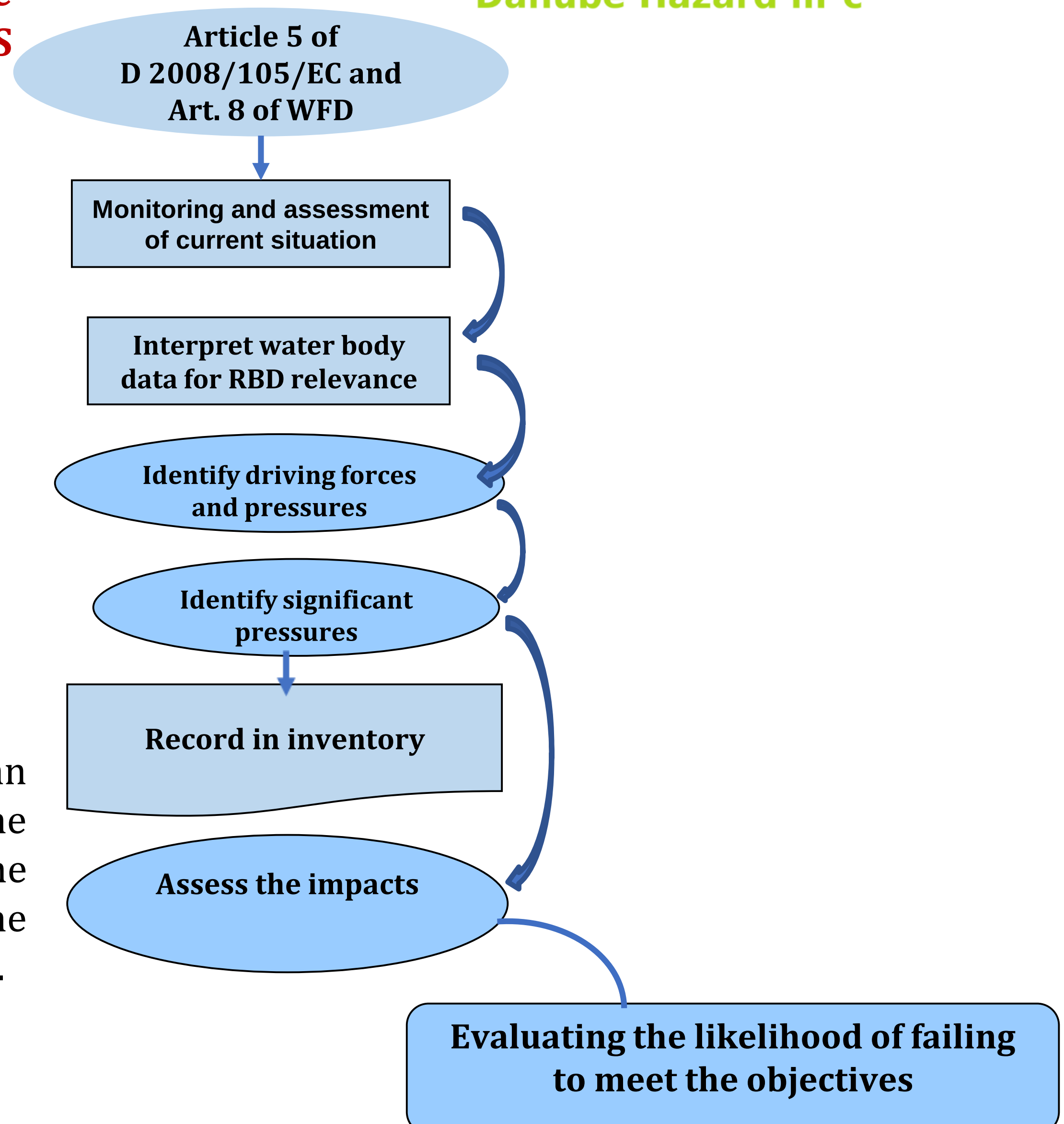
Topic 1

b. Start assessment per substance presence of discharge with EQS exceedance



DPSIR approach

Member States shall carry out an assessment of the susceptibility of the surface and groundwater bodies to the all pressures identified, including the specific priority substances pressures.

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Topic 1.
c. Key EU and national legal requirements concerning management of HS in water - 1

Main aspects of the legal requirments on:

- ✓ Immissions oriented general policies i.e., concerning the quality of water bodies
- ✓ Emissions oriented policies i.e. concerning the point source discharges (industrial & municipal)
- ✓ Policies, concerning non-point source (diffuse) discharges - mostly preventive, emissions oriented

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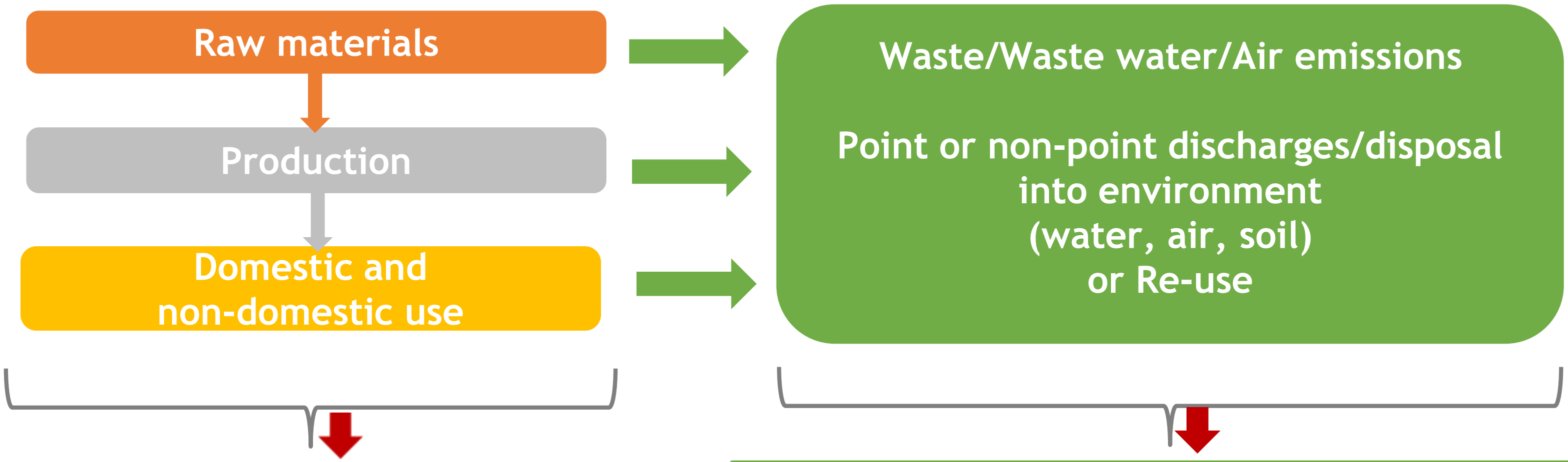
Topic 1
c. Key EU and national legal requirements - 2



PRODUCTION AND USE POLICIES

- ❖ D 2019/904/EU - on the reduction of the impact of certain plastic products on the environment
- ❖ 2006 REACH Regulation - rules for the registration and regulation of the production and import of substances
- ❖ Regulation 1272/2008 on classification, labelling and packaging of substances and mixtures
- ❖ Regulation 2020/741 on minimum requirements for water reuse
- ❖ Regulation 2019/1021 and Stockholm convention on Persistent Organic Pollutants
- ❖ Other

ENVIRONMENTAL (WATER RELATED) POLICIES

- ❖ **General policies** concerning water bodies:
  - D 2000/60/EC Water Framework Directive
  - D 2006/118/EC on the protection of groundwater against pollution and deterioration
  - D 2008/105/EC amended by D 2013/39/EU as regards priority substances in the field of water policy
  - D 2009/90/EC - technical specifications for chemical analysis and monitoring of water status
  - Regulation (EC) No 166/2006 on the establishment of a European Pollutant Release and Transfer Register
- ❖ **Point source discharge**: D 2010/75/EU on industrial emissions (IED); D91/271 (Urban wastewater treatment directive)
- ❖ **Diffuse source discharge**: D 2009/128 on sustainable use of pesticides and Regulation (EC) No 1185/2009 on pesticide statistics

The key EU legislative documents concerning production, use and release of HS

Topic 1
c. Key EU requirements and comparison of national legislative framework - 3

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- ✓ The national legislative frameworks of both EU and non-EU project partners' countries, are fully harmonised with the key relevant EU directives, except for Directive 2010/75/EU (IED) which is still in process of adoption by Ukraine.

but…

- ✓ In many cases the transposition of the EU Directives into the national legislation is realized through more than one national document which demands additional harmonization between the different acts and thus makes the general management more complicated.
- ✓ For industries which are not subject of control pursuant to Directive 2010/75/EU (IED) the emissions standards for wastewater discharges vary from country to country in terms of number of monitored substances and respective limit values for concentrations. This creates unequal conditions for industrial development and complicates the application of "polluter pays" principle.

Topic 1
c. Key EU requirements and comparison of national legislative framework- 4

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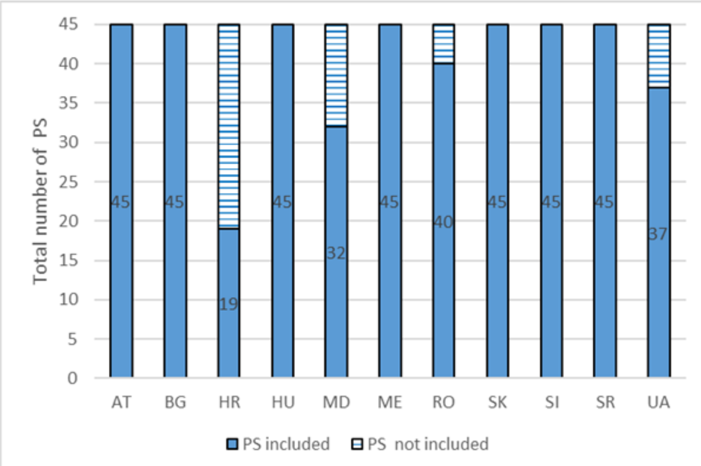
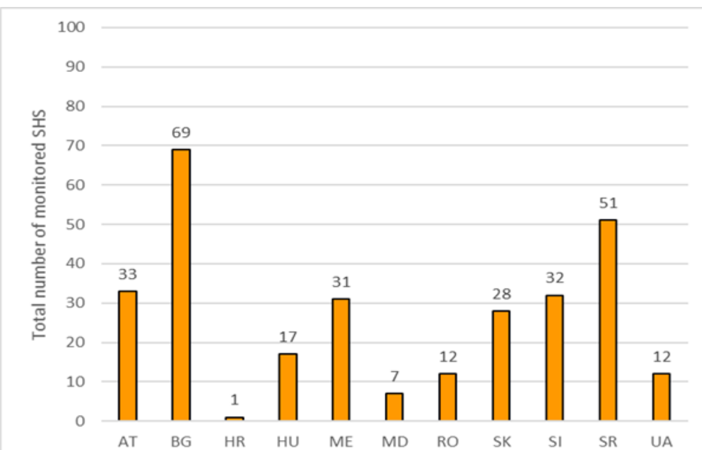
Common features of the conceptual design of the national policies

- ✓ Each country has regulations for monitoring of imissions of chemical substances (including HS) in surface water and groundwater bodies.
- ✓ Each country has a regulatory framework for minimum emission standards to be met by the operators discharging wastewater in municipal sewer networks (*indirect discharges*) and surface water bodies (*direct discharges*).
- ✓ The wastewater discharges are subject to individual permit granted by the responsible national authorities. The installations listed in Annex I of the IED are subject to specific regulations pursuant to the requirements of IED;
- ✓ There are fees for discharge into sewer networks and they are established by the sewer operators. In all the countries, except in Austria, there are fees for wastewater discharge into river bodies.
- ✓ The results of monitoring and control over the emitters are organized in electronic registers and data bases, which however are not always online or public available.

Topic 1
c. Monitoring of hazardous substances in surface water - 5





- 11 PSs included in the national monitoring programs in all the countries: ***Anthracene, Cadmium and its compounds, Endosulphan, Hexachlorobenzene, Hexachlorobutadiene, Hexachlorocyclohexane, Mercury and its compounds, Nonylphenols (4-Nonylphenol), Pentachlorobenzene, Trifluralin and Heptachlor and heptachlorepoxide.***

- 5 PSs are the least monitored: ***tributyltin compounds (cation), PFOS, dioxins and dioxin-like compounds, bifenox, HBCDD.***

- ***Only 10 other SHSs are monitored in more than half of the countries studied: 4 heavy metals and metalloids (arsenic, chromium, copper and zinc); organic substances (o, m, p-xylene, phenols, Bisphenol A;PCBs; cyanides) and one herbicide – terbuthylazine;***

Topic 1
c. Monitoring of hazardous substances in ground water - 6

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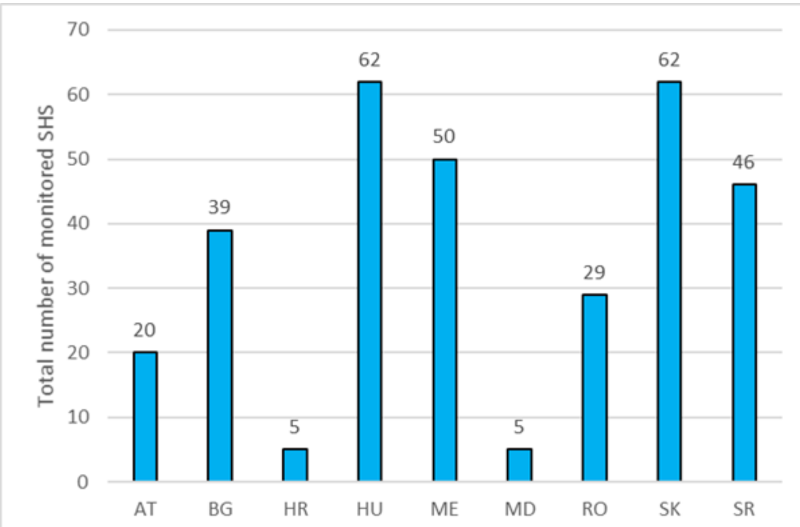


Hazardous substances that are monitored in groundwater in over 50% of the countries

Type	Hazardous Substance name
Metals	Arsenic, Cadmium**, Lead*, Mercury**, Nickel*
Plant protection products	Aldrin, Allachlor*, Atrazine*, Dieldrin, Simazine*
Industrial origin	Trichlorethylene

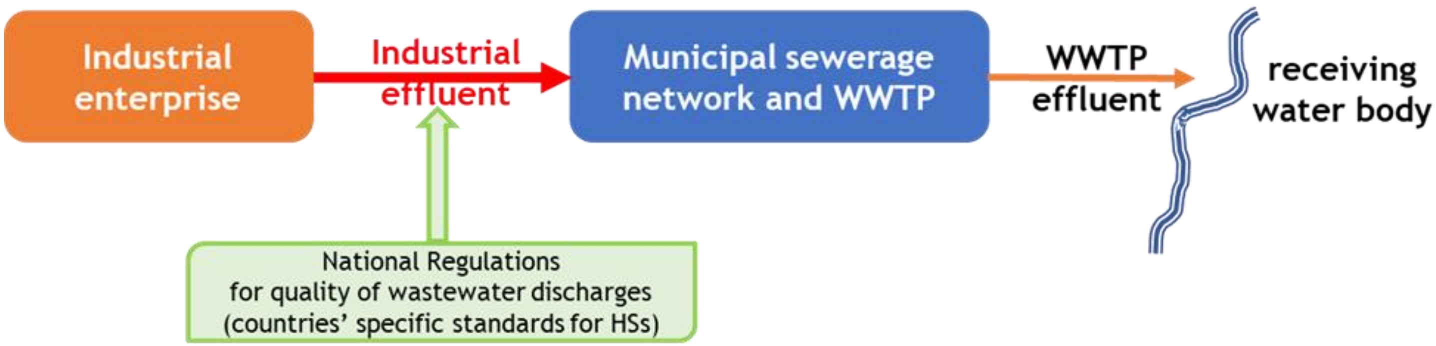
- **Priority substances, ** Priority hazardous substances**

➢ Directive 2006/118 (the ground water directive) recommends each country to develop threshold values at least for the following hazardous substances: ***arsenic, cadmium, lead, mercury, trichloroethylene and tetrachloroethylene.***

➢ Such threshold values have been determined in Austria, Bulgaria, Croatia, Hungary and Romania. In Montenegro, Moldova, Slovakia and Serbia the development of EQS for these substances is not yet completed.

Topic 1
c. Regulation of point source discharges - 7

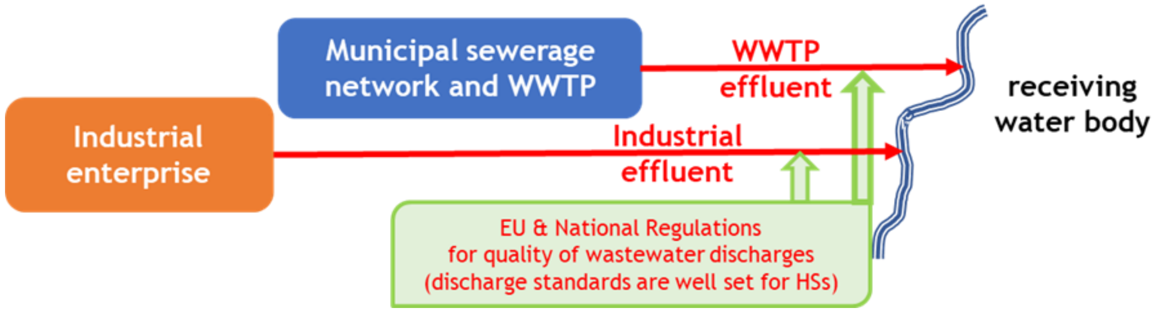
- **Approaches for regulation of industrial discharges into sewer networks**



- In Bulgaria, Montenegro, Romania and Slovakia there are general rules for discharge of industrial wastewater into sewer networks. In Bulgaria there are also different emission standards for discharge into sewer networks with and without WWTP.
- In Austria, Croatia, Hungary and Slovenia there are general rules for emission standards, complemented however by additional requirements (e.g. different concentrations or extended list of substances) for certain types of industrial branches and/or technological process.

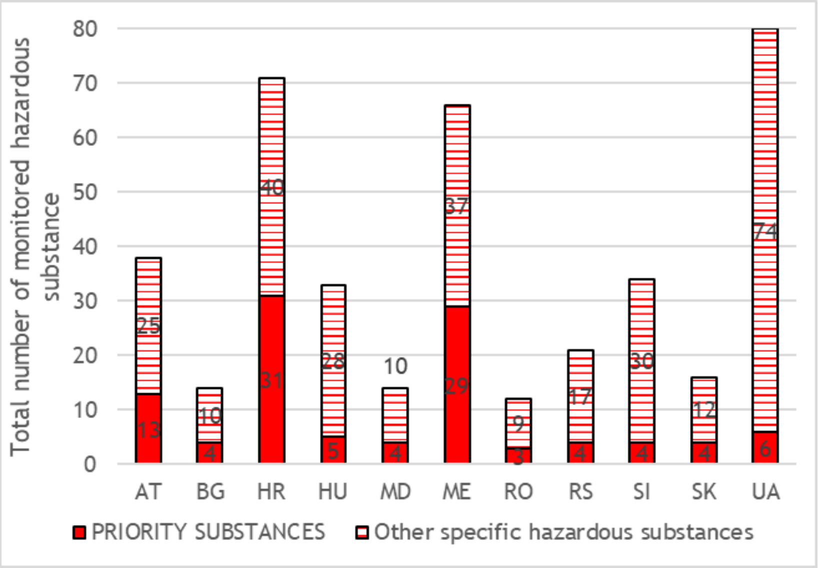
Topic 1
c. Regulation of point source discharges - 8

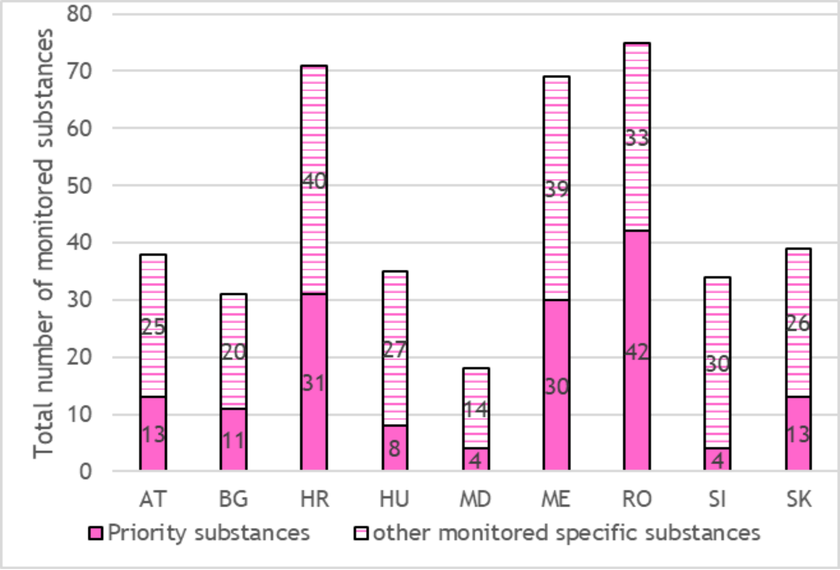
➢ Approaches for regulation of direct industrial discharges



- *In Austria, Croatia, Hungary and Slovenia the approach is similar as for the indirect industrial discharges. In Bulgaria, Romania and Slovakia the emission standards target specific industrial branches. In Montenegro a significant number of parameters must be measured when obtaining discharge permit. Afterwards a shorter list of specific parameters is established in the mandatory monitoring program.*
- *The control of hazardous substances in the WWTPs discharges varies substantially in the different countries and is not consistent for all the WWTPs. The most monitored substances seem to be the heavy metals, although there are countries like Montenegro and Romania which monitor a longer list of SHSs.*
- *The control of hazardous substances discharged through the combined sewer overflows is not regulated in any of the investigated countries. Only Austria reports for "state of the art" standard of the Austrian Water and Waste Management Association.*

Topic 1
c. Regulation of point source discharges - 9





- *Only four priority substances -* **cadmium, lead, nickel and mercury** *- are regulated in over 80% of the investigated countries.*
- *Specific hazardous substances monitored in over 80% of the countries are:* **arsenic, chrome (6+), copper; cobalt and zinc.**
- *The emission standards very significantly from country to country, sometimes in an order of magnitude*

Topic 1
c. Regulation of diffuse pollution -10

- **Approaches for regulation of diffuse pollution (in particular from agricultural activities)**

- *All the countries have well developed regulatory basis for preventive control, in particular from agricultural activities (e.g. various permissions and certifications related to plant protection products activities), following the requirements of Directive 2009/128/EC for establishing sustainable use of pesticides.*

- *The onsite control of the plant protection products application is predominantly passive however, e.g., relying on good agricultural practices, keeping of appropriate records for pesticides application. Only Austria and Slovakia report for programs for control of plant protection products through analyses of soils.*

- *In all the National Action Plans for sustainable use of pesticides are envisaged measures for protection of aquatic environment and drinking water against pollution with hazardous substances. Besides some conventional measures (e.g., establishment of protection zones, ban of some PPPs on certain zones, etc.), some countries (Hungary, Romania and Slovakia) propose development/improvement/ enhancement of the informational system concerning PPPs application.*

Topic 1

d. Role of monitoring and the main pathways in the context of HS management - Monitoring

- Article 8 of the WFD and Annex V: Member States shall ensure the **establishment of programmes for the monitoring of water body status** to establish an overview of water status within each river basin district
- The monitoring requirements depend to a large extent on **the pressures and impacts** that have been identified for the specific water body
- **Requirements can change** with ongoing assessments and changes in anthropogenic pressures and impacts (Guidance document No 3)
- Hazardous Substances monitoring provides the basis of early detection of new stress (status) and for a **chemical risk assessment** in surface waters
- If necessary, monitoring results can be used for the derivation and evaluation of appropriate **Programs of Measures**

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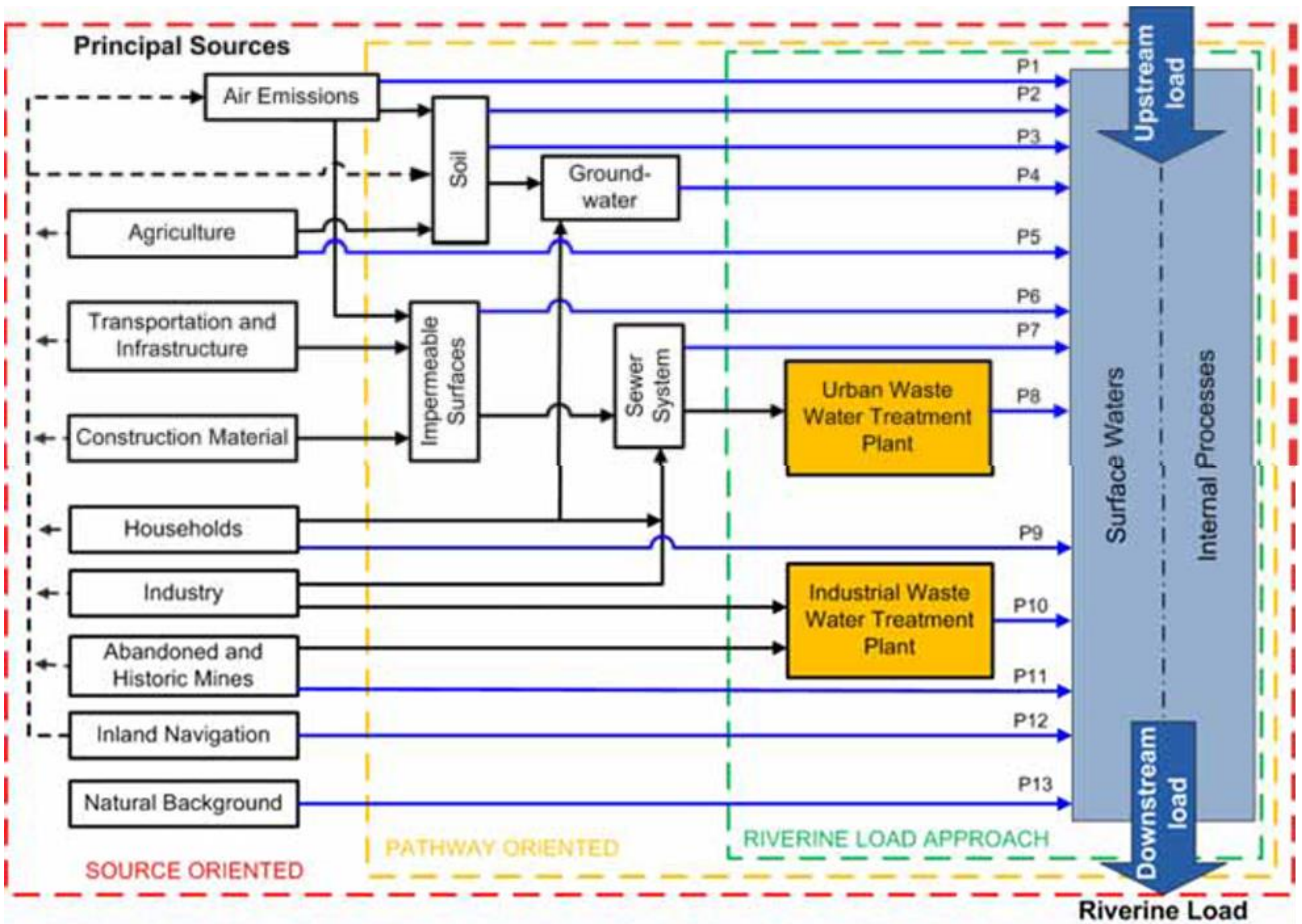
Topic 1

d. Role of monitoring and the main pathways in the context of HS management – Emission Inventory

- Article 5 of the EQS Directive: MSs are obliged to establish an **inventory of emissions, discharges and losses (IEDL)** of all Priority Substances and pollutants (Part A Annex I: 45 substances and group of substances); Guidance document 28 on the preparation of the IEDL of HS
- The reference space is **the River Basin District (RBD) level or part of a River Basin District**
- Reported loads discharged to the aquatic environment should give **transparency** with regard to pollution and on the **need for measures**
- The criteria recorded cover:
  - Assessment of ecological and chemical status objectives
  - Significant point source pollution (urban, industrial, agricultural installations & activities)
  - Significant diffuse source pollution (urban, industrial, agricultural and other installations)

Topic 1

d. Role of monitoring and the main pathways in the context of HS management – Pathways



P1: Atmospheric Deposition
P2: Erosion
P3: Surface Runoff from Unsealed Areas
P4: Interflow, Tile Drainage and Groundwater
P5: Direct Discharges and Drifting
P6: Surface Runoff from Sealed Areas
P7: Storm Water Outlets, Combined Sewer Overflows and Unconnected Sewers
P8: Urban Waste Water Treated
P9: Individual - Treated and Untreated- Household Discharges
P10: Industrial Waste Water treated
P11: Direct Discharges from Mining Areas
P12: Direct Discharges from Navigation
P13: Natural Background

https://circabc.europa.eu/sd/a/6a3fb5a0-4dec-4fde-a69d-5ac93dfbbadd/Guidance%20document%20n28.pdf

Topic 1

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d. Role of monitoring and the main pathways in the context of HS management – Pathways

TIER	BUILDING BLOCKS	EXPECTED OUTPUT	RESULTS FOR THE INVENTORY
STEP 1: ASSESSMENT OF RELEVANCE			
	Information sources identified in Art. 5 of EQS directive, see section I.1	Decision of relevance	List of relevant and less relevant substances
STEP 2: APPROACHES FOR RELEVANT SUBSTANCES			
1. Point source information	• Data on point sources • Emissions factors	• Availability of data • Quality of data • Identification of gaps	• Point source emissions • Listing of identified data gaps
2. Riverine load approach	add: • River concentration • Data on discharge • In stream processes	• Riverine load • Trend information • Proportion of diffuse and point sources • Identification of gaps	• Rough estimation of total lumped diffuse emissions • Verification data for pathway and source orientated approaches • Listing of identified data gaps
3. Pathway orientated approach	add: • Land use data • Data on hydrology • Statistical data • .... •	• Quantification and proportion of pathways • Identification of hotspots • Information on adequacy of POM	• Pathway specific emissions • Additional spatial information on emissions
4. Source orientated approach	add: • Production and use data e.g. from REACH • SFA • Substance specific emission factors • .... •	• Quantification of primary sources • Complete overview about substance cycle • Information on adequacy of POM	• Source specific emissions • Total emissions to environment and proportion to surface waters

https://circabc.europa.eu/sd/a/6a3fb5a0-4dec-4fde-a69d-5ac93dfbbadd/Guidance%20document%20n28.pdf

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Topic 1

d. Role of monitoring and the main pathways in the context of HS management - modelling

- To **avoid high costs and spatial constraints** of monitoring, modelling is mentioned as a suitable instrument to:
  - bridge information gaps
  - provide regionalized system analyses with quantification of pathways and sources
  - Give better insights in the role of diffuse pollution and the specific pathways
  - Calculate the effect of scenarios (e.g. of mitigation measures)
- **Models differ** widely in complexity, spatial and temporal resolution
- In DHm3c the **MoRE Emission Model** (pathways – Tier III) and **SOLUTIONs model**, an emission based coupled model approach (pathways & sources – Tier III + IV) is used
- Model input data differ significantly from general monitoring data, e.g. used for emission-based (point sources) or in-stream based assessment

Topic 1

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d. Role of monitoring and the main pathways in the context of HS management- modelling & monitoring

- The aim of the model approaches in DHm3c is an integrated assessment of selected substances on sub-catchment level
- To address different pathways or sources, model quality highly depends on substance specific information in surface waters and other environmental or engineered compartments
- Data supporting this approach (if available at all) are often fragmented and show considerable spatial and temporal discrepancies
- Analytical standard procedures are often insufficient and show limits of quantification higher than needed
- Furthermore data should be adapted to the spatial scale (10^{th} to 100s of km2) and to the temporal scale (annual)

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Topic 1

d. Role of monitoring and the main pathways in the context of HS management- modelling & monitoring

- In seven pilot regions DHm3c monitoring strategy focusses on a well concerted investigation of different substances to improve data on:
  - Surface waters (low/medium and high flow conditions)
  - Deposition
  - Soils
  - Urban and industrial WWTPs
- Aim to:
  - Calculate more precise annual surface water loads, especially for those substances with tendency to adsorb to particles (high flow evaluation)
  - To form the basis for a preparation of a regionalized data base (e.g. using statistical or geo-statistical methods) and to optimize parametrization of most important pathways
  - To provide a sound data base my merging own measurements with existing data from literature and other projects
  - Consequently, to improve model validation and exactness


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TECHNISCHE UNIVERSITÄT WIEN

Institute of Chemistry

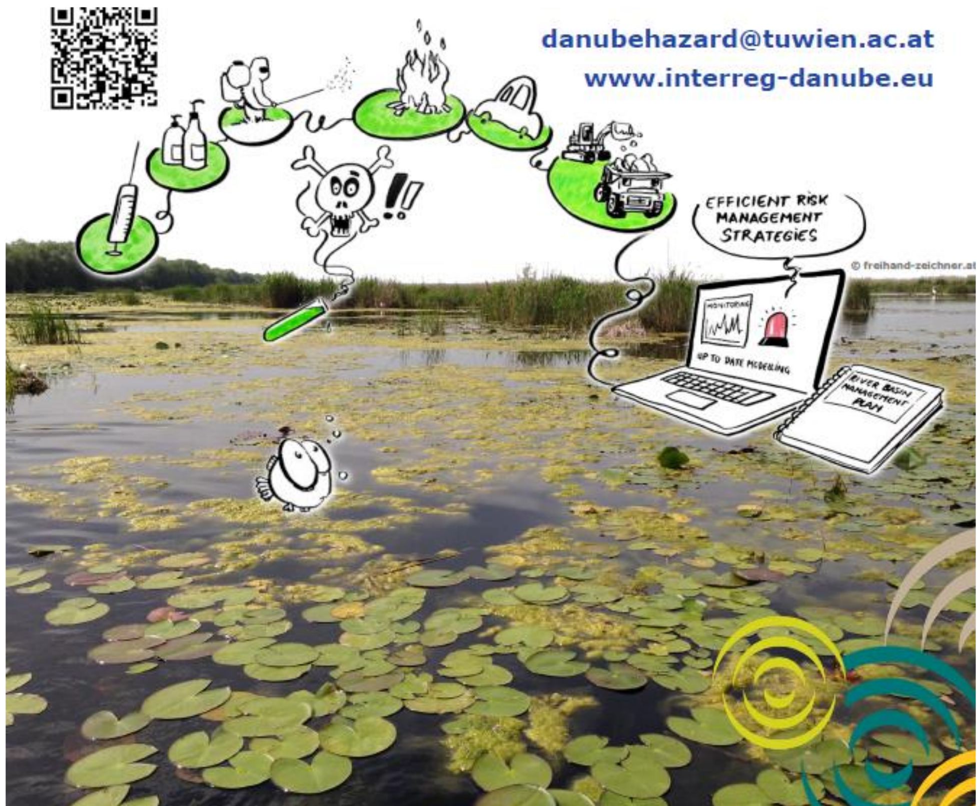
Bulgarian Water Association

Center for Eco-Toxicological Research

ICPDR IKSD

International Commission for the Protection of the Danube River

Internationale Kommission zum Schutz der Donau



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ENVIRONMENT AGENCY AUSTRIA

Administrația Națională Apele Române

Jožef Stefan Institute, Ljubljana, Slovenia

MŰEGYETEM 1782

Project co-funded by European Union funds (ERDF, IPA, ENI) and National Funds of the participating countries

AGENDA

Topic 1. Hazardous substances aspects of water quality monitoring and inventorying of pollution sources and pathways

Topic 2. Monitoring of the hazardous substances

Topic 3. Technical aspects of HSs sampling and measuring

Topic 4. Contribution of the results of our DHm3c monitoring to the inventory of hazardous substance pollution

Topic 5. Modeling of Hazardous Substances

Topic 2: Monitoring of Hazardous Substances – general aspects

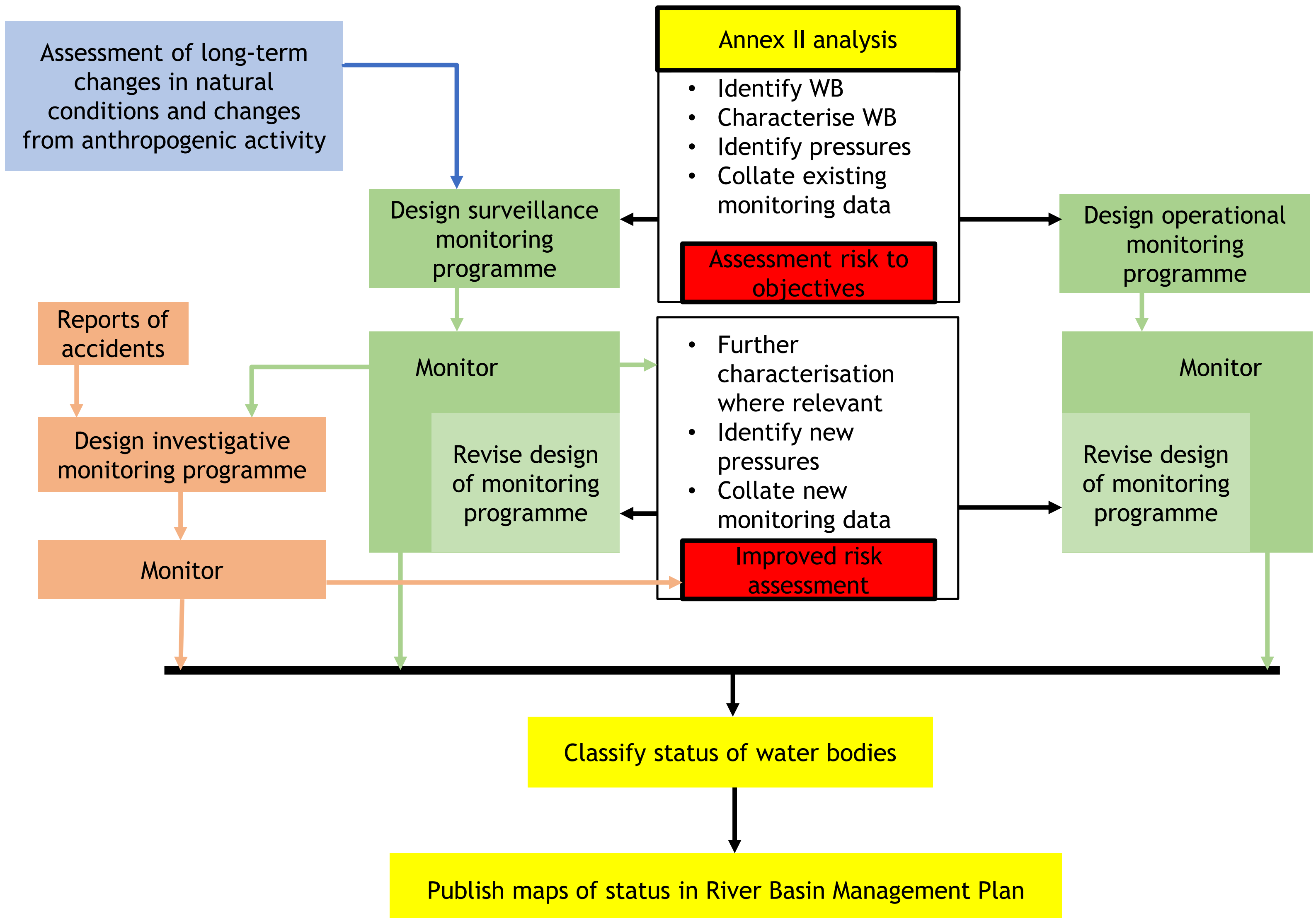
a) Monitoring under the WFD, types of monitoring
b) Criteria and technical aspects of different monitoring types under the WFD
c) Selection of hazardous substances to be monitored and selection of the monitoring sites (representativeness)
d) Criteria for laboratories performing monitoring

Topic 2
a. Monitoring under the WFD

Objective of monitoring is to establish a coherent and comprehensive overview of water status within each *River Basin District* and must permit the classification of all surface water bodies:

- ecological status or ecological potential: five classes – high/maximum, good, moderate, poor, bad
- chemical status: 2 classes – good or bad
- *River Basin District* – member states should identify individual river basins within their territory and assigns them to River Basin Districts

Topic 2
a. Relationship between Monitoring and Status Assessment



Topic 2
Map of Chemical Status of Danube River Basin District (Slovakia)

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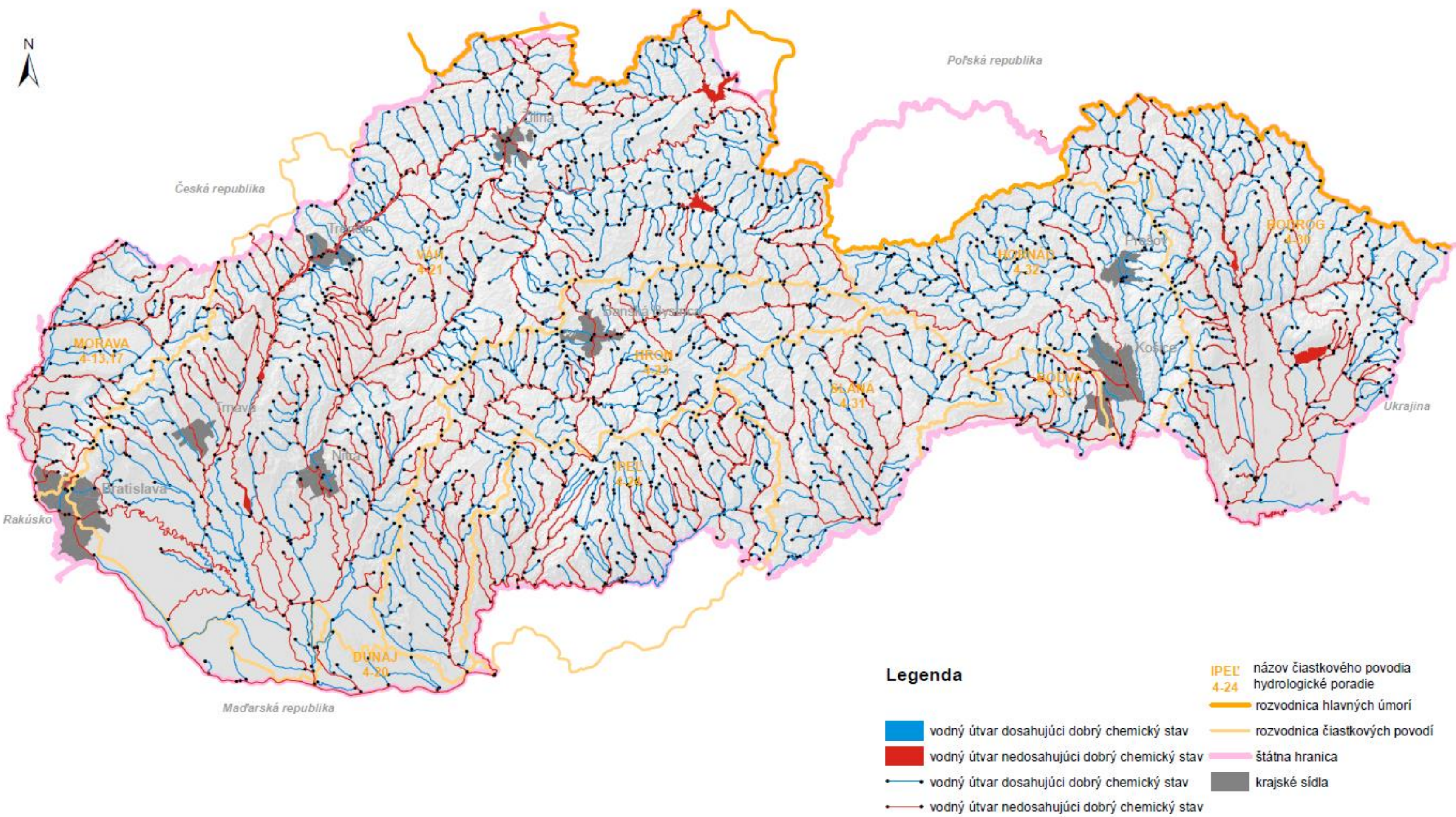
Plán manažmentu správneho územia povodia Dunaja
Chemický stav útvarov povrchovej vody – obdobie 2013 až 2018 — Mapa 5.4



Tematický obsah zostavený podľa zákona č. 364/2004 Z. z. organizáciami rezortu životného prostredia SR.
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Podklad - digitálny terénny model SR (25 m) © 2000 CEI-SAŽP v súlade so zákonom č. 205/2004 Z. z.

Mierka 1:1 100 000
1 cm = 11 km
0 7,5 15 30 45 60 km

Topic 2

Map of Ecological Status/Potential of Danube River Basin District (Slovakia)

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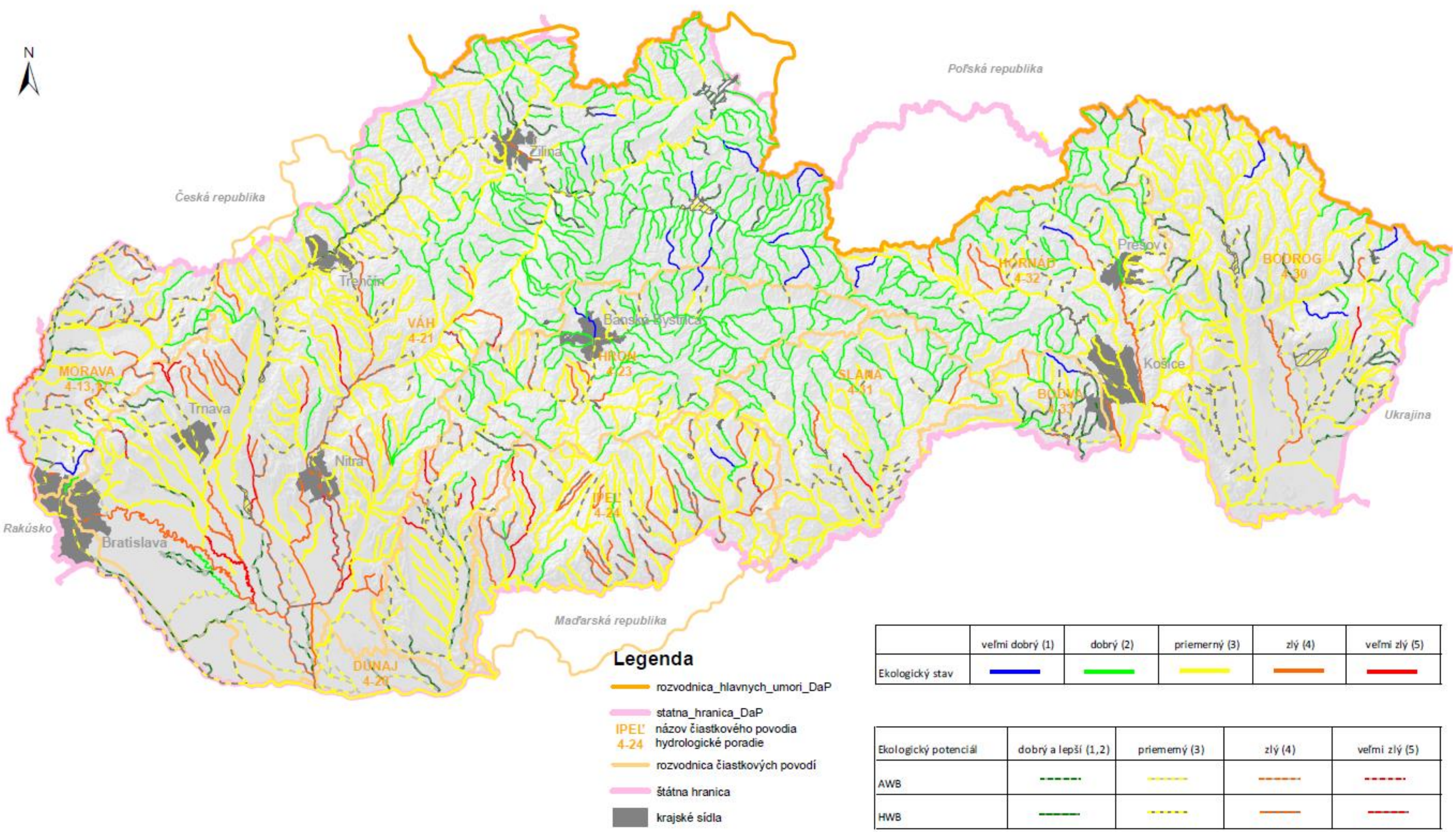
Plán manažmentu správneho územia povodia Dunaja

Ekologický stav/potenciál útvarov povrchovej vody – obdobie 2013 až 2018 Mapa 5.3



	veľmi dobrý (1)	dobrý (2)	priemerný (3)	zlý (4)	veľmi zlý (5)
Ekologický stav					

Ekologický potenciál	dobrý a lepší (1,2)	priemerný (3)	zlý (4)	veľmi zlý (5)
AWB				
HWB				

Tematický obsah zostavený podľa zákona č. 364/2004 Z. z. organizáciami rezortu životného prostredia SR.
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Mierka 1:1 100 000
1 cm = 11 km
0 7,5 15 30 45 60 km

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b. Types of Monitoring under the WFD

Surveillance monitoring:

Supplementing and validating the impact assessment (detailed in Annex II of the WFD);

Efficient and effective design of future monitoring programmes

Assessment of long term changes in natural conditions

Assessment of long term changes resulting from widespread anthropogenic activity

Operational monitoring

Establish the status of those bodies identified as being at risk of failing to meet their environmental objectives

Assess any changes in status of such bodies resulting from the programmes of measures

Investigative monitoring-

Where reasons for any exceedances (of Environmental Objectives) is unknown

Where surveillance monitoring indicates that the objectives set for a body of water are not likely to be achieved and operational monitoring has not already been established

To ascertain the magnitude and impact of accidental pollution

Topic 2

b. Design of Surveillance Monitoring

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Quality elements:

- Biological quality elements;
- Hydro-morphological quality elements
- General physico-chemical quality elements
  - Thermal and oxygen conditions, salinity, acidification status, nutrient conditions
- Other specific pollutants (e.g. river basin specific pollutants)
  - Priority substances (discharged into river basins or sub-basins), other substances identified as being discharged in significant quantities into the water body

Topic 2

b. Design of Surveillance Monitoring

- Selection of monitoring points:
  - Should cover adequately: water bodies probably at risk, probably not at risk and not at risk of failing the environmental objectives.
  - Sampling points should include major rivers as well as points downstream end of relevant sub-catchments.
  - Sampling points before the water body cross the state border - In case of transboundary waters, selection of monitoring point should be consulted between member states involved.
  - Monitoring points should be representative for the water body, should not be directly influenced by discharges
- Is not intended for:
  - Mapping a analysing water quality problems
  - Testing the effectiveness of programme of measures
  - Obtaining detailed or complete overview of the quality of all types of water

Topic 2

b. Design of Operational Monitoring

- Contrary to surveillance monitoring, operational monitoring is characterized by spatial and temporal monitoring network, problem-oriented parameter selection and sampling.
- May be modified during the planning period
- Frequency can be reduced
- Can be stopped when good status is achieved and there is no risk of failing the environmental objectives
- Monitoring parameters
  - Any priority pollutants and other pollutants discharged into the water body in significant amounts and relevant physico-chemical parameters relevant for reliable interpretation of obtained results.

Topic 2

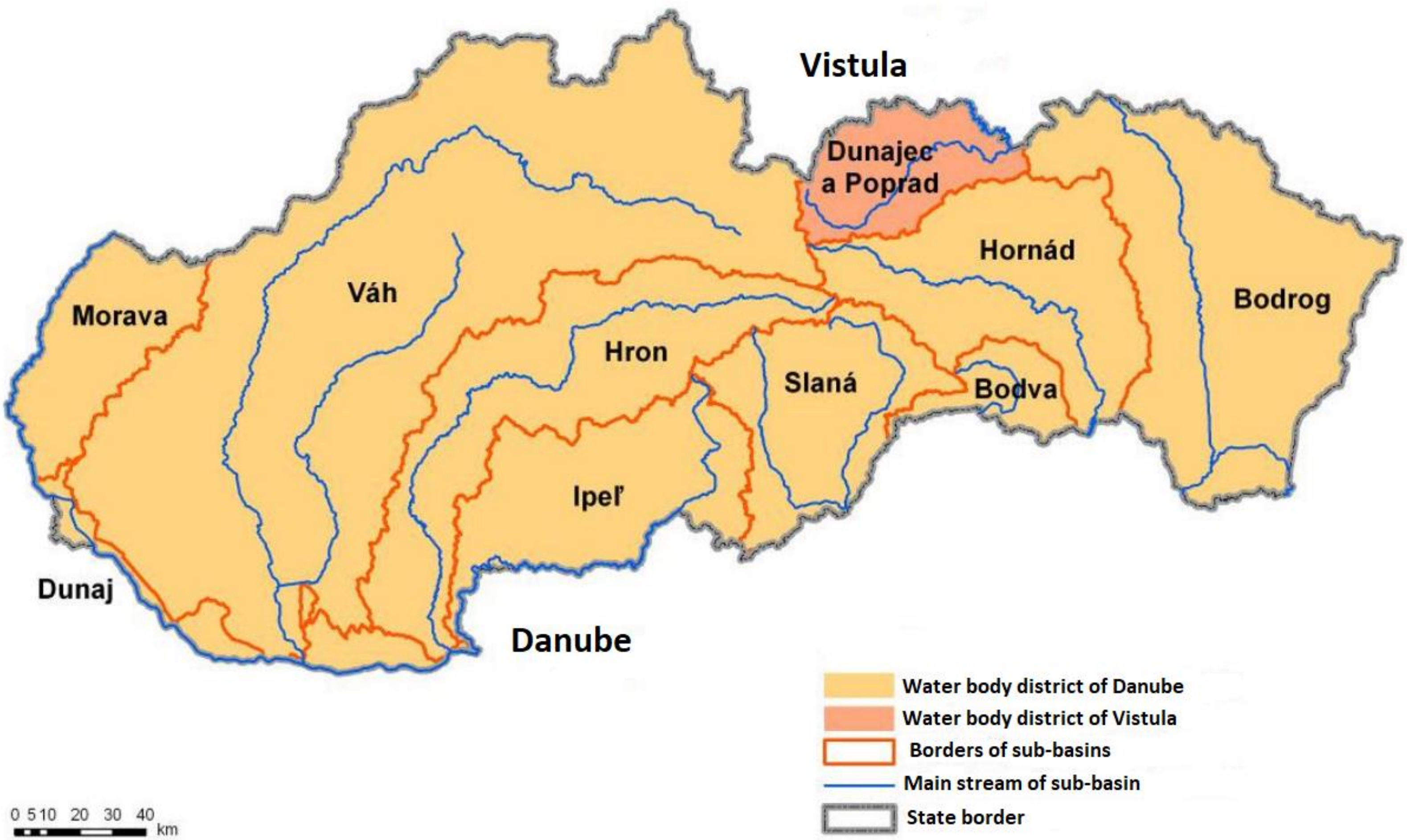
b. Surveillance and Operational Monitoring Network – Slovak example

- Permanent monitoring network – 87 monitoring stations covering all sub-basins, all types and whole gradient of pollution, status and potential
- Aim – to obtain long term homogenous data for various assessments
- All types of monitoring (Surveillance, Operational and Investigative)
- Will be used for the whole period of 6 years, some parameters will be monitored with monthly frequency
  - Transnational water (SK-HU, AT, -CZ, -PL, -UA) – Priority Substances, Other pollutants
  - Danube Trans National Monitoring Network – Priority Substances, Other pollutants
  - Sites aimed for reporting to European Environmental Agency
  - Sites aimed for reporting according to Directive on the reduction of national emissions of certain atmospheric pollutants (NECD, 2016/2284/EU)
  - Sites for water quantity monitoring
  - Sites for long-term monitoring of surface water quality (PS - biota and sediments)
  - Sites for Watch List monitoring

Topic 2

b. Example – Monitoring Programme in Slovakia

- Water bodies districts: Danube, Vistula
- Number of water bodies in Slovakia in total: 1351



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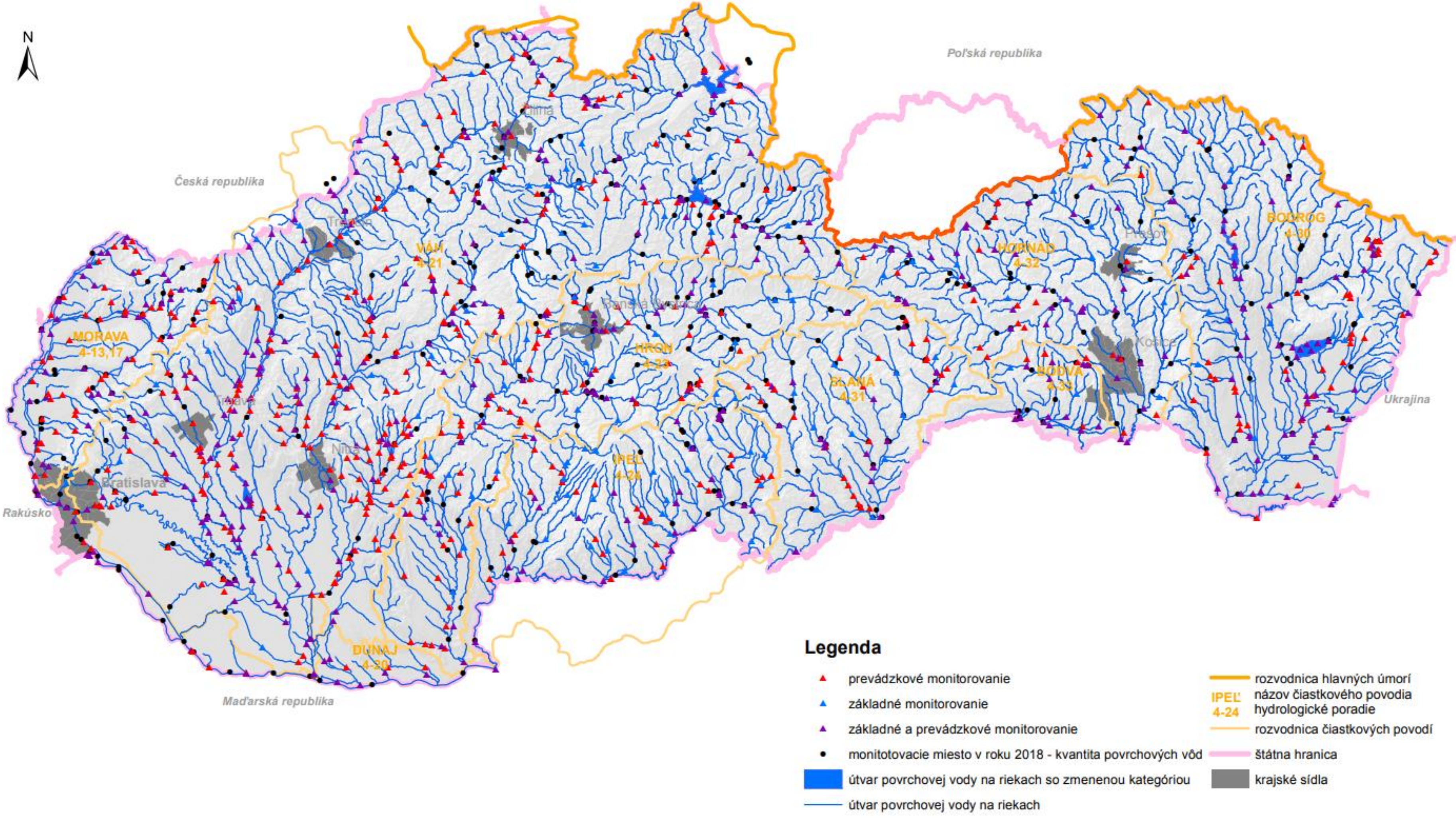
b. Surveillance and Operational monitoring network of Danube water basin district in Slovakia



b. Design of Investigative Monitoring

- Starting point of Investigative Monitoring is when surveillance or operational monitoring reveals that EQS values are exceeded, but causes are unknown or poorly understood.
- Can be performed in case of accidental pollution
- No general guidance is available, case by case approach, expert knowledge and judgment is required.
- Monitoring points, matrix, parameters, sampling frequency and duration of monitoring should be adjusted to the specific case.
- Can be stopped as soon as the cause of no-compliance has been identified.

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b. Minimum frequency of sampling according to WFD

Quality element	Rivers	Lakes
Biological		
Phytoplankton	6 months	6 months
Other aquatic flora, macro invertebrates, fish	3 years	3 years
Hydromorphological		
Continuity	6 years	
Hydrology	continuous	1 month
Morphology	6 years	6 years
Physico-chemical		
Thermal cond., oxygenation, salinity, nutrient status, acidification status	3 months	3 months
Other pollutants	3 months	3 months
Priority substances	1 month	1 month

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c. Selection of Hazardous Substances

- **Priority substances and priority hazardous substances**, certain other pollutants –2000/60/EC (WFD), 2008/105/EC, 2013/39/EU, New update in preparation
  - Assessed as Chemical Status of the water body
- **Other pollutants** – this category of hazardous substances has several names such as: Other pollutants, Specific synthetic/non-synthetic pollutants, but for reporting the term River Basin Specific Pollutants is used.
  - These pollutants are pollutants discharged in significant quantities and should have similar properties as Priority Substances with regards to their toxicity, accumulation in biota or sediments and persistence,
  - Groups of substances for other pollutants are listed as Indicative list of the main pollutants in Annex VIII of the WFD
  - Member State should develop EQS (also named as Chemical (Environmental) Quality Standards) for these substances
  - Assessed as a part of Ecological Status or Ecological Potential because these substances are regulated on national level as well as schemes for assessment of Ecological Status/Potential are developed on national level

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c. Monitoring of Priority Substances in Biota

- Directive 39/2013/EU sets EQSs also for biota for following compounds:
- BDE, fluoranthene, hexachlorobenzene, hexachlorobutadiene, mercury and its compunds, PAH (benzo(a)pyrene), dicofol, perfluorooctane acid and its derivateves (PFOS), dioxins and dioxin-like compounds, hexabromocyclododecane (HBCDD), heptachlor and heptachlor epoxide.
- Member states can under specific circumstances apply EQS also for another matrix or for other taxons of biota. In this case, member states must to established an EQS that offers at least the same level of protection
- Frequency of monitoring should be 1 year.
- When potential risk to or via, the aquatic environment from acute exposure has been identified as a result based on comparison with EQS being applied to biota or sediment, Member State shall ensure that monitoring in surface water is also carried out.

Topic 2

c. Long-term Trend Analysis

- Directive 105/2008/ES requests monitoring of long-term trends on selected compounds tending to accumulate in sediments or biota.
- Anthracene, brominated biphenylether, carbon-tetrachloride, C10-C13 chloroalkanes, di(2-ehtylhexyl)-phthalate (DEHP), fluoranthene, hexachloro-benzene, hexachloro-butadiene, hexachloro-cyclohexane, lead and its compounds, mercury and its compounds, pentachloro-beznene, polyaromtic hydrocabons (PAH), tributyltin compounds, dicofol, perfluorooctane sulfonic acid and its compunds (PFOS), quinoxyfen, dioxins and dioxin-like compounds, hexabromocyclododecane (HBCDD), heptachlor and heptachlor epoxide.
- Member States shall determine the frequency of monitoring in sediment and/or biota, this should be once in 3 years

Topic 2

c. Watch List

- Is established to support the future prioritization exercises
- Compounds present on the Watch List should be monitored at least once per year
- Number of monitoring stations is calculated based on the number of inhabitants and the area of Member State.
- Monitoring stations should be representative taking into account the use patterns of the compound and possible occurrence.
- The maximum number of compound (groups of compounds) on the WL is 14.
- Duration of monitoring of each compound or group of compounds shall not exceed 4 years.

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d. Criteria for Laboratories

- Regulated by Commission Directive 2009/90/EC
- Laboratories performing chemical analysis for assessment of chemical status apply quality management system according to EN ISO/IEC-17025 or other equivalent standard accepted at international level
- Laboratories shall demonstrate their competences:
  - Participation in proficiency testing (ISO/IEC guide 43-1, or other standard accepted at international level)
  - Analysis of available reference materials

Topic 2

d. Criteria for Laboratories

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- For sampling of various water matrices used for monitoring, transport, conservation and storage family of standards ISO 5667 is used
- Samples shall be transported in dark at temperature 3±2 °C
- Samples shall be stored in dark at temperature 3±2 °C
- Sample should be processed within 48 hours after sampling or suitable conservation should be applied (e.g. freezing)

Topic 2

d. Criteria for Laboratories

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- Minimum performance criteria for method of analysis:
  - Uncertainty of measurement 50 % or below (k=2) estimated at the level of EQS
  - Limit of quantification (LOQ) equal or below of 30 % of the EQS

Topic 2

Cost Effectiveness

- Monitoring programme should be cost-effective
  - No guideline on what is cost effective is available
  - In general multiresidues analytical methods are considered to be cost effective (WFD, CIS Guidance No. 19)
  - WFD requests to analyze priority substances with frequency 12 x year what is very costly with regards to sampling and samples logistics
  - Some EQS values are extremely low – very costly methods of sample preparation and hi-end (in other words: very expensive) instruments must be used


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WP T4 - Capacity building
National training course

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Topic 3: Technical aspects of sampling and measuring of Hazardous Substances in different pathways

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AGENDA

Topic 1. Hazardous substances aspects of water quality monitoring and inventorying of pollution sources and pathways

Topic 2. Monitoring of the hazardous substances

Topic 3. Technical aspects of HSs sampling and measuring

Topic 4. Contribution of the results of our DHm^{3}c monitoring to the inventory of hazardous substance pollution

Topic 5. Modeling of Hazardous Substances

Introduction

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Approach for monitoring

WFD[1] monitoring

Main goal: status assessment
Specific goals: trend detection (surveillance monitoring), assessing the effect of the implementation of measures (operational monitoring)
Not provide information about loads and pollution sources!

Inventory supporting monitoring

Main goal: load assessment
Addressed for measuring of concentrations and loads in different pathways (e.g. point and diffuse pollution sources)
Provide information for substance balances and input for modelling.

1 - Water Framework Directive

Introduction

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Objectives of the inventory supporting measurements

Targeted measurement of hazardous substances **concentrations and loads in rivers** and **other environmental and anthropogenic compartments**

Danube Hazard m³c specific goals:

- Select indicator substances for measurement
- Select representative areas
- Demonstrate a cost-effective sampling approach to support inventoring and modeling of HS

Monitoring in Danube Hazard m³c

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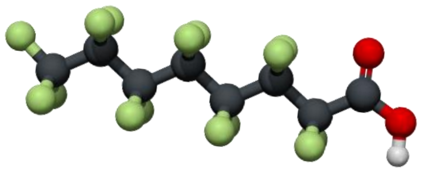
Preselected "indicator" substances
(representative for different sources and relevant in the Danube Basin)

Agriculture

- Tebuconazol (fungicide)
- Metolachlor, Metolachlor -ESA, Metolachlor – OA (herbicide)

Industrial chemicals



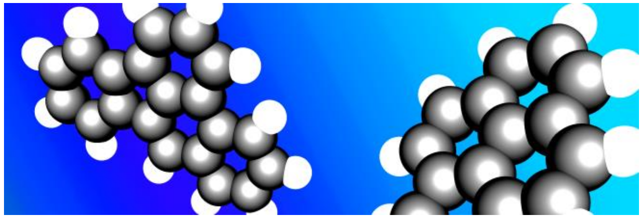
- PFOS, PFOA
- Octylphenol, Bisphenol-A, Nonylphenol

Pharmaceuticals

- Diclofenac
- Carbamazepine

Substances of both natural and anthropogenic origin

- Toxic metals (As, Cd, Cu, Cr, Pb, Hg, Ni, Zn)
- PAH16



Monitoring in Danube Hazard m³c

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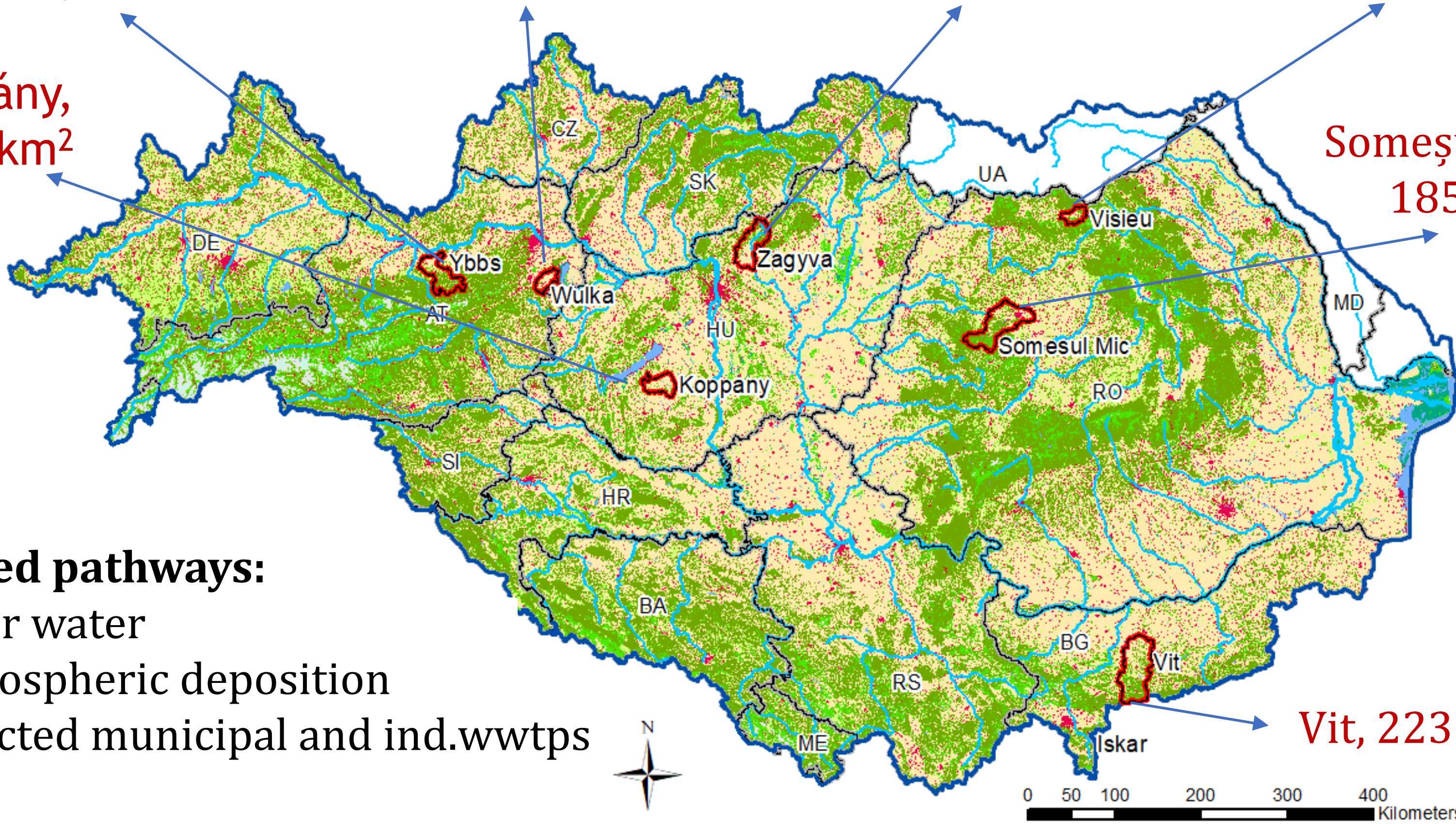
Measurement campaigns were carried out over one year in 7 pilot regions, which were selected to cover differences and major aspects of the Danube River Basin



Sampled pathways:

- River water
- Atmospheric deposition
- Selected municipal and ind.wwtps
- Soil

Technical aspects of the monitoring

Topics for discussion

- Sampling strategies applied in different matrices (rivers, rainwater, wastewater, soil)
- Equipment for sampling
- Sample preparation, common procedures and protocols (SOP)
- Development of special requirements – lessons learned
- Preliminary results

Sampling methods

Grab (spot) sampling

Most typical sampling method which consists of the lab personnel travelling to the sampling point, taking a limited amount (usually 1 litre) of the matrix in some bottle/case, and analysing it in the lab.
Efficiency depends on the frequency (which has its limits).
Traditional monitoring programmes rely predominantly on this method.

Grab sampling of rivers (ISO 5667-3 2018)

- A vessel mounted in a telescopic holder, or a simple bucket,
- Immerse an open-mouthed bottle of sampling system into a flow stream approximately 30 cm below the river surface,
- The inlet of the sampling bottle should face the direction of the river flow.
- Bottles should be filled maximum to 85% of the bottle volume!

Sampling methods

Composite samples

Extension of grab sampling: **samples are grabbed with a higher frequency, mixed together, and the so generated mixed sample (composite) is analysed.**

This is usually done with **an automated sampling device.**

The concentration values of the composite sample are representative of the whole period in which the samples were taken. Samples can be added to the composite **at equal time intervals** (time proportional, e.g. every hour) or **depending on some hydrological property** (e.g. flow proportional). In the second case, automated flow measurements are needed at the sampling location. Linking sampling frequency to turbidity values (measurable online) is also a possibility (Lewis, 1996).

Mixed sampling approach for river monitoring

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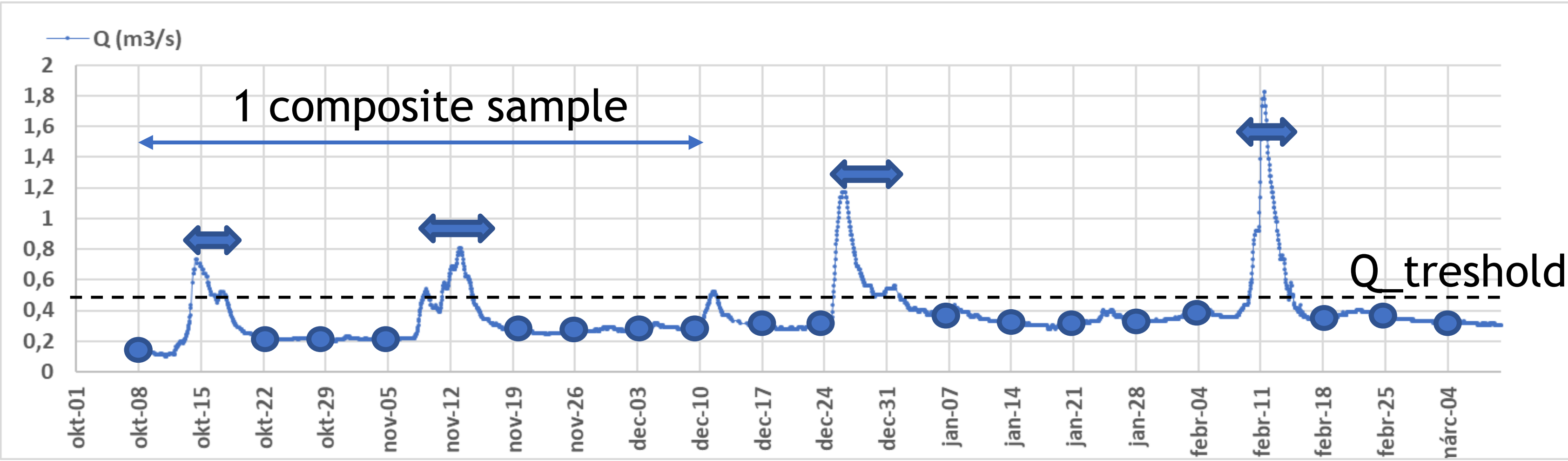

Low and mindflow conditions: weekly spot sampling, 8 samples (2 months) = 1 composite

High flow events: flow proportional sampling with autosamplers

Automatic sampling

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- Enable time-, volume-, flow-, and event-proportional sampling
- Vessels: 12…24, or composite container
- Temperature control for the sample storage chamber
- Power supply required (AC, battery, solar panel)
- Regular maintenance must be provided!

Portable samplers

Stationary sampler

Equipment for automatic sampling (1)

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The video is showing the operation of the autosampler

Wulka pilot region, Austria

Sampling methods

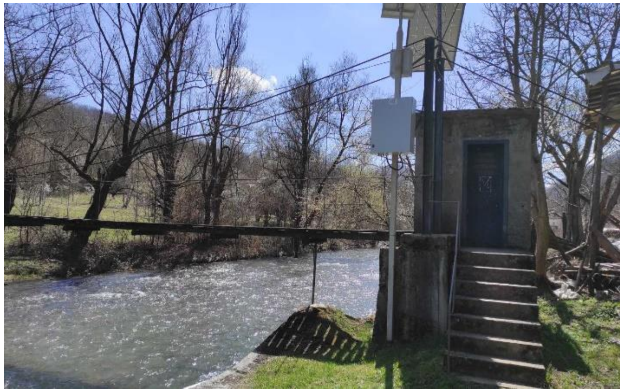
Flow & turbidity-triggered sampling

Turbidity threshold sampling uses real-time turbidity and river level information to:

i) automatically collect targeted water quality samples during high flow events and
ii) to estimate suspended sediment loads during a specific time period.

The system uses a **programmable data logger** in conjunction with a **water level measurement device, a turbidity sensor**, and a pumping sampler. Specialized software enables the user to control the sampling process by setting threshold values for sample collection.

Thresholds are usually chosen so that the square roots of NTU values are evenly spaced to adequately define loads for small storms without oversampling large storms. A programmable data logger, typically recording at 10- or 15-minute intervals, instructs an automatic pumping sampler to collect a sample whenever a threshold is crossed (Lewis and Eads, 2009).



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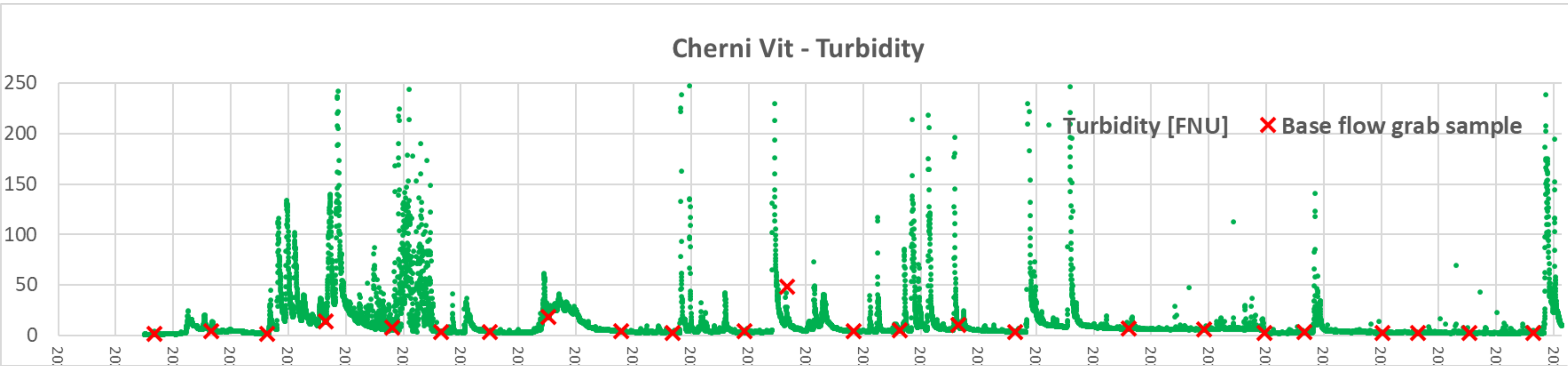
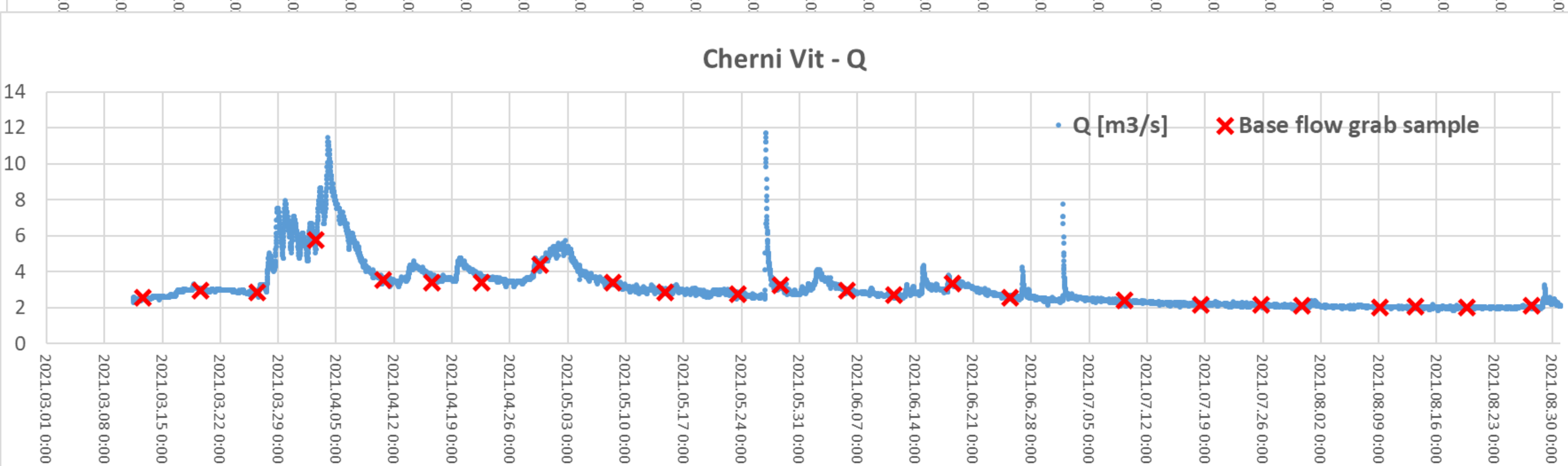
Example:

Weekly spot sampling supported by continuous flow and turbidity measurement at Station Cherni Vit (Bulgaria)





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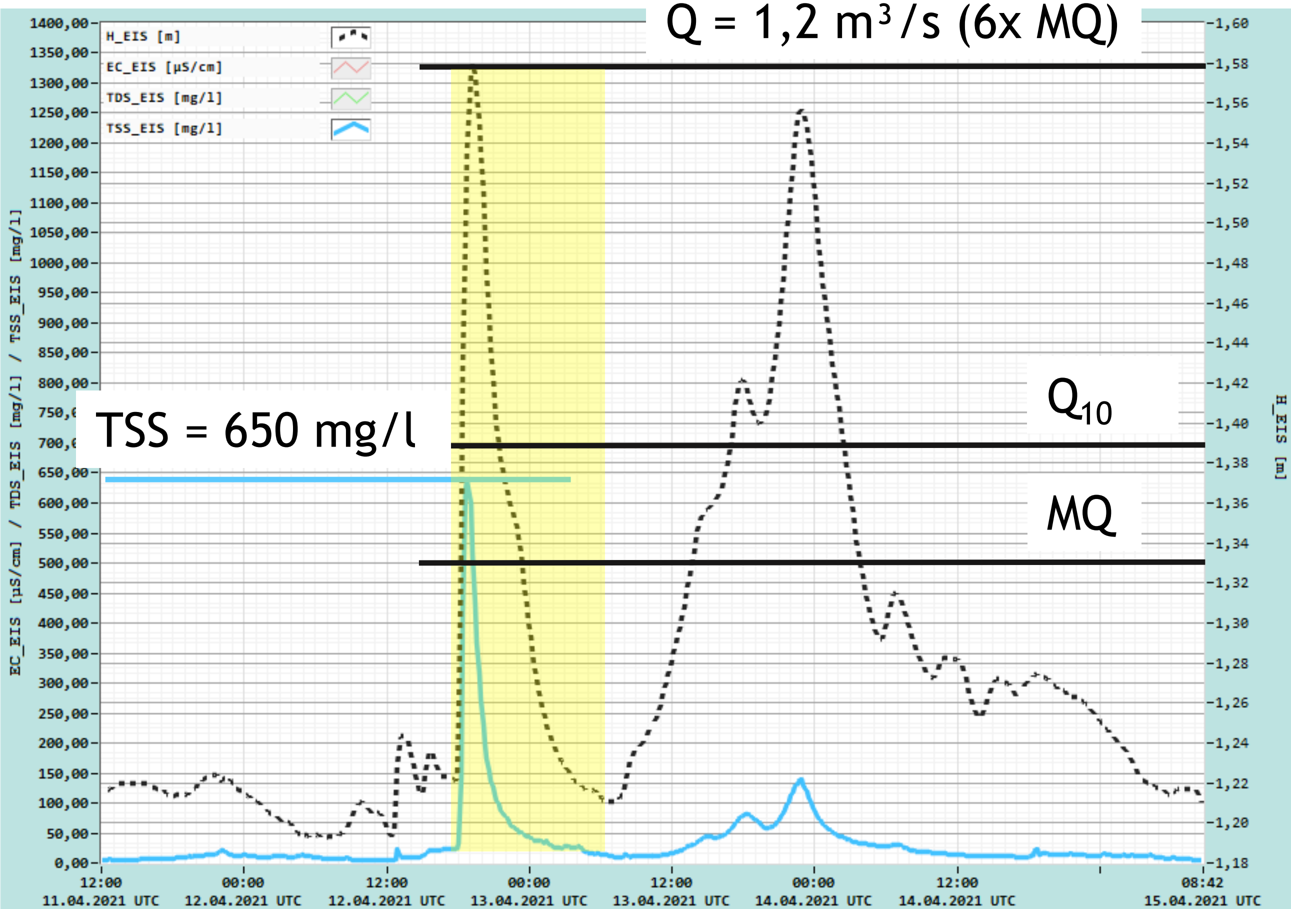
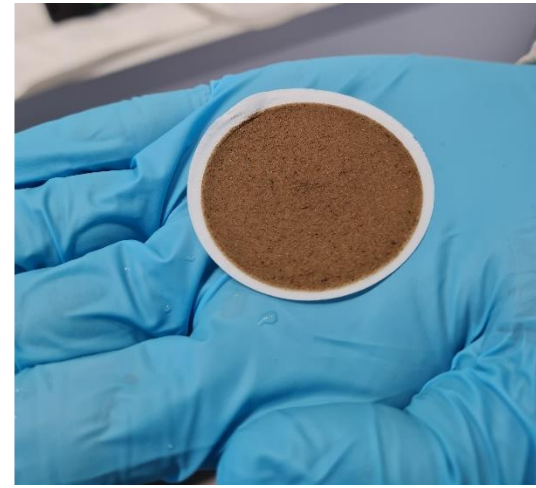
Example 1: Sampled high-flow event in Wulka pilot region, Austria





Abbreviations: MQ – 50% probability discharge (medium flow)
TSS – Total suspended solids Q10 – 10% probability discharge

Example 2: Sampled high-flow event in the Ybbs - pilot region, Austria

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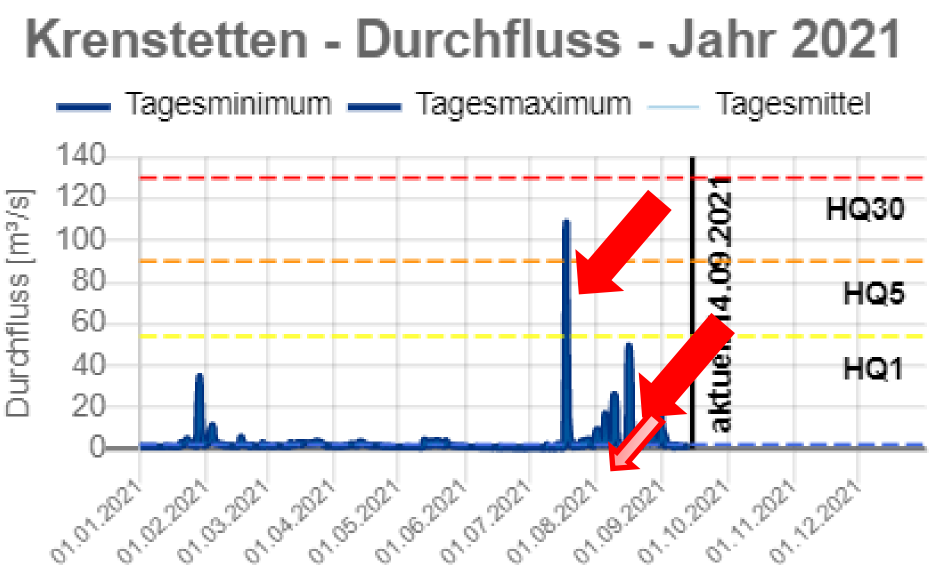
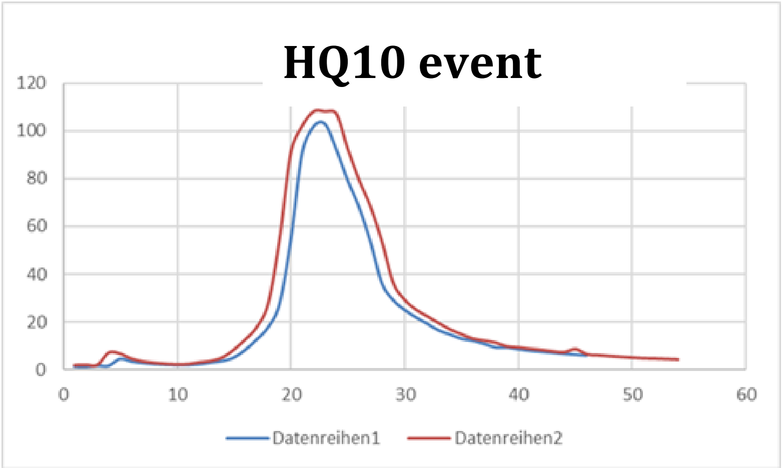
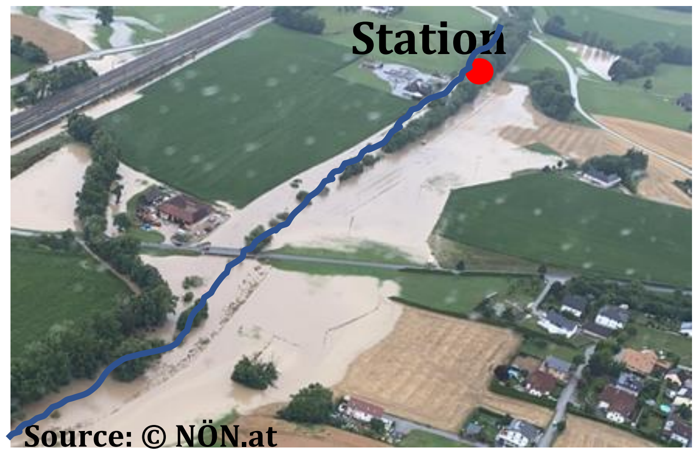




- More than 100 m³/s; MQ: 2,1 m³/s
- Whole HQ10 event continuously measured (45h: 24l)
- HQ1 event completely measured



Abbreviations: HQx – high flow with x % probability

Equipment for automatic sampling (2)

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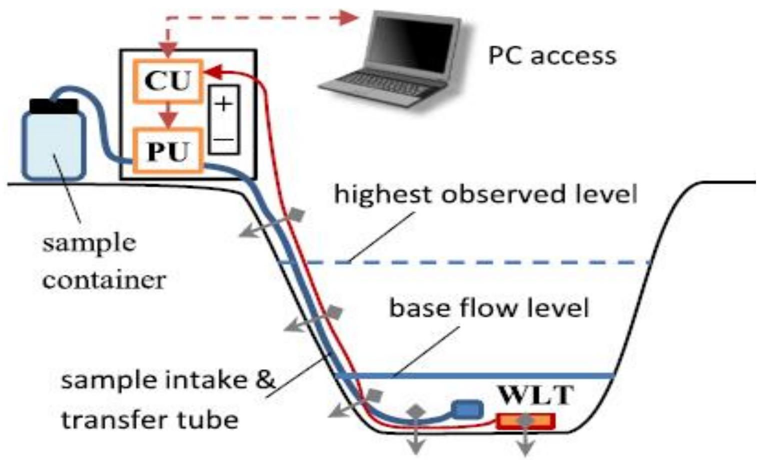
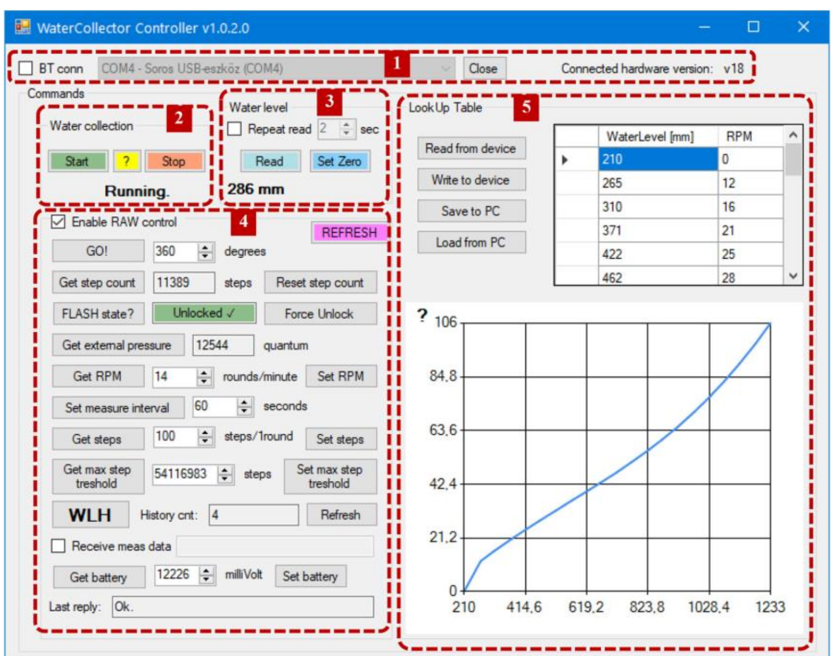
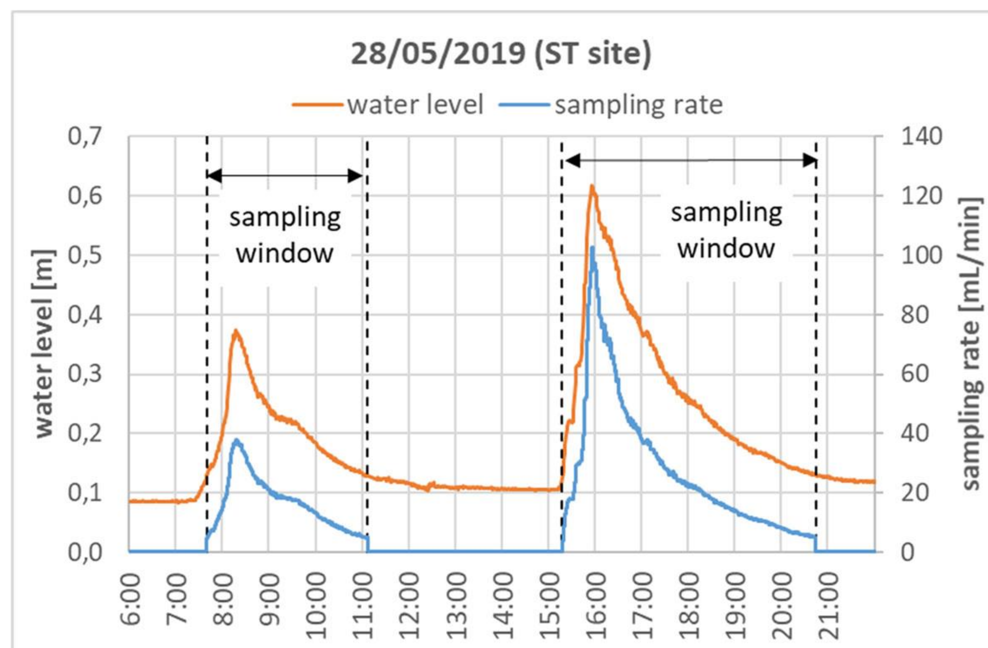


Autonomous flow-proportional water sampler developed for continuous composite sampling of runoff events (Budai et al., 2020)





Example 3: Flow proportional sampling of a high-flow event in the Upper Zagyva pilot region, Hungary

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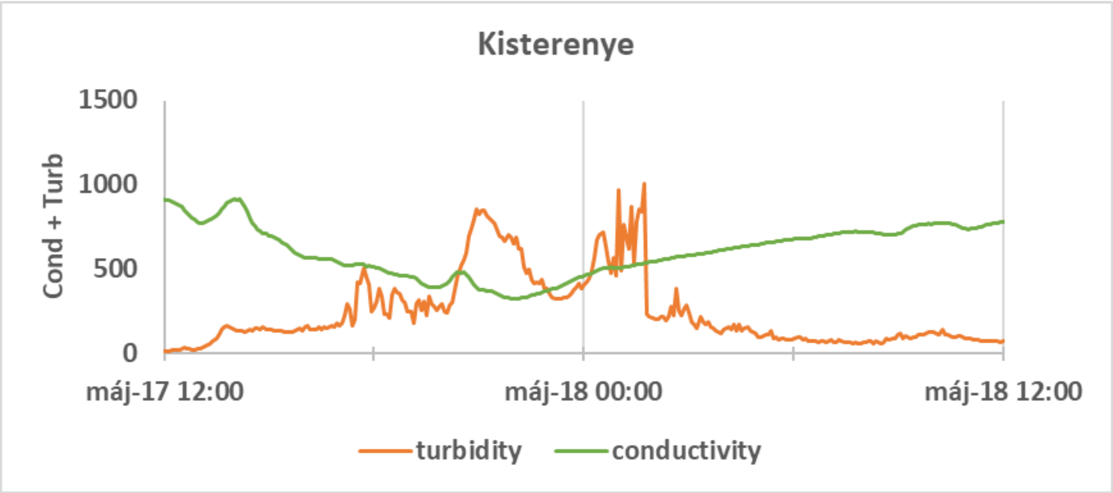

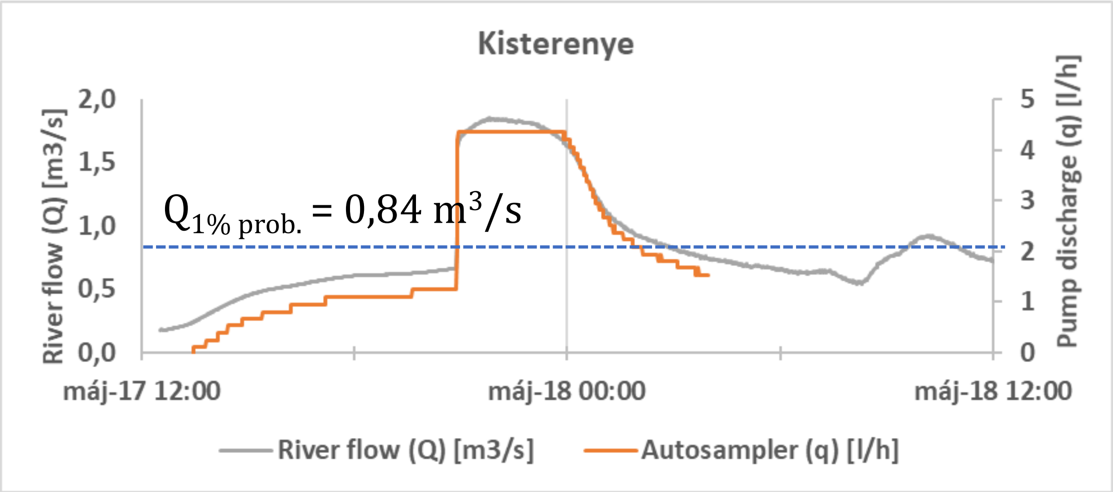

Sampled total volume: 21,9 l

Online stations: BME (Hungary)

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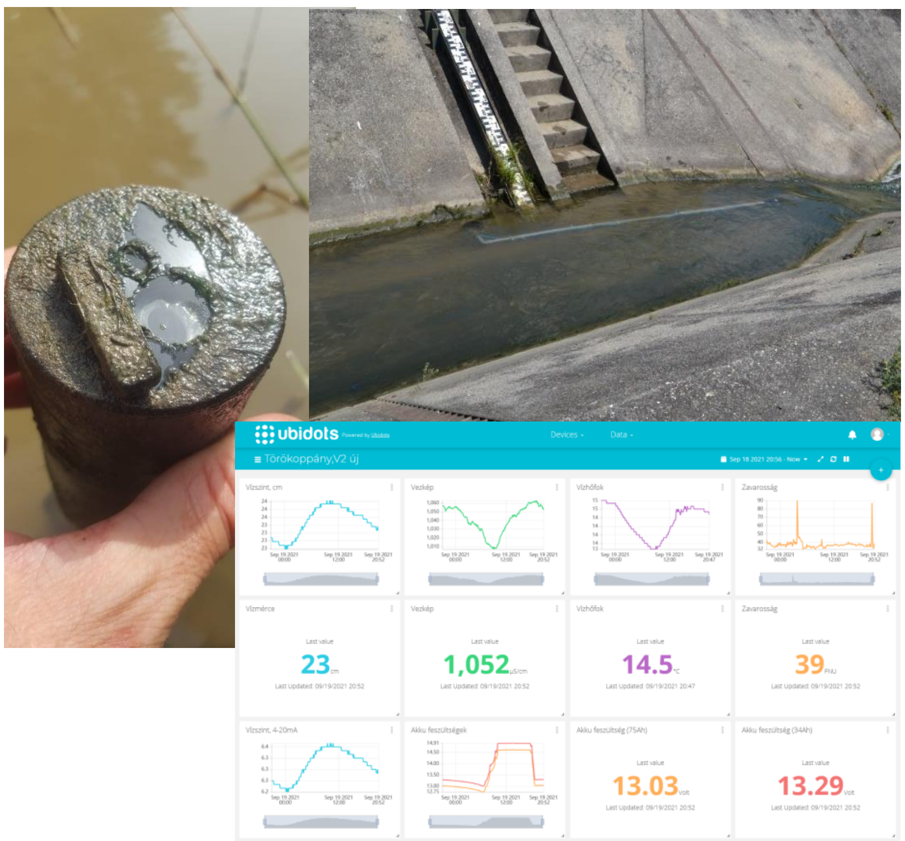
- Probes were installed in existing river gauges
- Hach sensors (SOLITAX t-line SC Turbidity probe with self-cleaning windows, 3798-S Conductivity and temperature probe)
- Transmitting device for online data communication
- Power supply by solar panels and wind power
- Online access to data



Online stations: TU-Wien (Austria)

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Station Nodbach

Turbidity sensor before and after cleaning

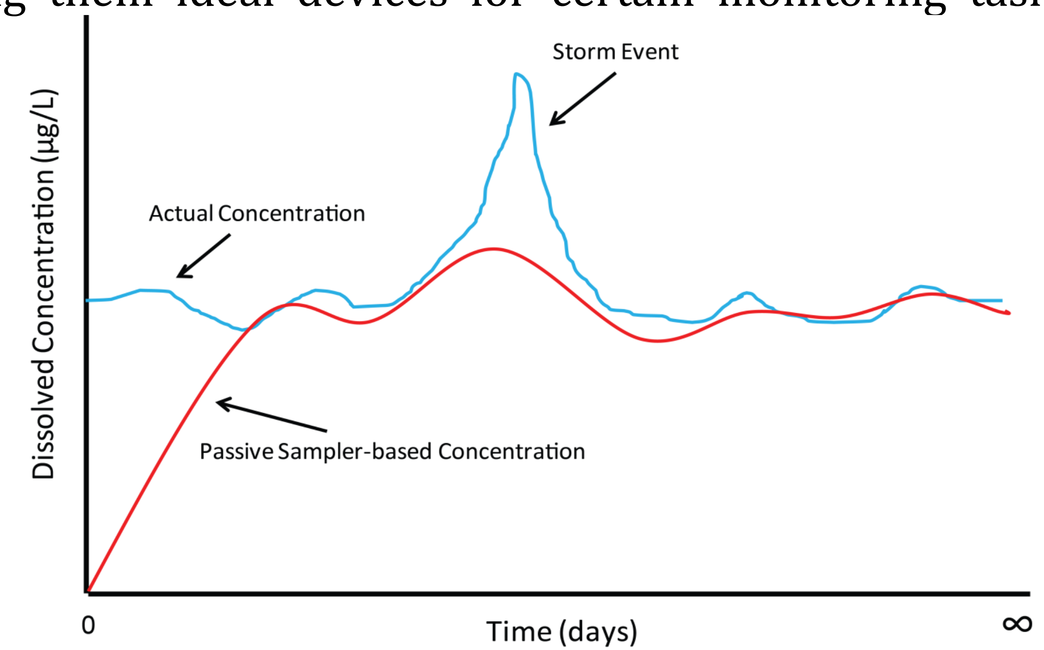
Sampling methods: passive sampling

Substance passive samplers

The advantages of passive samplers over other sampling and measurement strategies include the ability **to integrate pollutant levels over extended sampling periods** (up to several weeks), as well as inherent speciation capabilities, allowing for critical in situ speciation of metals. Thanks to the **enrichment principle, they can provide better detection limits**.

Passive samplers are **relatively low-cost** and do not require secure locations or additional infrastructure, making them ideal devices for certain monitoring tasks (Knutsson, 2013).

Water passive samplers developed by the Canton of Thurgau (Switzerland)



Conceptual diagram of the dissolved water column concentration of a hydrophobic contaminant (US-EPA, 2012)

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Sampling methods: passive sampling

Particle-bound concentrations in rivers

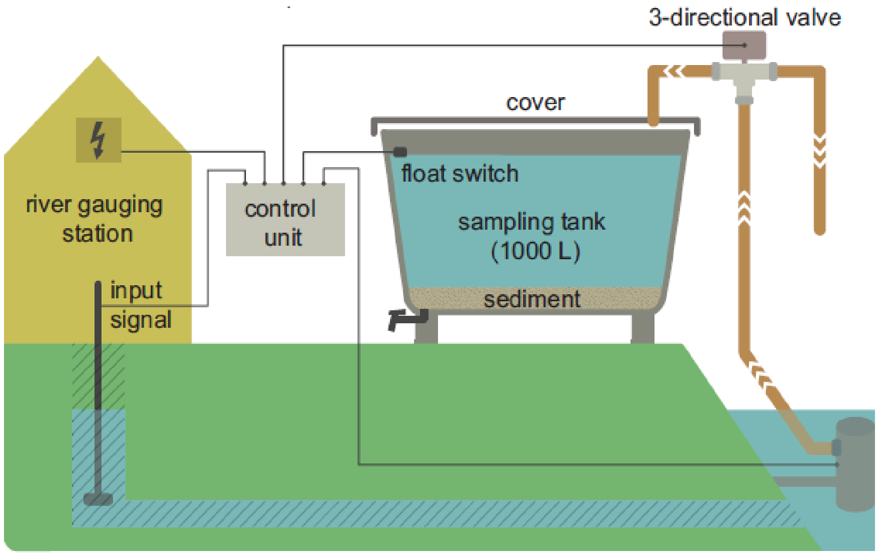
Sediments are an important source of information for the level of legacy pollution in a water body and for the internal pool of contaminants that could be mobilized or leached into the water column, **Suspended Particulate Matter (SPM)** reflects the current contamination level. Moreover, in comparison to sediments, SPM **contains a higher percentage of fine-grained fraction**, in which particulate-bound contaminants mainly accumulate.

)

Devices for the collection of Suspended Particulate Matter (SPM):

Passive sampler according to Phillips et al (2000)

Devices for the collection of Suspended Particulate Matter (SPM): High volume samplers



Large volume sampler arrangement at a river gauge (Kittlaus and Fuchs, 2015). The stainless-steel tanks optimizes the deposition and the separate collection of SPM. The possibility of automatic control allows the targeted sampling at different flow and turbidity conditions.

Large Volume Solid Phase Extraction (LVSPE) device used in the Joint Danube Survey in 2013.

Image: André Künzelmann (UFZ, Leipzig, Germany)

Sampling of wastewater treatment plant effluents

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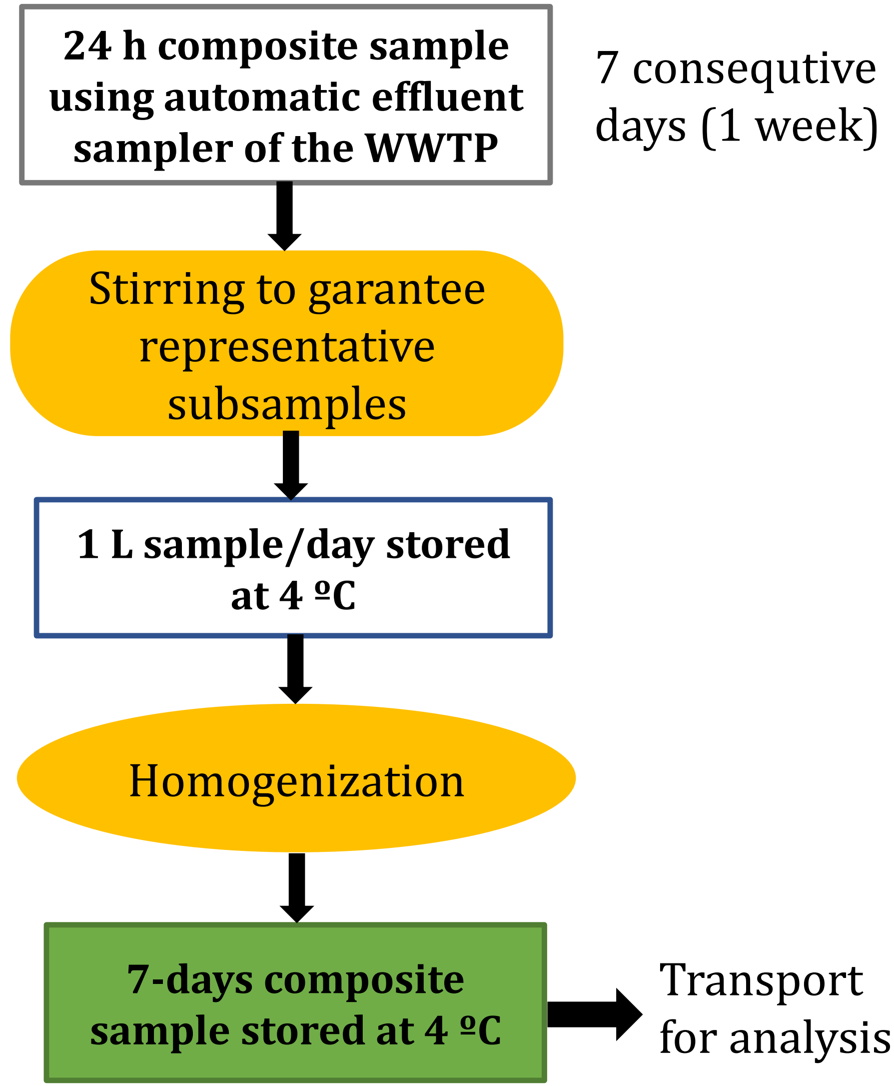
Scheme of sampling procedure:

- Knowledge concerning household and industry connected to the WWTP is needed.
- In general, it is beneficial to do the sampling for at least one week and to repeat it seasonally.

Household effluents are in general quite homogeneous in time, although there is a daily pattern and the population number can fluctuate seasonally or weekly. Industrial discharges are widely diverse and can fluctuate extremely.



Atmospheric deposition sampling

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Bulk deposition

The **simplest and cheapest** method to monitor atmospheric deposition. The sampling device is a tray or a bucket. The diameter of the platter or funnel should be chosen depending on the amount of precipitation($\sim$ 20 – 70 cm). **Both spontaneously settled dust and particles bound to precipitation are collected.**

Wet deposition

Similar to bulk deposition, but the sampler is equipped with a humidity sensor and a lid, which is closed except during precipitation events (Pekey et al., 2007).

Wet and dry deposition

Wet and dry deposition happen alternatively with the placement of a second bucket: the lid covers either the wet or the dry bucket (Amodio et al., 2014).

Precipitation measurement and atmospheric deposition sampling

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Composite samples were collected for 4 x 1 months representing 4 seasons

Atmospheric deposition sampling

Challenges addressed during the sampling:

- To cover seasonal effects of pollutant distribution and precipitation amounts, a whole year of sampling is deemed necessary. To reduce the associated staff resources, selected months can be sampled to cover to a satisfactory extent the seasonal variations.
- The bigger the sampling devices get, the more complicated the handling and storage become. Thus, the sampled volume should be a compromise aimed to collect the necessary amount without losing part of samples during intense events.
- The samples need to be taken out of the sampling device immediately after the rain events to avoid evaporation and degradation. They need to be stored in a freezer until analysis. The samples should be protected from direct sunlight at all times by wrapping them in aluminum foil.
- The contamination of samples from soil or vegetation must be avoided. Thus, the samplers should be placed in an open space at least 1.5 m above ground.
- Disturbance of the mean spatial rainfall and dry deposition pattern should be avoided by keeping distance to higher objects (buildings, trees…).
- The location of the samplers should ensure their protection from vandalism.

Sampling protocol (SOP) - Instructions for sample identification, handling, storage, preservation and transport to the labs

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New methodology for the preparation of composite samples had to be developed (how to preserve samples for such a long time)

- Preparation: weekly aliquot + a proportional amount of stabilizing compound is added
- Material used for storage
- Cleaning of the vessels
- Temperature of storage, freezing (if possible)
- Requirements for filtering (to avoid contamination)
- Blank samples (procedure blanks, autosamplers)

Chemical analysis is performed for the same parameters from all samples in the same lab

Compound	Sample matrix	Lab.	Volume and bottle material	Preservation
Hg and other metals (total and dissolved*)	All matrices	JSI	0.5 l Teflon or PE 0.16 L of filtered water	0.16 mL of HCl s.p. (30%) or 0.16 mL of HNO3 s.p. (65%) Frozen
16 PAH total and dissolved*	River, Atm.Dep. Wastewater	NARW	1 L Amber glass	The inner surface of plastic cups covered with aluminium foil, Cooling (2-4 °C)
16 PAH	SPM, Soil	UBA	1 kg, Rex glass	Lyophilisation
PFAs (PFOS, PFOA, PF4C – PF12C, PF4S – PF10S)	All matrices	Wessling Hungary Ltd	250 ml, PE	Frozen for composites, otherwise cooling: max 6 days
4-ter Octylphenol, Nonylphenol			1 L dark glass	Cooling (2-4 °C) and max 2 months
Metolachlor (incl. Metabolites), Tebuconazole			2x40 ml EPA vial	Cooling (2-4 °C) max 2 months
Diclofenac, Carbamazepine Bisphenol A			1 L dark glass	Cooling (2-4 °C) max 2 months

* Only from river waters

Sampling protocol (SOP)

Lessons learned - impacts of freezing on the measurements of dissolved metals

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- White precipitation was observed when thawing of the sample.
- Water chemical parameters showed a strong change after freezing the samples as composites: **obvious signs of $CaCO_3$ precipitation**. This is proven indirectly, by increased pH, reduced Electric Conductivity, several fold increase in turbidity and around 40-60% loss of hydrogen carbonate, and strong loss of calcium in water samples.
- **Risk of loss of particle bound contaminants from the samples**, high risk of measurement errors.
- Results of the **experiment by JSI**: Ni, Cu and As form more soluble carbonates/complexes, while Cr, Zn, Cd, Pb and Hg form insoluble carbonates.

Solution: Filter the samples onsite right after sampling delivery to the own lab, using specific pure filter: Sartorius Ministart NML, syringe filter, 28 mm, 0.45 um pore size.

Sampling protocol (SOP)

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PAH measurements

Problems:

- The bigger PAH are not found in the samples after our SOP procedure
- The dissolved concentration is often above the total concentration

Experiment:

- See the effect of aging of the samples (measurement after several weeks)
- See if the bottle that was used causes any problems (Teflon cap bottle was used in parallel)
- See if the use of preservative (Hexane) could improve the sampling and preservation method

Discoveries:

- ➢ Strong variance in low concentration ranges
- ➢ Tendency to underdetermination during storage
- ➢ No indication for SOP change regarding bottle

Solution: Stop filtering, focus on total PAH (only whole samples are measured), immediate shipping to reduce the storage time, Strong analytical efforts to fully reflect long chain PAH in TSS, LOQ of 1,6 ng/L is essential

TSS versus long chain PAH

Wulka/Nodbach (including earlier sampling)

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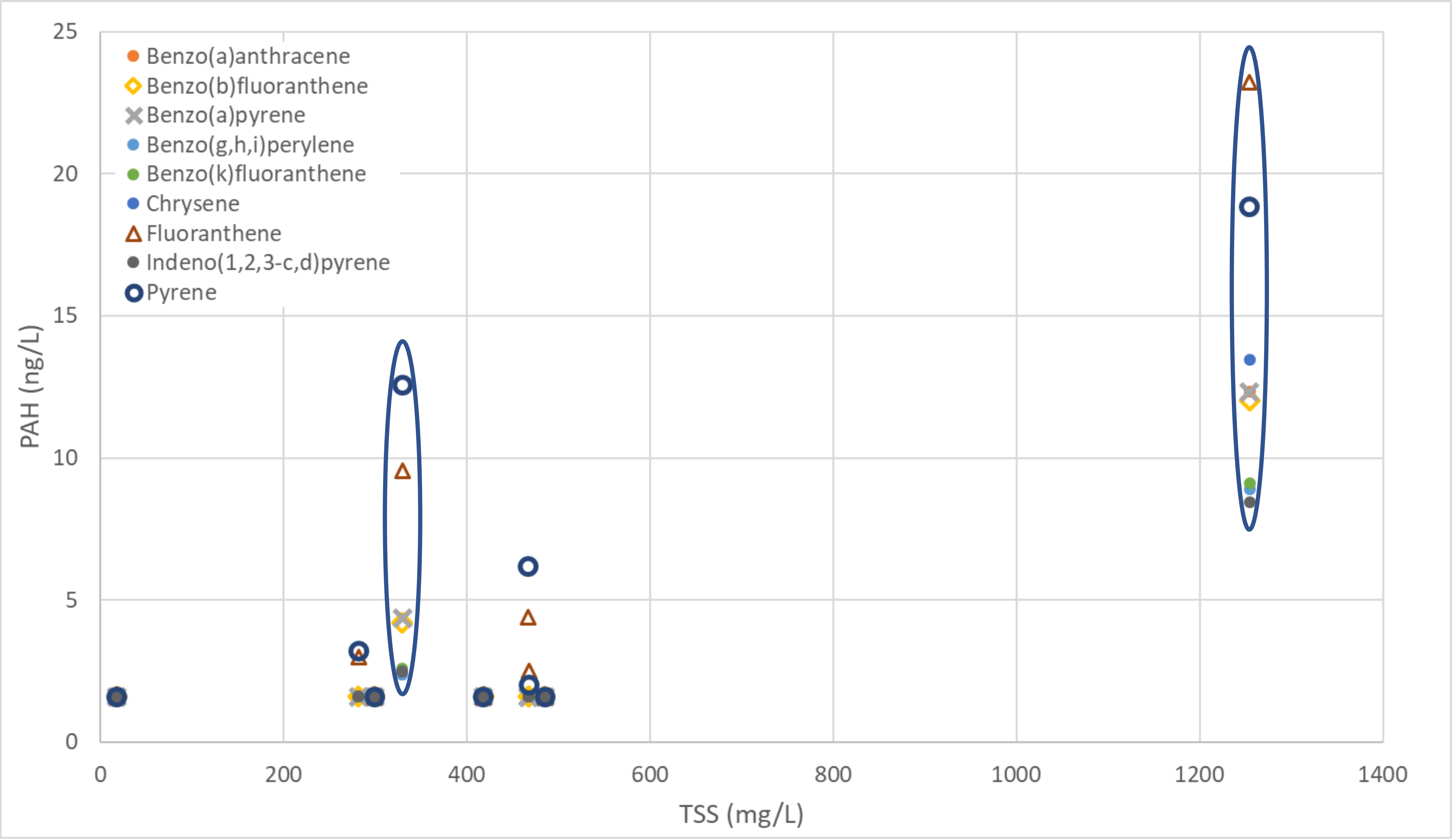

PAH storage experiment results

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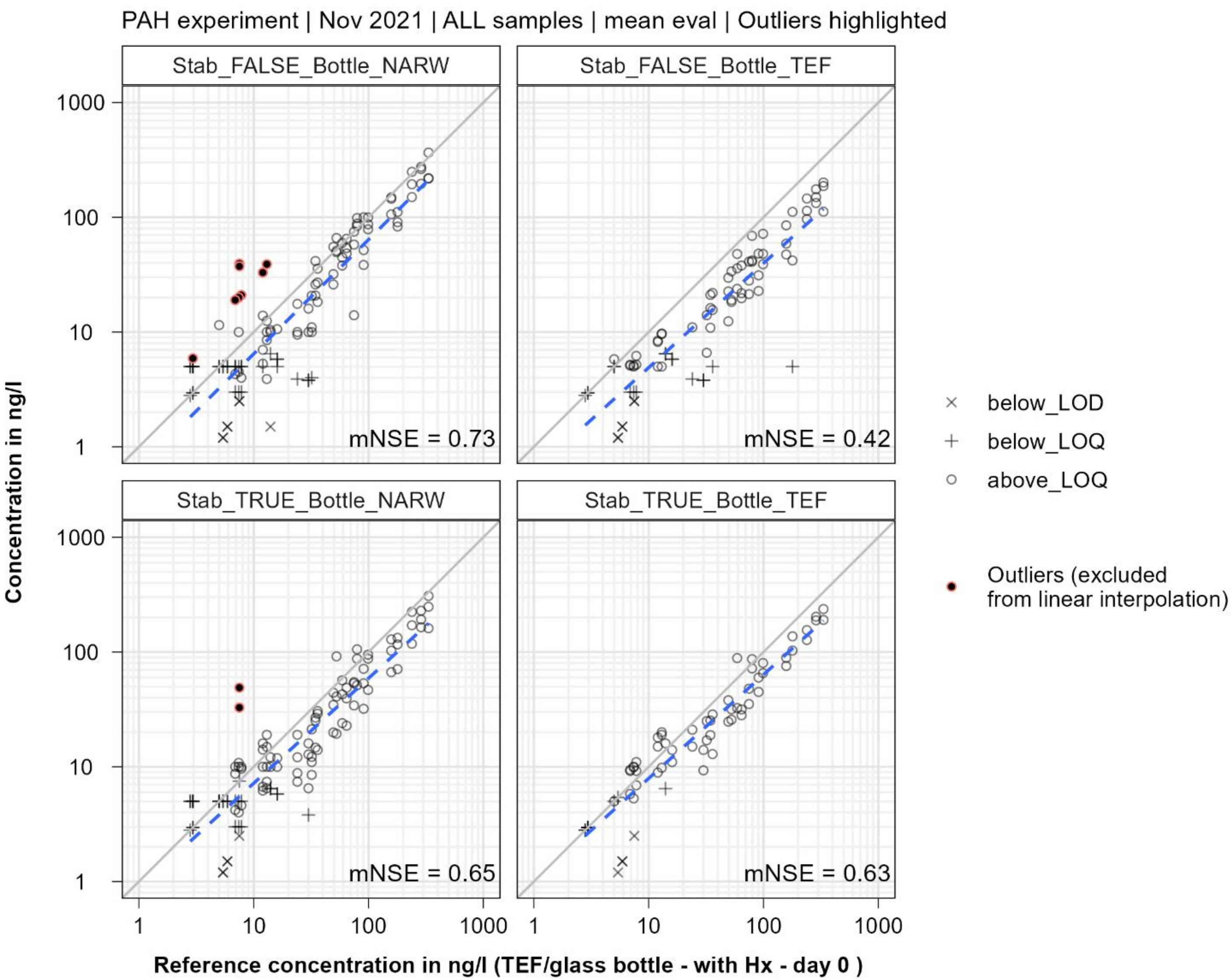

Preliminary results: HS concentration measured in different matrices

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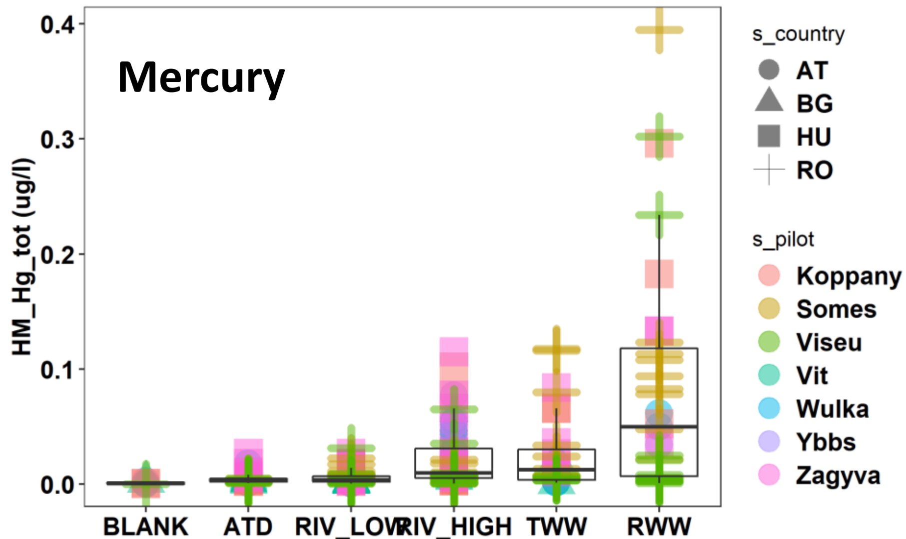

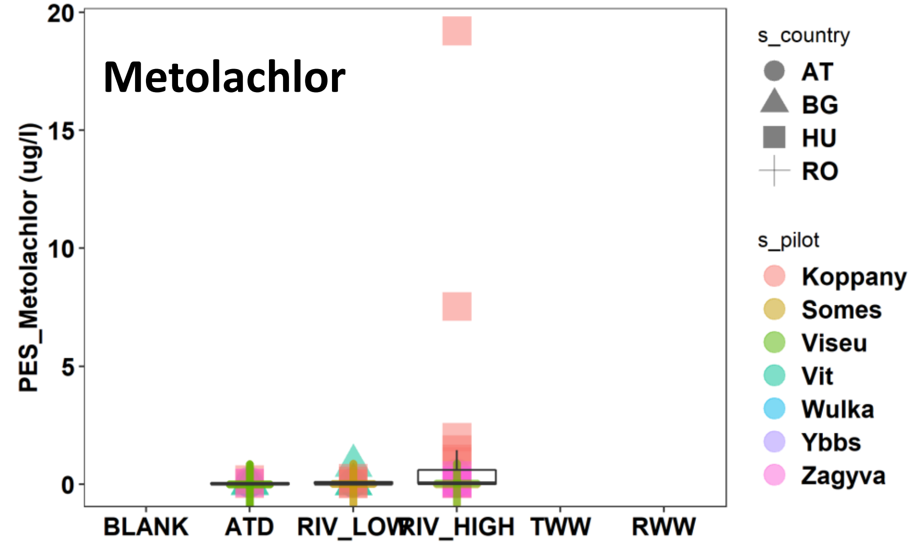

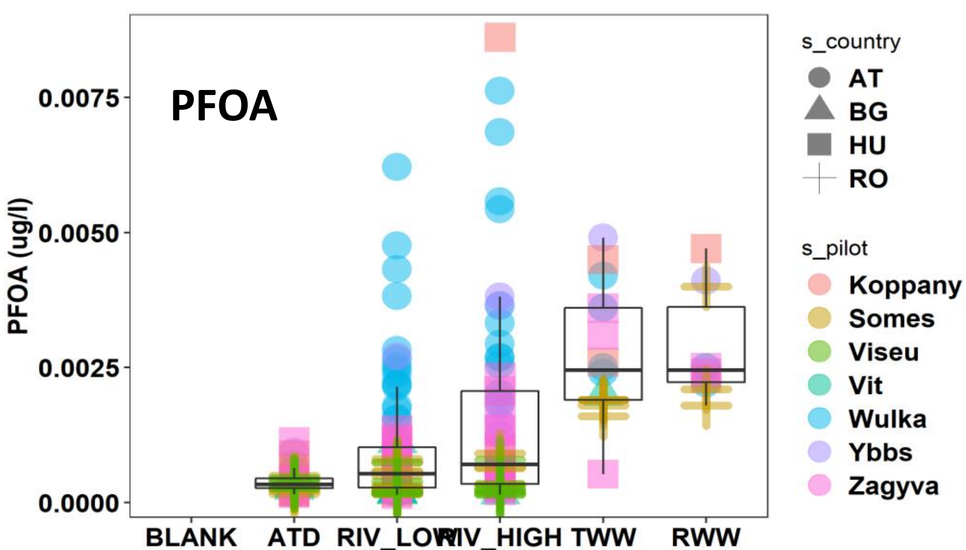

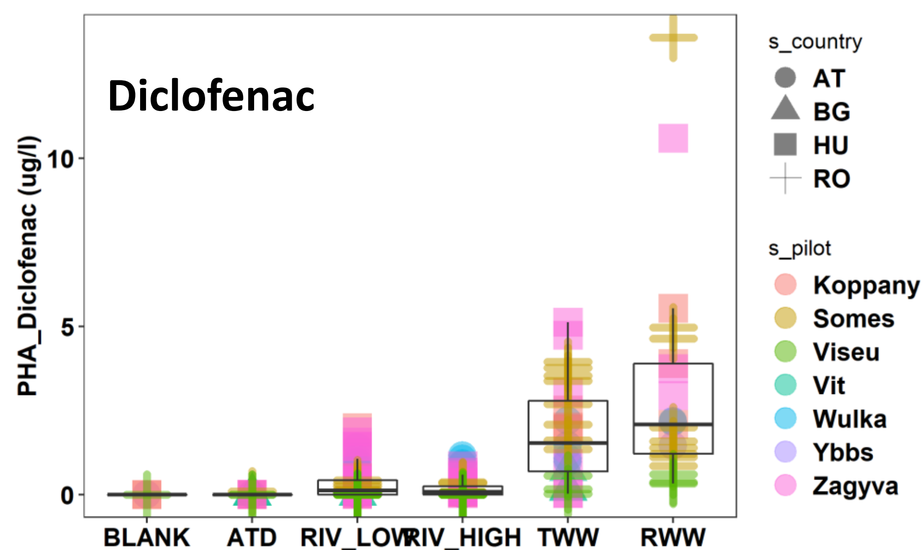

Preliminary results: impact of high-flow events on river concentrations

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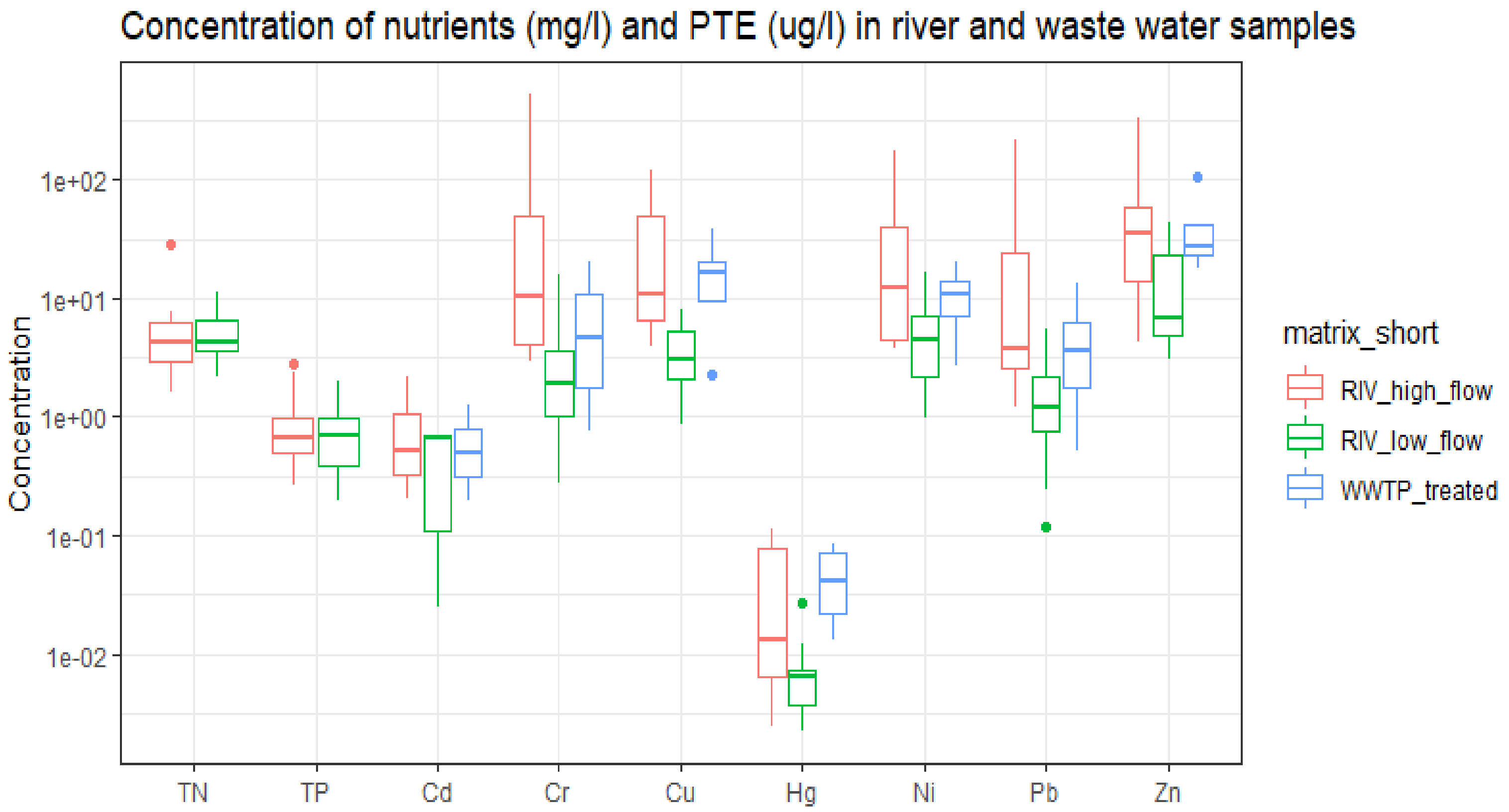
Traditionally measured elements like total nitrogen (TN) and total phosphorus (TP) do not indicate the high variability during high-flow events as heavy metals; the latter seem more capable of differentiating between different hydrological circumstances.



Soil sampling

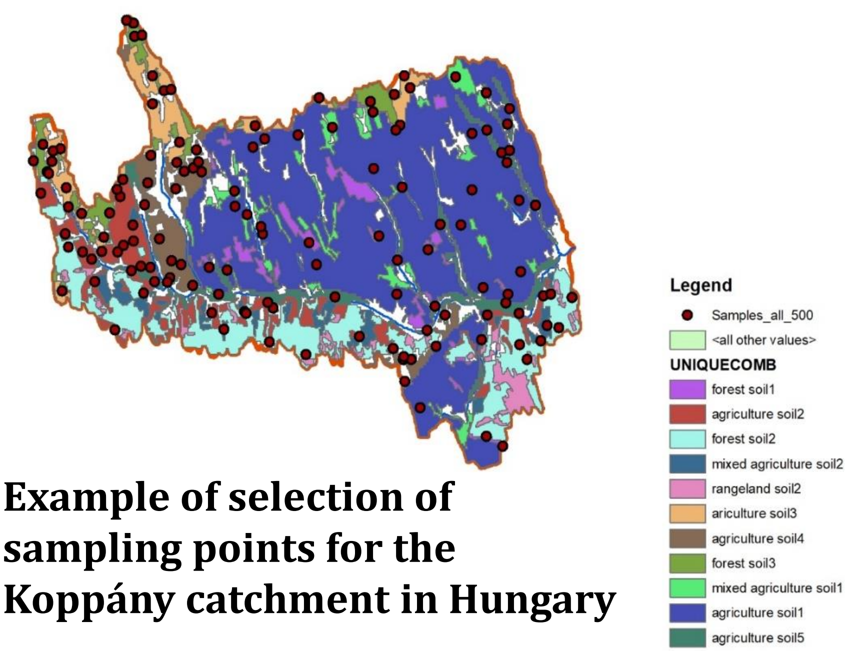
Sampling strategy

Collect composite samples for each major land-use type, with a total of 10 composite samples in each pilot region. The minimum threshold for the major land uses is set to 5 % of the total area.

Each composite sample should be composed of at least 20 samples. For one land use type, the sample locations should be distributed along the catchment in a way that **all major soil types** in the catchment are included.

Land use and soil classes should be overlapped by GIS application for each sub-catchment to create land units for composite sampling.

The specific **sampling points shall be distributed randomly** within the land units by GIS techniques, and finally, the sample positions should be adjusted manually to position it near to the roads where it can be approached.



Example of selection of sampling points for the Koppány catchment in Hungary

Soil sampling

Tools and methods

Soil samples can be taken for chemical analysis by simple auger tools, no specific drill is necessary: **Pürckhauer ground augers** specifically suitable for dense, hard soils. **Edelman augers** for softer soils.


Pürckhauer auger

The **upper soil layer should be sampled** beause this soil profile is the most important as runoff will play a much bigger part than subsurface flow in the emissions of such chemicals. For **grasslands and forest soils, the upper 10 cm** shall be sampled, whereas **for agricultural soils, the upper 30 cm** is relevant due to the tillage mixing of the soil layer.

Litter (plant residues) should be removed from the surface prior to sampling. The depth should be similar at each location.

Soil samplers should be cleaned between sampling spots.

All soil samples are collected in clean and sealable glass jars to prevent contaminant reaction with the container's material.

Generating the composite samples by merging equal aliquots of the sub-samples straight after sampling on site.


Edelman auger

Execution of soil sampling campaigns

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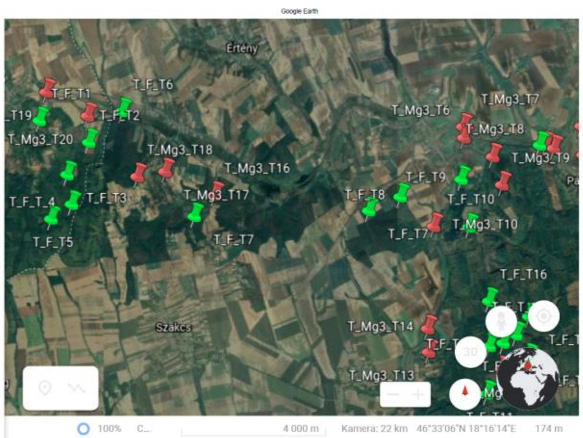
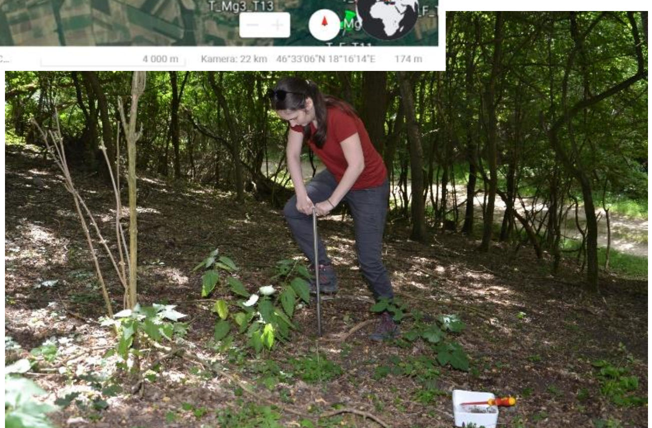
1. Planning the sampling points by GIS
2. Sampling and preparation of **representative composites** describing the variability in soil characteristics and land use (1 composite is made of 20 samples each, each of the 20 samples is composed in turn of 1-5 subsamples, to be taken close to each other)
3. **Lyophilisation before chemical analysis**





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Thank you for your attention!

Logo of hosting partner/speakers organisation (not wider/higher than EU flag)

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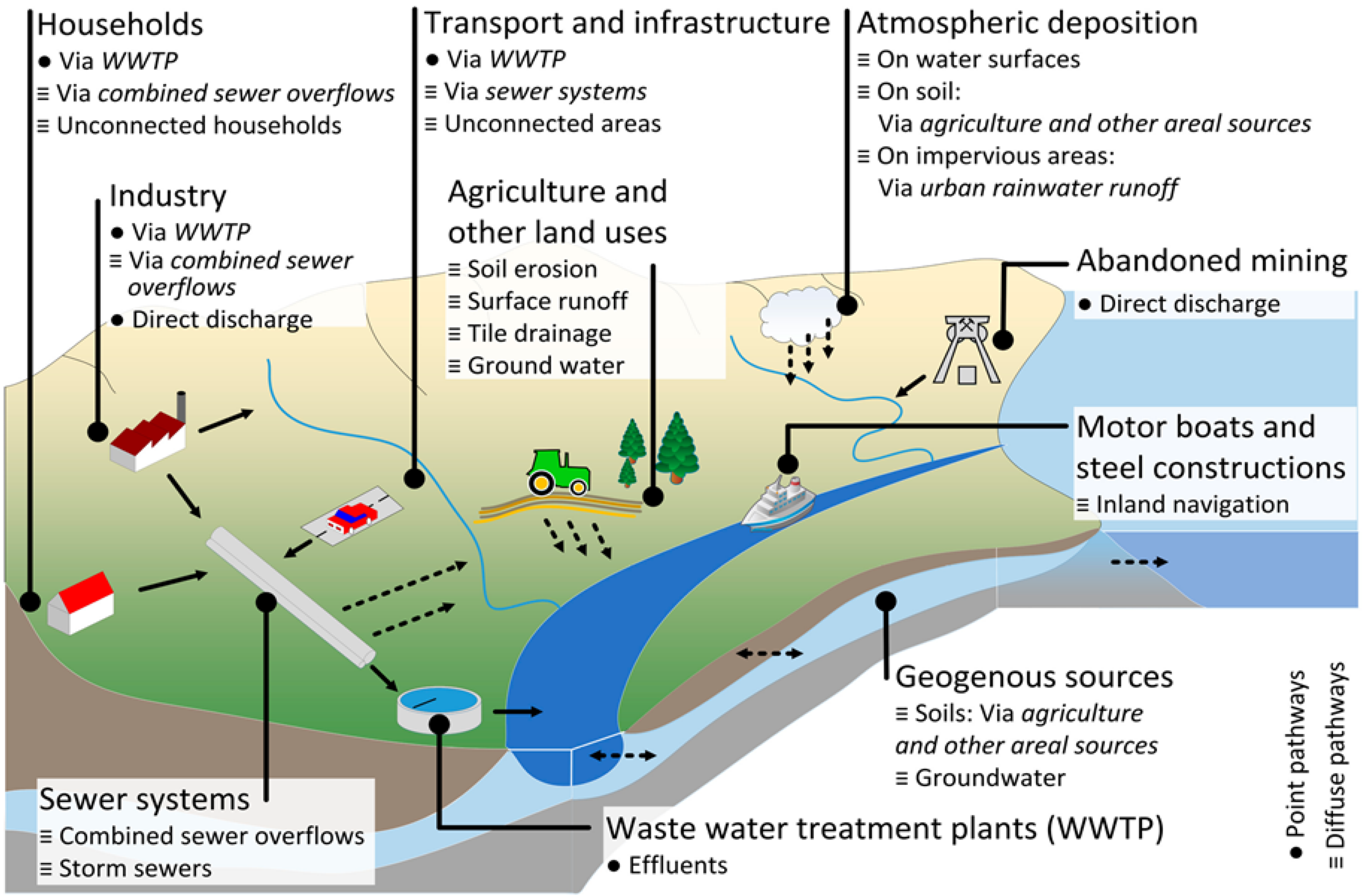
Danube Hazard m^3c National training on inventorying and monitoring

Inventory of hazardous substance pollution with specific focus of the DH m^3c approach

[Venue], [Date]

Project co-funded by European Union funds (ERDF, IPA, ENI) and National Funds of the participating countries

Emission pathways



Fuchs et al. (2017) Modeling of Regionalized Emissions (MoRE) into Water Bodies: An Open-Source River Basin Management System. Water, 9(4), 239

Inventorying: legal requirements

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According to the Article 5 of the Directive 2008/105/EC (EQS Directive), Member States shall establish an inventory, including maps, if available, of emissions, discharges and losses of all priority substances for each river basin district or part of a river basin district lying within their territory including their concentrations in sediment and biota, as appropriate.

Main objectives of the inventorying:

- Inform on the relevance of priority substances at spatial scale in the RBD
- Enable compliance check with WFD regarding the reduction of discharges, emissions and losses

Inventorying: two-step process

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TIER	BUILDING BLOCKS	EXPECTED OUTPUT	RESULTS FOR THE INVENTORY
STEP 1: ASSESSMENT OF RELEVANCE			
	Information sources identified in Art. 5 of EQS directive, see section I.1	Decision of relevance	List of relevant and less relevant substances
STEP 2: APPROACHES FOR RELEVANT SUBSTANCES			
1. Point source information	• Data on point sources • Emissions factors	• Availability of data • Quality of data • Identification of gaps	• Point source emissions • Listing of identified data gaps
2. Riverine load approach	add: • River concentration • Data on discharge • In stream processes	• Riverine load • Trend information • Proportion of diffuse and point sources • Identification of gaps	• Rough estimation of total lumped diffuse emissions • Verification data for pathway and source orientated approaches • Listing of identified data gaps
3. Pathway orientated approach	add: • Land use data • Data on hydrology • Statistical data • .... •	• Quantification and proportion of pathways • Identification of hotspots • Information on adequacy of POM	• Pathway specific emissions • Additional spatial information on emissions
4. Source orientated approach	add: • Production and use data e.g. from REACH • SFA • Substance specific emission factors • .... •	• Quantification of primary sources • Complete overview about substance cycle • Information on adequacy of POM	• Source specific emissions • Total emissions to environment and proportion to surface waters

Step 1

Step 2

Tier approaches in Step 2

Technical Report - 2012 – 058 Common Implementation Strategy for the Water Framework Directive (2000/60/EC) *Guidance Document No. 28 Technical Guidance on the Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances*

Tiers 1-4

Technical Report - 2012 – 058 Common Implementation Strategy for the Water Framework Directive (2000/60/EC) *Guidance Document No. 28 Technical Guidance on the Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances*

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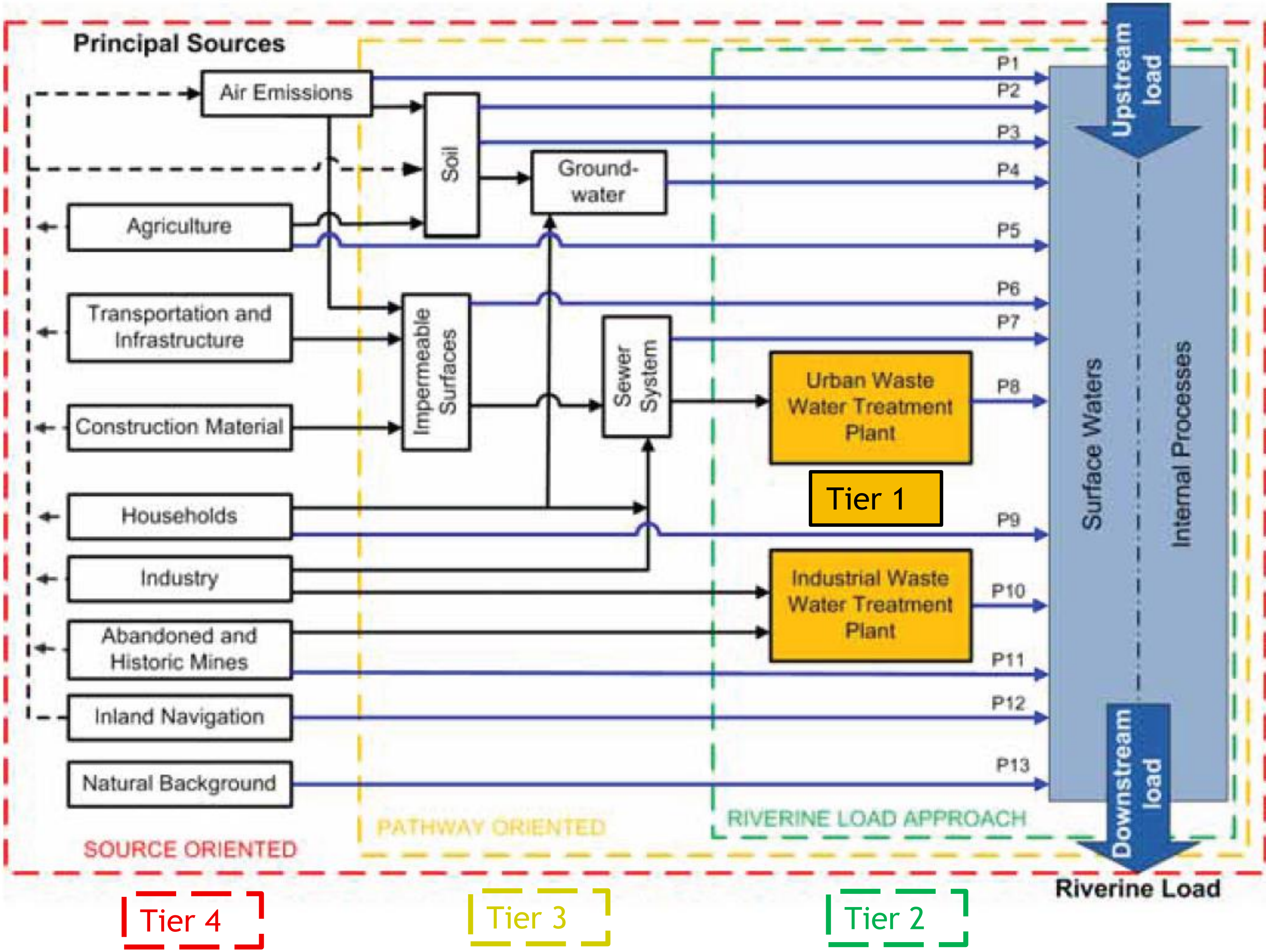

Step 2: Riverine load approach

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- It is based on concentration (both for the water and the suspended solids phase) and discharge data in rivers considering the basic processes of transport, storage or temporary storage and degradation of substances.
- The resulting riverine load provides information about the recent status of pollution and if long-term information is available then temporal trends too.
- In combination with the information gained in tier 1 (inventory of point source emissions) it allows estimating which share of loads derive from diffuse emissions.
- Results of the riverine load approach indicating high pollutant concentrations, an increasing trend, or a high relevance of diffuse emissions signal the need for a more detailed analysis using the approaches in tiers 3 (pathway oriented) and 4 (source oriented).

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Step 2: Pathway oriented approach

- It uses more specific information about land use, hydrology and basic transport processes involved The data requirements are higher than for the lower tiers.
- This tier allows identification of the main emission pathways and regional hotspots of emission and provides the quantification of specific emissions (e.g. area specific loads, storm water runoff loads).
- It will, therefore, provide the basis for an accurate inventory.
- For substances following a ubiquitous emission pattern or for which efficient mitigation measures are not available it might be appropriate to enter the next tier (source oriented approach).

For example with the MoRE model used in the project

Step 2: Source oriented approach

- It is based on substance-specific information on production, sales and consumption which to some extent are available e.g. through REACH.
- It allows the drawing of a comprehensive picture of the life cycle of a substance.
- The benefit of this approach is that the information gained is precise enough to implement not only end-of-pipe solutions but also source controls and precautionary measures.

Integrated for example within the DHSM model (based on the SOLUTIONS model) used in the project

Inventorying in the DRB

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Main outcomes of the policy review carried out within the Danube Hazard m^{3}c project

Step 1 in the Danube River Basin

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Similar approach for the assessment of relevance across the DRB

Examples of criteria used in more countries within the DRB:

- Focus on ubiquitous persistent bioaccumulating and toxic substances (uPBTs)
- Cause for not achieving good condition in at least one water body
- Concentrations exceed half of EQS in more than one water body
- Detection of increasing trend (rising concentrations in water bodies)
- Identification of sources and activities, which may lead to problems within following cycles of RBMP

Step 2 in the Danube River Basin

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Major differences and stages of implementation across the DRB.

Examples of different strategies in different countries

- Application of all three approaches, depending on data availability and suitability of each method in specific cases (e.g. HU)
- Only use of riverine load approach, without deeper analysis of sources and diffuse pathways (e.g. SI and SK)
- Focus on the pathway oriented approach (e.g. AT)
- No inventory developed yet (e.g. ME and MD)

Problem: in most cases, diffuse emissions are estimated as „black box“ via subtraction of point emissions from riverine loads

- weaker plausibility check of calculated loads and of mass balance
- Impossible to identify and implement effective measures against diffuse emissions

Inventorying in the DRB: spatial scale

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Major differences in the selected spatial scale across the DRB:

- At country level (e.g. SK)
- At river basin district (RBD) level (e.g. SI, HU, BG)
- At sub-basin level (e.g. RO)
- At catchment scale, with catchment area sizes as uniform as possible (e.g. in AT ~ 100 km^2)

Problem: in most cases spatial resolution not high enough to enable modelling, scenario analysis, effective implementation of measures

Inventorying in the DRB: natural background concentration

The natural background concentration with metals is considered within the DRB, although with **some differences**:

- Partly different metals are considered (e.g. Hg, Se and U only in some countries)
- Different approaches (e.g. AA-EQN considered as sum of background concentration and concentration due to anthropogenic emissions; exclusion of areas with significant background concentration from compliance of limit values, etc.)

Inventorying in the DRB: non substance specific data

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- Essential to estimate emission loads and river loads in combination with substance-specific data (concentrations)
- In part already available at DRB scale thanks to e.g. to inventories created for modelling with MONERIS and for the SOLUTIONS project
- Still work to be done: partly incomplete, inconsistent our outdated, costly and dependent on external providers (e.g. hydrology)

Discharges from industries and wastewater treatment plants

Discharges from mining sites

Erosion, soil and sediment transport

Water balance, hydrological model, precipitation amounts

Inventorying in the DRB

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Database developed in the Danube Hazard m³c project

Focus on substance-specific data

Inventorying in the DRB: database

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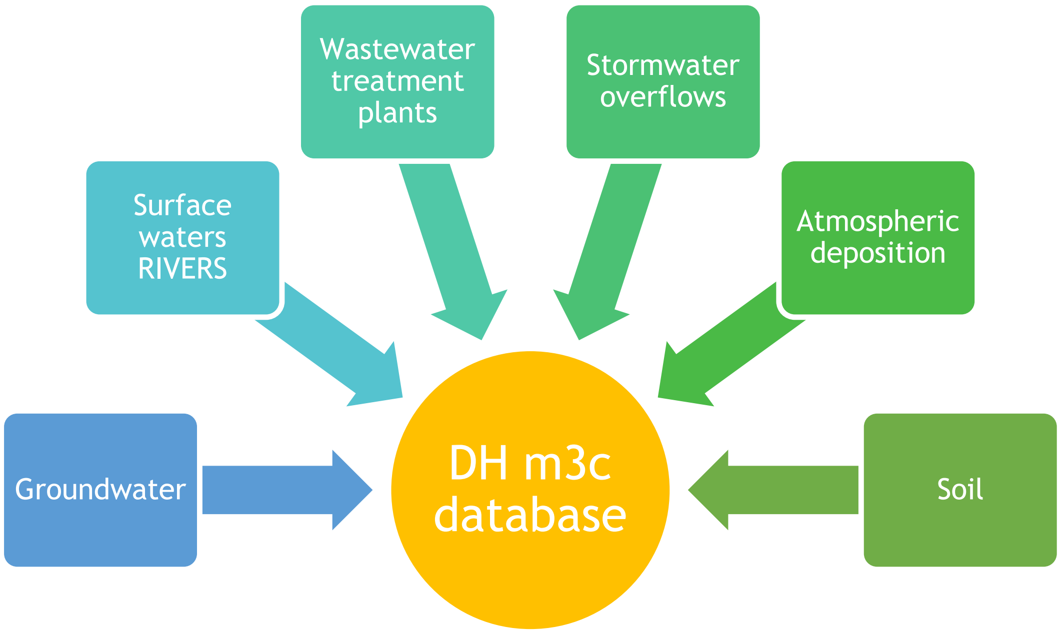

- 1st goal: to merge, harmonize and analyze available information in the DRB
- 2nd goal: to showcase the development of an integrated inventory covering substance-specific data (concentration levels) and essential metadata in surface water bodies, but also in environmental compartments related to major emission pathways

Inventorying in the DRB: metadata

Usage of data in an inventory goes far beyond check of compliance with limits and thresholds

→

Without appropriate, accurate and exhaustive metadata, data of an inventory has very little informative value and is of almost no use

Without adequate metadata:

1. limited or impossible quality-plausibility check of data
2. impossible extrapolation, identification of patterns and correlations to use inventory as input data for emission modelling at catchment scale and in general for understanding and linking emissions from different environmental compartments to pollution levels in rivers
3. as consequence of 1. and 2. very limited value for informed decision making and identification of effective management strategies

Inventorying in the DRB: metadata

No matter for which environmental compartment, values of hazardous substances concentrations must be complemented with:

- Date, location (**coordinates**)
- Analytical method, **Limit of Quantification** (LOQ), Limit of Detection (LOD)
- Unit of measure
- Representativeness (grab, composite, spatially or temporally aggregated value of multiple samples)
- Data source

Inventorying in the DRB: rivers

Fraction (total vs. filtered water, suspended particulate matter)

Essential info for estimation of loads and for linkages to different transport processes

Flow level and turbidity level/SPM content at sampling time

River features (average flow, average SPM, water body category, catchment area)

Inventorying in the DRB: soil

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Soil texture, soil genetic type, organic matter and dry matter content

Essential info for extrapolation over large areas for load estimation through soil erosion processes

Land use

Fraction (e.g. top soil 0-30 cm, top soil 0-50 cm)

Inventorying in the DRB: WWTP discharges

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WWTP type, capacity, connected PE/inhabitants

Essential info for extrapolation over similar WWTP without monitoring data and for estimating removal rates and loads

Processes-technologies (treatment stages, P removal type, chlorination, ozonation, etc.)

Recipient type and discharge point

Average discharge volumes of treated wastewater

Inventorying in the DRB: stormwater overflows

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Sewer type (combined, separated)

Presence of any retention, treatment step

Catchment area, recipient and discharge point

Essential info for extrapolation over other outlets without monitoring data and for estimation of loads at basin-catchment level

Average discharge volumes of stormwater

Inventorying in the DRB: atmospheric deposition

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Type of site (e.g. urban, natural background, forest, agricultural)

Essential info for estimation of loads and for linkages to different areas in basins-catchments

Precipitation quantity at time of sampling

Average annual precipitation at sampling site

Inventorying in the DRB: results

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Idea 1: show specific graph on data and metadata availability for the different environmental compartments in the country of the training and comparison to the availability in the other countries covered in the database

Inventorying in the DRB: results

Idea 2: show example of usage of river data for load calculation. For instance we could show the importance of having info on high-flow, lowflow concentration levels and on turbidity and flow data. We could show the load calculation of a substance taking this info into account and without having it.

Inventorying in the DRB: results

Idea 3: show example of usage of WWTP data to identify patterns of concentration levels according to WWTP type, capacity, processes (thus removal rate) and thus to be able to extrapolate this info to non-monitored plants

Inventorying in the DRB: results

Idea 4: the same for soil concentrations, identify and extrapolate to soil types-land uses in a catchment

Inventorying in the DRB: results

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Idea 5: the same for atmospheric deposition, example of load calculations and usage

Inventorying in the DRB: lessons learned

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Still major gaps of information regarding HS concentration in many compartments	Need of targeted monitoring
Information from monitoring exists, but is not or hardly made available for inventory	Need of enhanced cooperation and data-sharing among institutions working in different fields
Still major barriers to harmonized transnational database	Need to find balance between harmonization and integration of intrinsic and necessary differences

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Monitoring carried out in the Danube Hazard m^3c project and its link to inventorying

Monitoring in pilot regions

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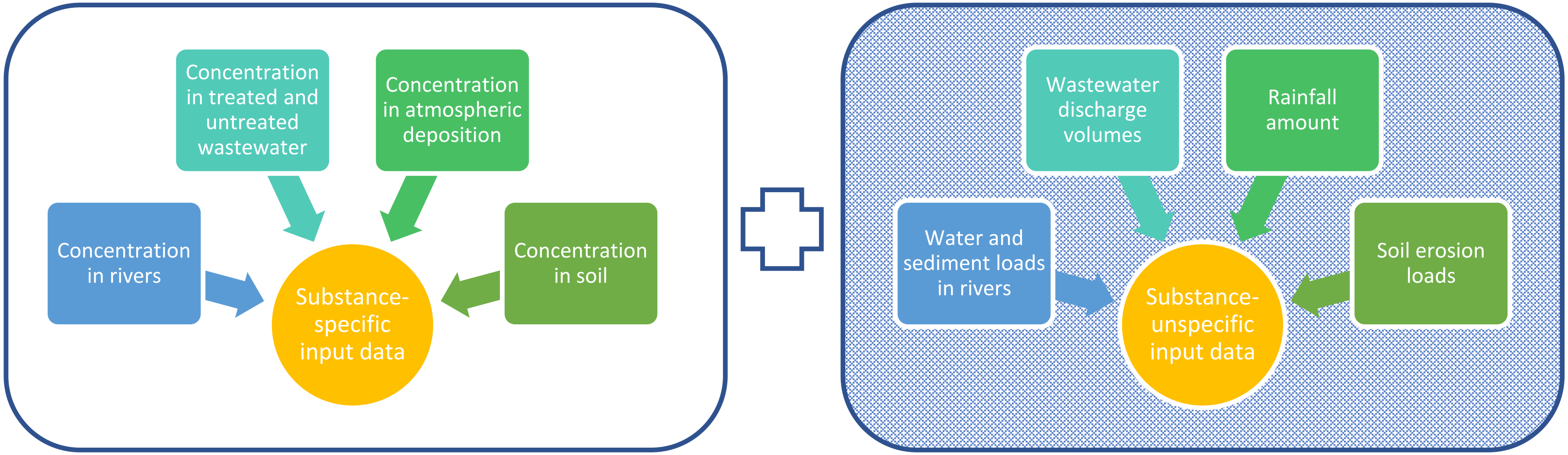

Monitoring results, combined with substance unspecific data (e.g. hydrology, WWTP discharge volumes, soil erosion loads) allow quantifying emission loads via different pathways in the MoRE model (pathway oriented approach for inventorying)

- 1st goal: to fill in critical knowledge gaps on concentration levels in the environment
- 2nd goal: to showcase in seven pilot regions the targeted use of integrated monitoring approaches (composite samples, simultaneously in different environmental compartments) as basis for the pathway oriented inventory development

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Monitoring in pilot regions

- Example of how we have used the results of monitoring to derive/prepare input data for MoRE

Idea 1: We sampled soils with different land use and geology, how did we use this info to extrapolate to the whole sub-catchments?

Monitoring in pilot regions

- Example of how we have used the results of monitoring to derive/prepare input data for MoRE

Idea 2: We sampled rivers at different flow levels and we monitored turbidity to estimate loads of suspended solids. How did we use this information to estimate substance loads in the rivers? Did we use it/link it to erosion processes?

WP T4 - Capacity building
National training course

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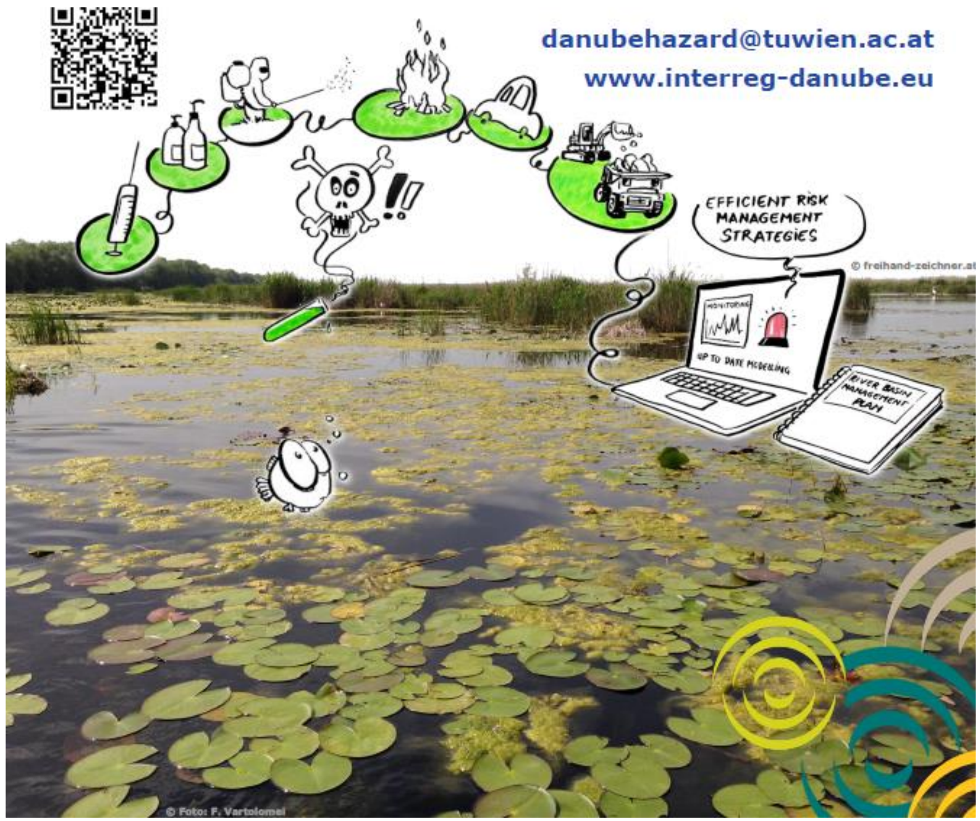
Institute of Chemistry

BULGARIAN WATER ASSOCIATION

Center for Eco-Toxicological Research

ICPDR IKSD
International Commission for the Protection of the Danube River
Internationale Kommission zum Schutz der Donau



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ADMINISTRAȚIA NAȚIONALĂ APELE ROMÂNE

Jožef Stefan Institute, Ljubljana, Slovenia

MŰEGYETEM 1782

Project co-funded by European Union funds (ERDF, IPA, ENI) and National Funds of the participating countries

AGENDA

Topic 1. Hazardous substances aspects of water quality monitoring and inventorying of pollution sources and pathways

Topic 2. Monitoring of the hazardous substances

Topic 3. Technical aspects of HSs sampling and measuring

Topic 4. Contribution of the results of our DHm3c monitoring to the inventory of hazardous substance pollution

Topic 5. Modeling of Hazardous Substances

Topic 5. Modelling of Hazardous Substances

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a. MoRe model - general info, what are the database needed, what are the expected results;

b. Solutions - general info, what are the database needed, what are the expected results;

c. what are our results -

- specific for the national pilot basin
- general for the Danube River basin

Topic 5: Modelling of Hazardous Substances - Content

- Value of Emission Modelling
- Model types - strength and weakness
- Practical model application in DHm3c (MoRE and SOLUTIONs)
  - Model structure
  - Data needs and data pre-processing
  - Pathways – calculation and adaptations
  - Contribution of model results to the WFD management cycle
- Limitations and opportunities for improvement

Topic 5: Modelling of Hazardous Substances - Value of Emission Modelling

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- Avoids high costs and bridges spatial constraints of monitoring
- Provides a regionalized system analyses with quantification of pathways and sources and closes information gaps (e.g. diffuse pollution)
- Shows need for action in catchments where no monitoring has been established
- Significantly contributes to the management cycle (pressures and impact assessment as well as for risk analyses)
- Authorizes decision makers to be pro-active by the possibility of prognoses
- Supports policy makers in the concrete design of the Program of Measures (by calculating the efficiency and effect of mitigation measures by scenario analyses)

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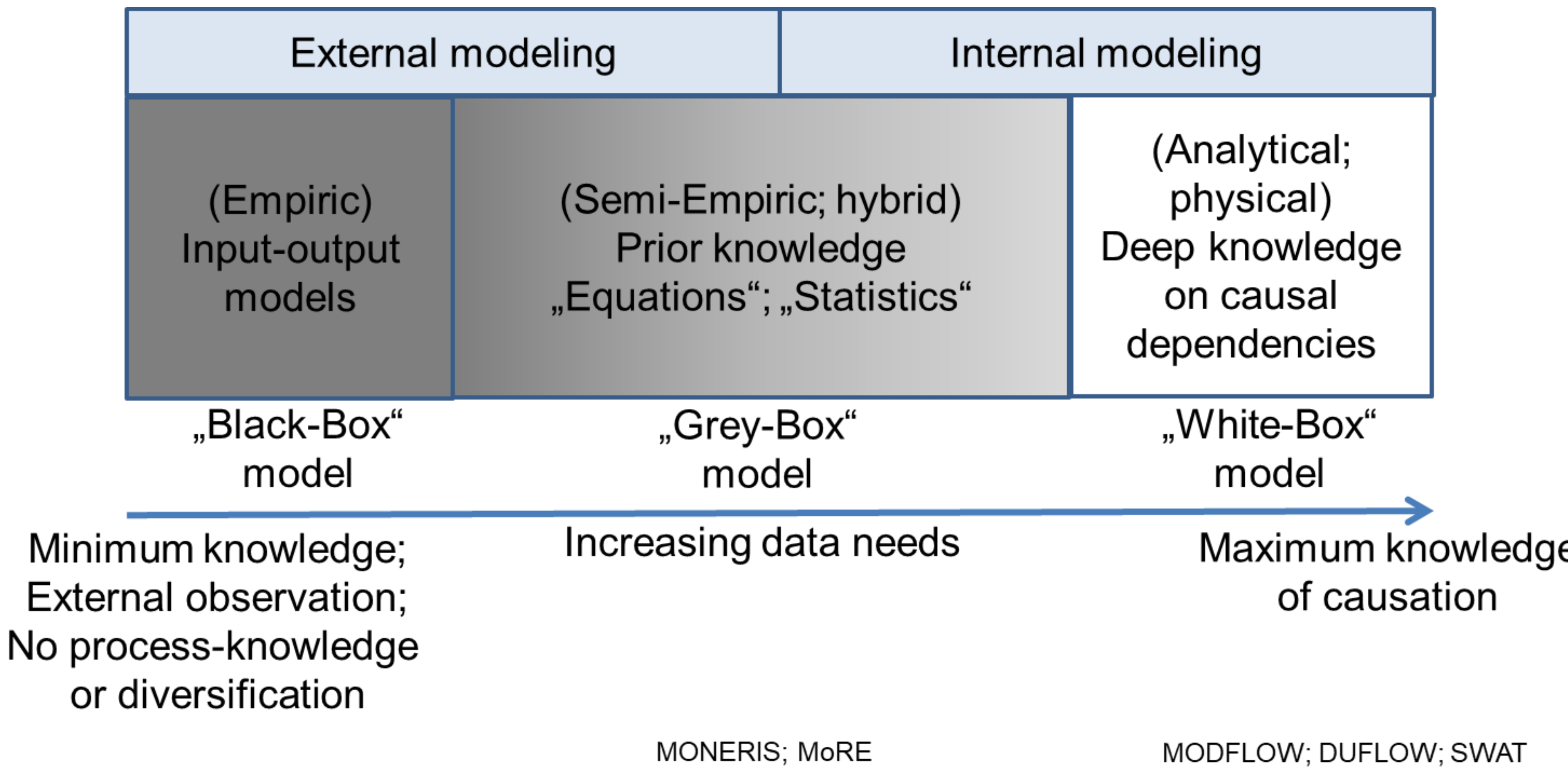
Topic 5: Modelling of Hazardous Substances- Model types strength and weakness



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Topic 5: Modelling of Hazardous Substances- MoRE Emission model - general

- Pathway-oriented, conceptual model (**M**odelling **o**f **R**egionalized **E**missions)
- Developed from MONERIS 2.01 model since 2009
- Mainly used to model heavy metals and organic polluters
- Is built on a PostgreSQL database in order to store the large datasets required for modelling
- Freely available
- Operates on medium scale (catchments with 50 - >100 km2)
- Annual time steps
- Transparent, comprehensive documentation of input data and approaches

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Topic 5: Modelling of Hazardous Substances- MoRE Emission model - setup

- Define Analytical Units (AU), considering:
  - Model resolution (50 – 200 km2)
  - Hydrography (discharge-tree)
  - Possibilities of Model validation (gauging stations and quality monitoring) at AU outlet
  - Best case: delineated AUs are related to the spatial scale of the status assessments
- Definition of discharge tree
- Parametrisation (basic input data and substance specific input data)
- Adapt pathways, formulas and calculation stacks to the site conditions and available data
- Implement different variants (mean, maximum, minimum) to consider uncertainties of input data
- Validate model results with annual load calculations at AU outlets

Topic 5: Modelling of Hazardous Substances- MoRE Emission model – sources, pathways

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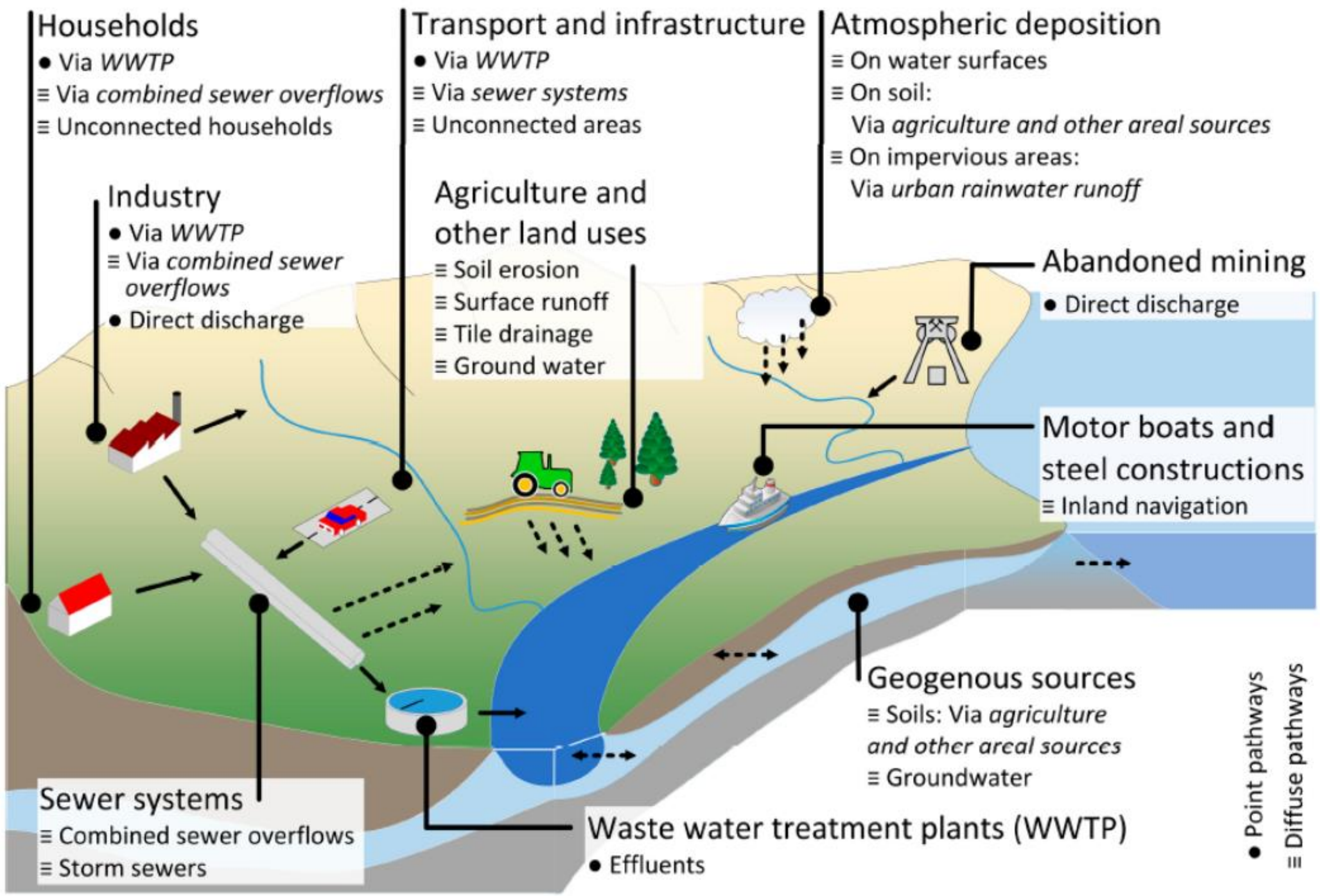
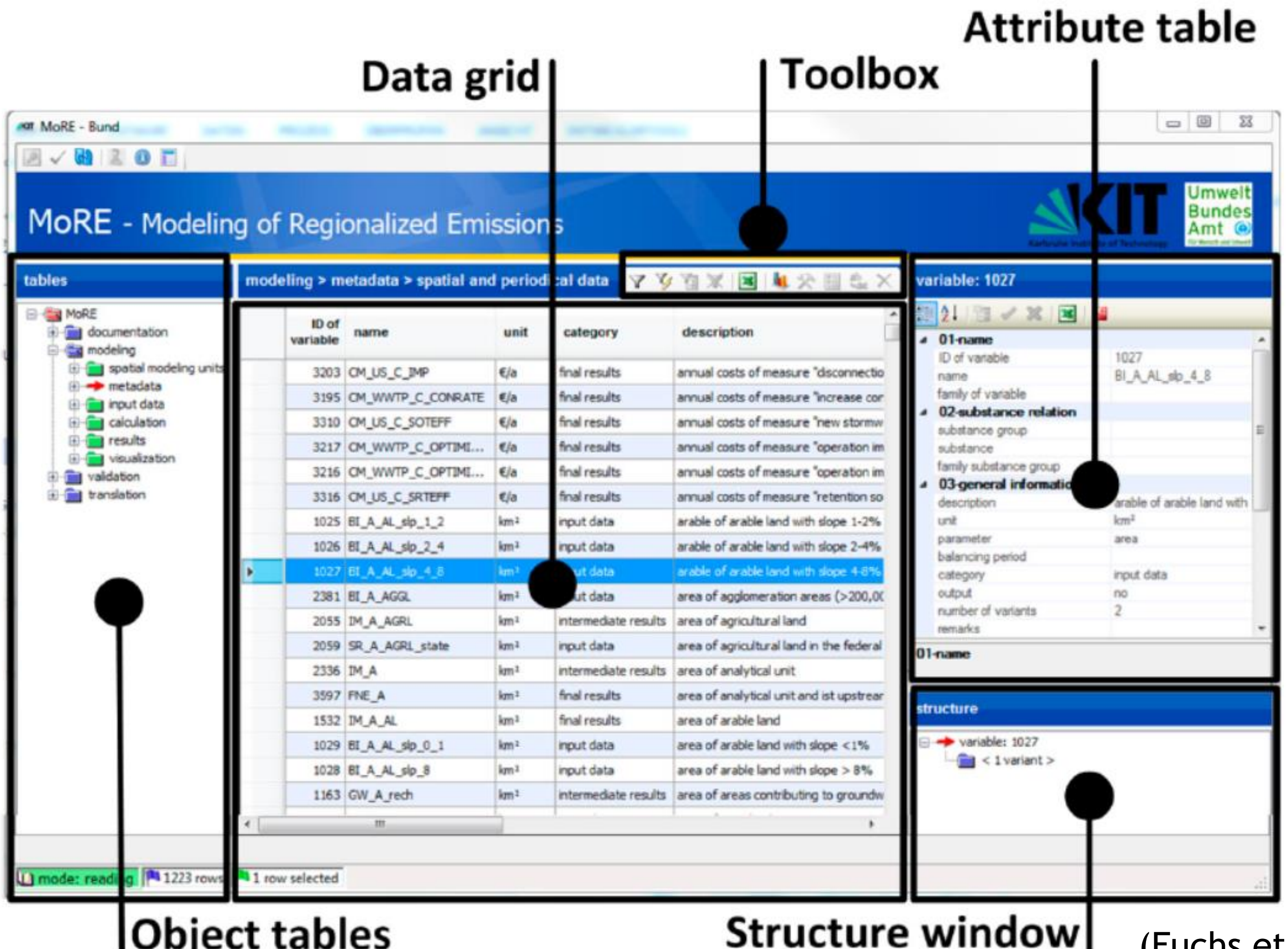


(Fuchs et al., 2017)

Topic 5: Modelling of Hazardous Substances-MoRE Emission model – user interface



(Fuchs et al. 2017)

Topic 5: Modelling of Hazardous Substances- MoRE Emission model – input data

Basic input data

- GIS or statistical data aggregated to Analytical Units (such as land use)
- Constant spatial data: (e.g. average altitude; average slope, hydrogeological conditions based on geology; soils; soil texture)
- Variable spatial data: (e.g. precipitation; discharge; water temperature; soil loss; surpluses, etc.)

Substance specific input data

- Specific concentration values in different technical or environmental compartments
- Point source data (with the opportunity of detailed meta data description are stored in a specific data base)
- Surface water concentration data and discharges to calculate annual loads or concentrations for model validation

Constants

- Predefined constants and parameters in complex calculation algorithms or as factor to calculate emissions (temporal and spatial independent)

Topic 5: Modelling of Hazardous Substances- MoRE Emission model – input data

Actual input data code	Name	Description	Unit	Parameter	Prioritization
Analitical Unit (AU)	**Topography**				
BI_A		Area of analytical units	km^2	Area	1
Topography	**Digital Elevation model**				
BI_ELEVA		Mean hights of subcatchments	m	Elevation	1
Landuse	**Landuse data set**	Landuse categories in actual version	km^2		
BI_A_AL_slope_0-1	Arable land	5 slope classes: 0-1; 1-2; 2-4; 4-8; >8 % if possible	km^2	Area	1
BI_A_PST	Pastures		km^2	Area	1
BI_A_WS_mr	Water surface	Main river (also lakes; reservoirs)	km^2	Area	1
BI_A_WS_trib	Water surface	Tributaries (also lakes; reservoirs)	km^2	Area	1
BI_A_FOR	Naturally covered areas	Woods; scrubland	km^2	Area	1
BI_A_O	Open areas	Mountainous area without vegetation; beaches; dunes	km^2	Area	1
BI_A_OPM	Surface mining	Mining areas	km^2	Area	1
BI_A_URB	Settlements	Total urban areas	km^2	Area	1
BI_A_IMP	Impervious urban area	Paved areas inside urban areas: settlements; industrial estates; car parks….	km^2	Area	1
BI_A_WL	Wetlands	Area of Bog; swamp; floodplains	km^2	Area	1
BI_A_OR	Country roads	Paved road area; not included in settlements	km^2	Area	1
BI_A_REM	Other remaining areas	Other areas not listed above	km^2	Area	1
Drainages	**Melioration cadastre**				
TD_SHR_a_td_agrl	Tile drained areas	From arable land and pastures	km^2	Area	2
Meteorological Data	**Climatic data**				
AD_EVAPO_lt	Evapotranspiration	Longterm mean annual evapotranspiration	mm	Data series	1
BI_PREC_apr	Precipitation	Monthly values	mm	Data series	1
Hydrological data	**River Discharges**				
BI_Q_net	Net runoff	Modelling period; annual data	m^3/s	Data series	1

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Topic 5: Modelling of Hazardous Substances – MoRE Emission model – data pre-processing

- Data preprocessing can range significantly in complexity

Basic input data

- Simple data aggregation to AU (e.g. landuse data, PE, EMEP raster data)
- Intersection and aggregation of different data sets (e.g. arable land with slope classes)
- Complex balance approaches, with an enhanced amount of different parameters (e.g. soil loss calculations (in slope classes of arable land) from the Revised Universal Soil loss equation (RUSLE))

Substance specific input data

- Data evaluation from different sources (studies, data bases (regional, national, EU scale))
- Own measurements in different technical/environmental compartments
- Regionalization of data by geo-statistical approaches (e.g. classification of background HM concentration by geological classes aggregated to AUs)
- Merging own data sets and data from other sources

Topic 5: Modelling of Hazardous Substances- MoRE Emission model – pathways calculations

- Different pathways are of different relevance based on substance group and process behavior → prioritization often possible (e.g. pharmaceutics)
- Calculations of pathways range from simple Q x c load calculations to more differentiated and partly complex approaches (e.g. Soil loss x SDR x Conc x ER)
- Facing variable data availabilities and On-site conditions the approaches must and can easily be adapted in the model approach
- New variables can be defined and described in a master data - data base, new formulas can be aggregated and defined to be used in new approaches
- The pathway approach can be documented in flow charts

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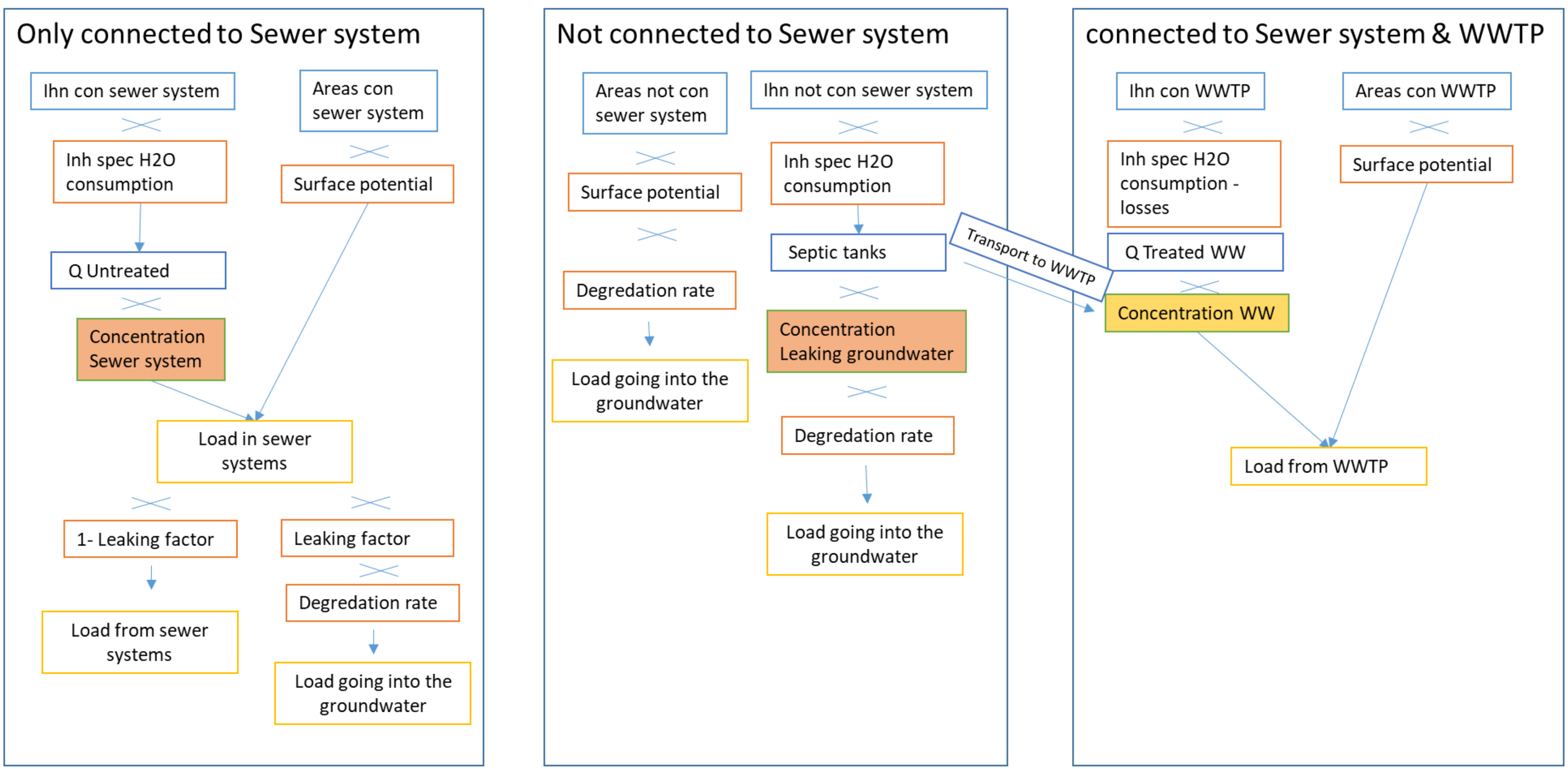
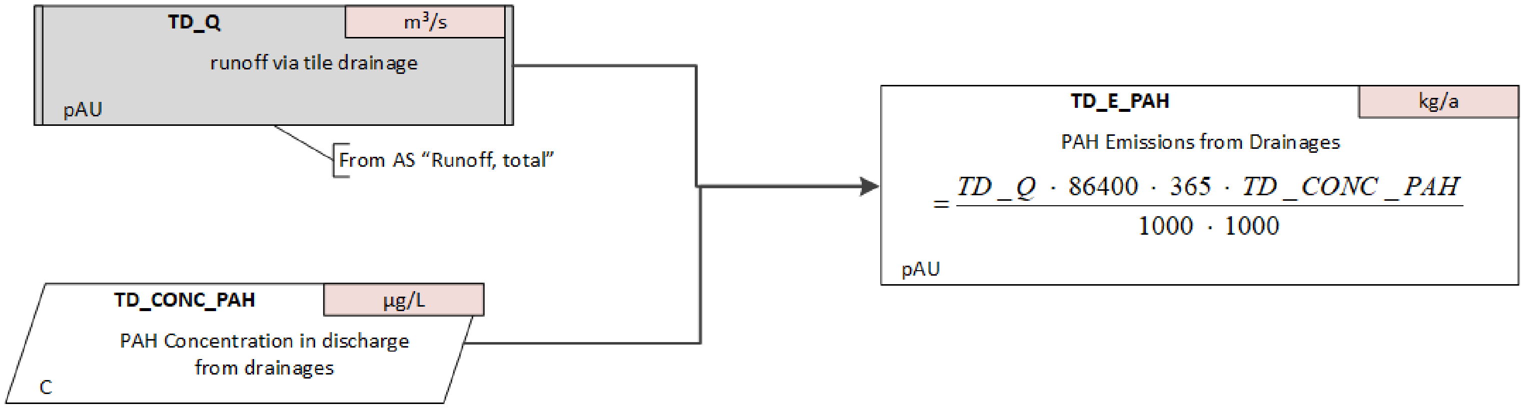
Topic 5: Modelling of Hazardous Substances- MoRE Emission model- example of pathways adaptations

Urban areas – example Bulgaria

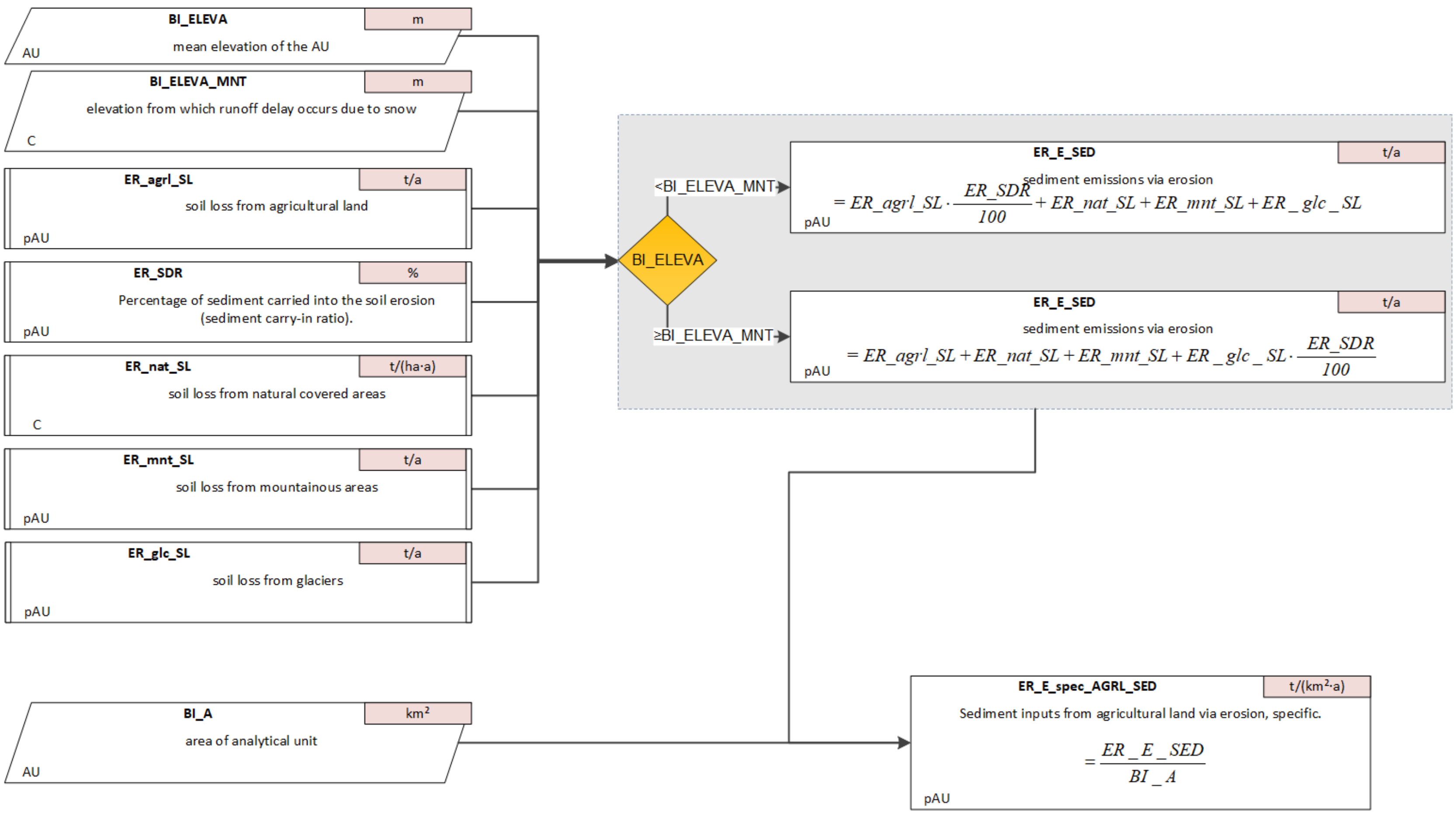


Topic 5: Modelling of Hazardous Substances- MoRE Emission model- example of flow charts

Emissions > PAH emissions via tile drainage > emissions via tile drainage



Topic 5: Modelling of Hazardous Substances- MoRE Emission model- example of flow charts



Topic 5: Modelling of Hazardous Substances- MoRE Emission model - results

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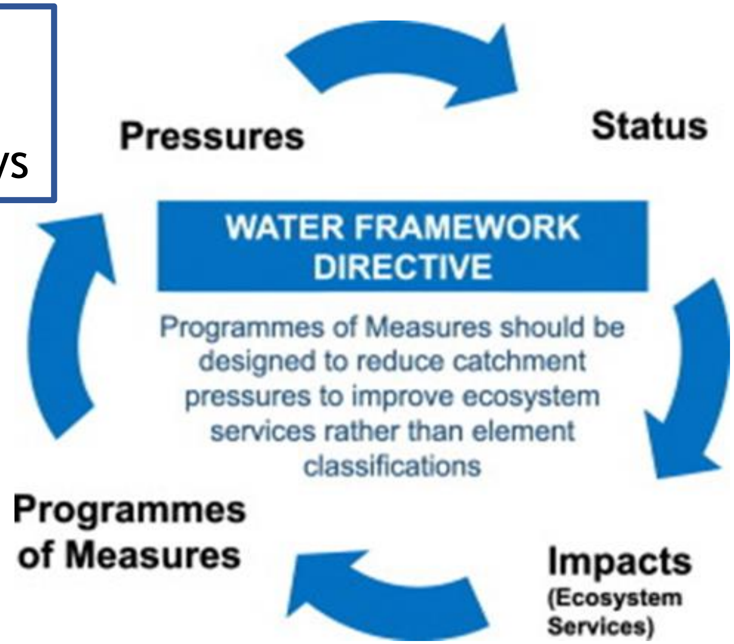
- Emission modelling can significantly contribute to parts of the WFD management cycle

Quantification of significant pressures from different pathways

Completion of more fragmented picture of monitorig



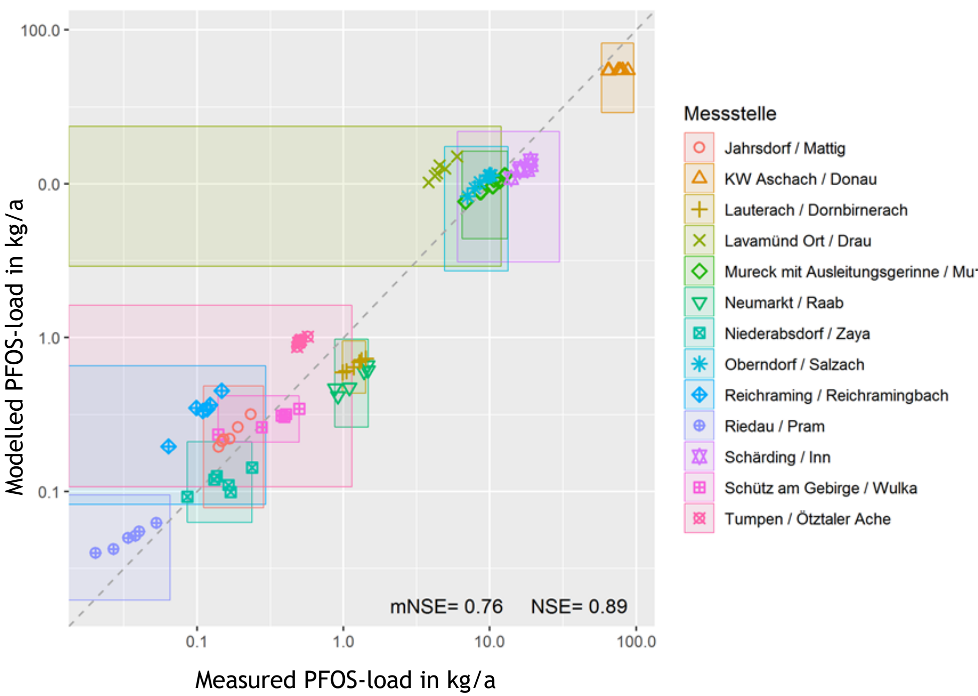
(T. Giakoumis and N. Voulvoulis, 2019)

Gain knowledge:
relevance of pathways
relevance of sources
potential reduction of Measures (by scenarios)

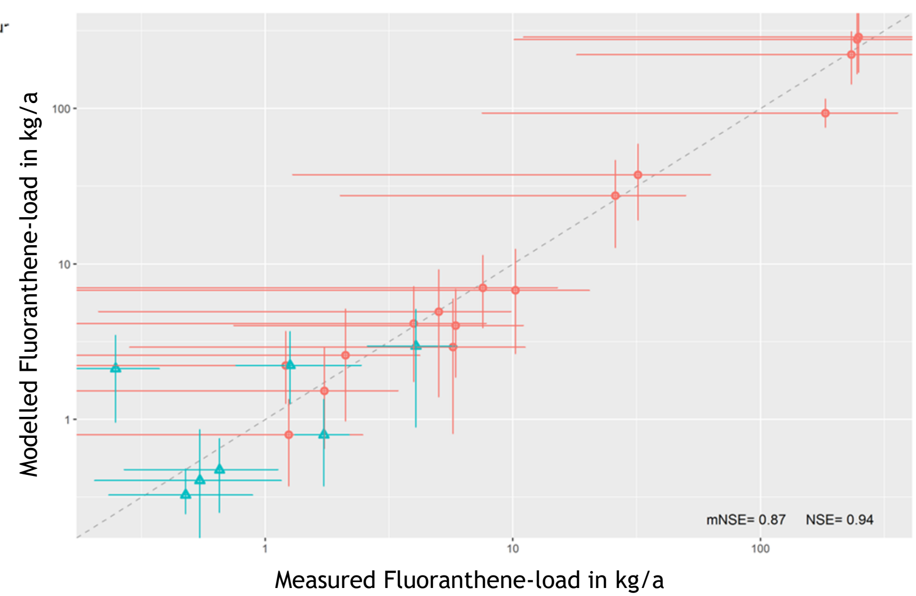
Possible risk analyses on scale of modelled Analytical Units

Topic 5: Modelling of Hazardous Substances - MoRE Emission model – results/validation

Validation considering uncertainties (by mean, min., max. variants) from project specific measurements



Validation considering uncertainties in merged data sets (project specific and national data base)



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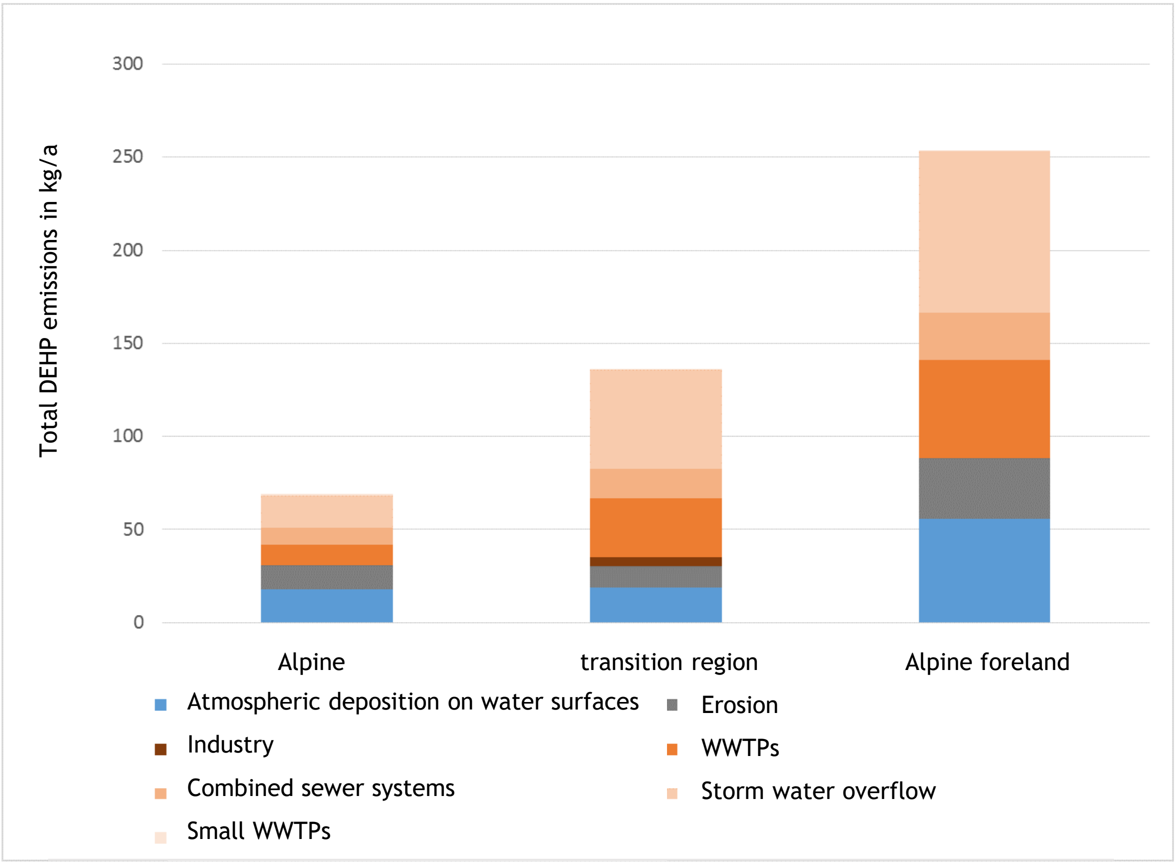
Topic 5: Modelling of Hazardous Substances- MoRE Emission model – results/pathways

DEHP in three main natural areas of the Inn catchment (not all pathways relevant)



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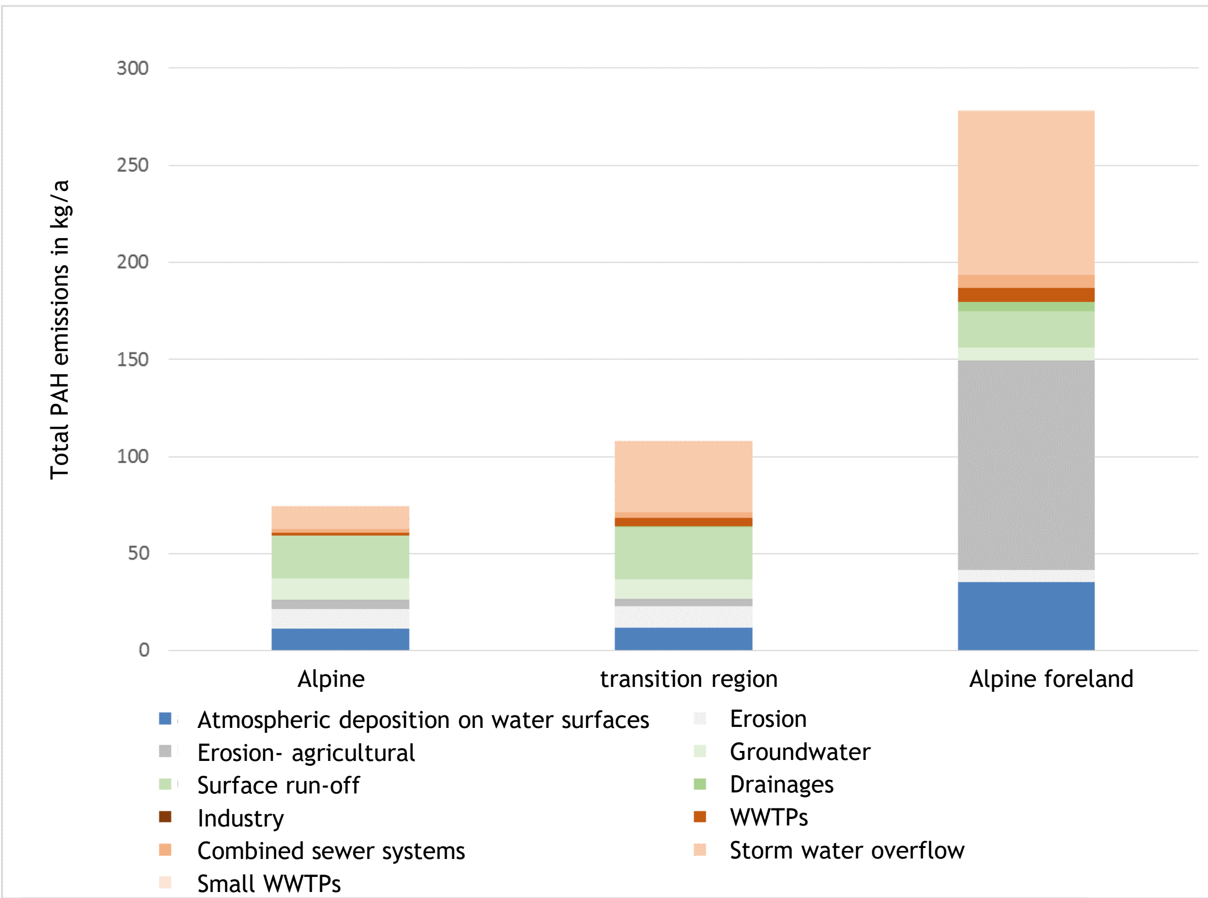
Topic 5: Modelling of Hazardous Substances- MoRE Emission model – results/pathways

PAK_{16} in three main natural areas of the Inn catchment (all pathways modelled)



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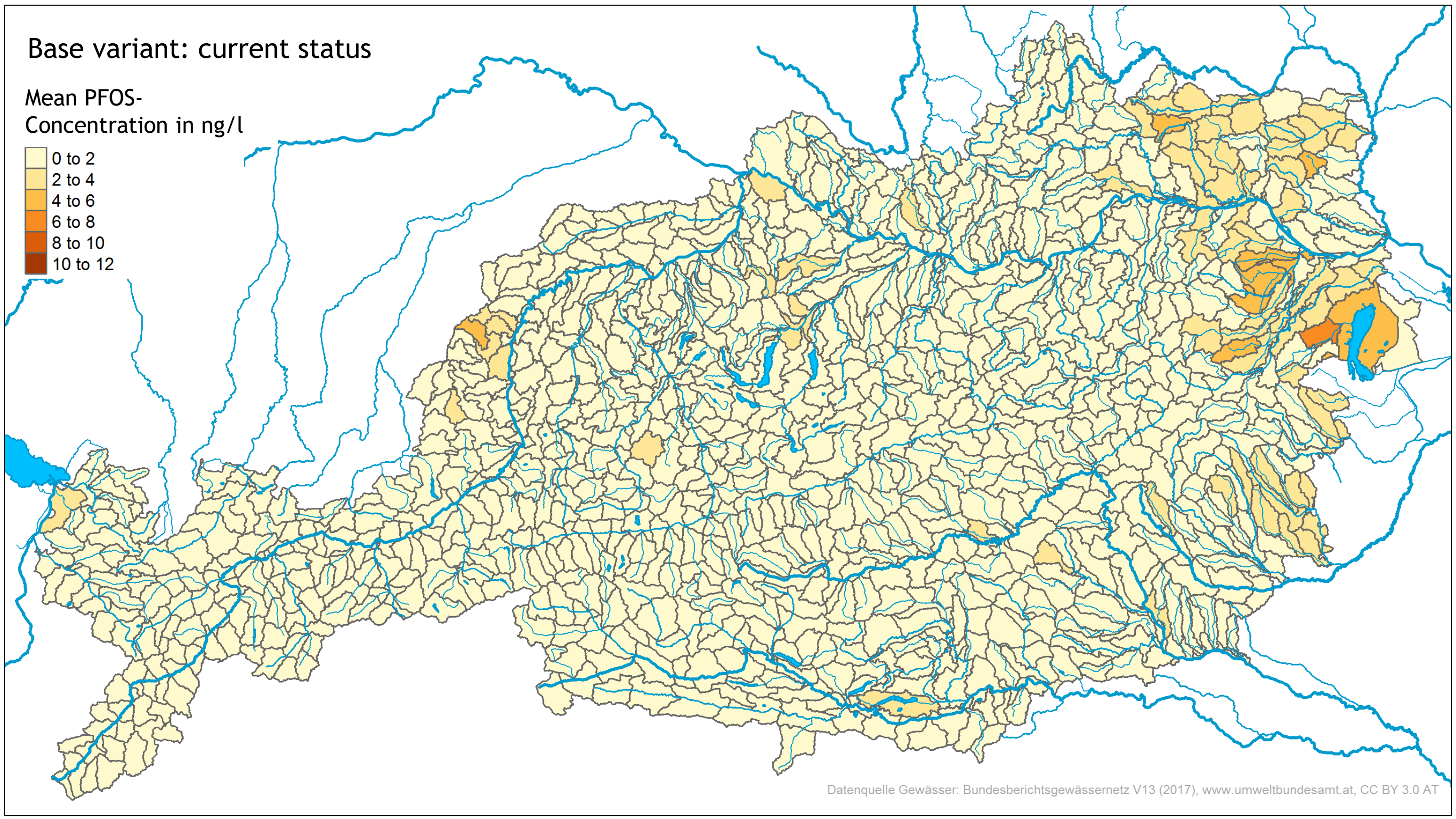
Topic 5: Modelling of Hazardous Substances- MoRE Emission model –results/status

Mean PFOS concentration in Austrian surface waters (base variant: mean values)



Topic 5: Modelling of Hazardous Substances- MoRE Emission model – results/risk analyses

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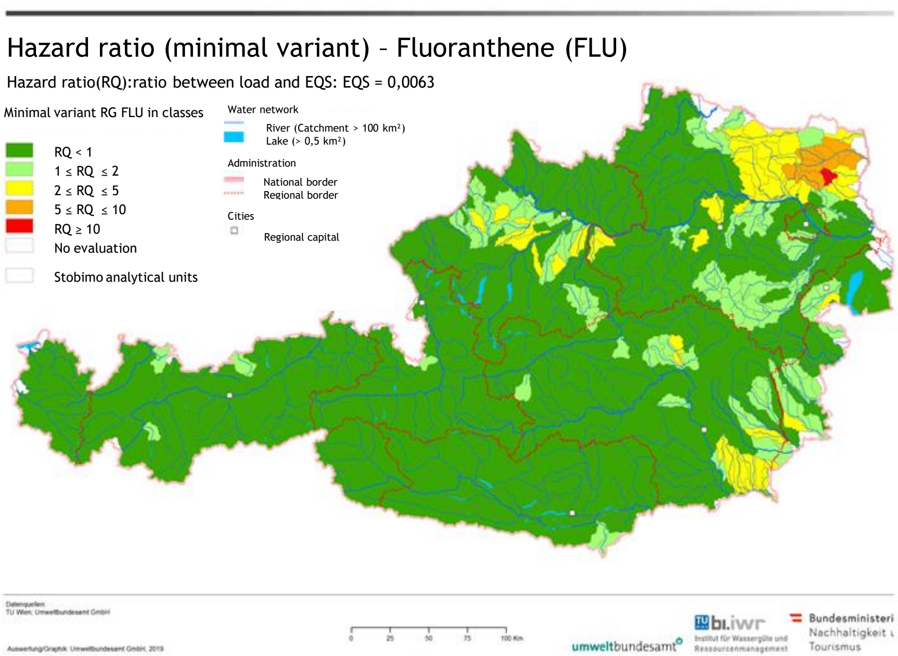
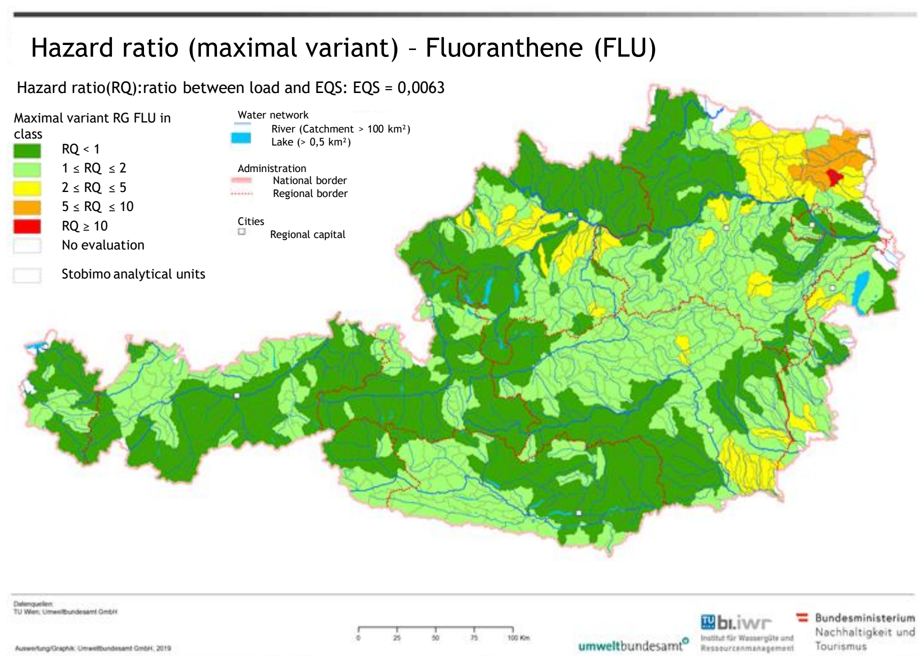
- Benefits in the project and for the management of hazardous substances in the Danube region





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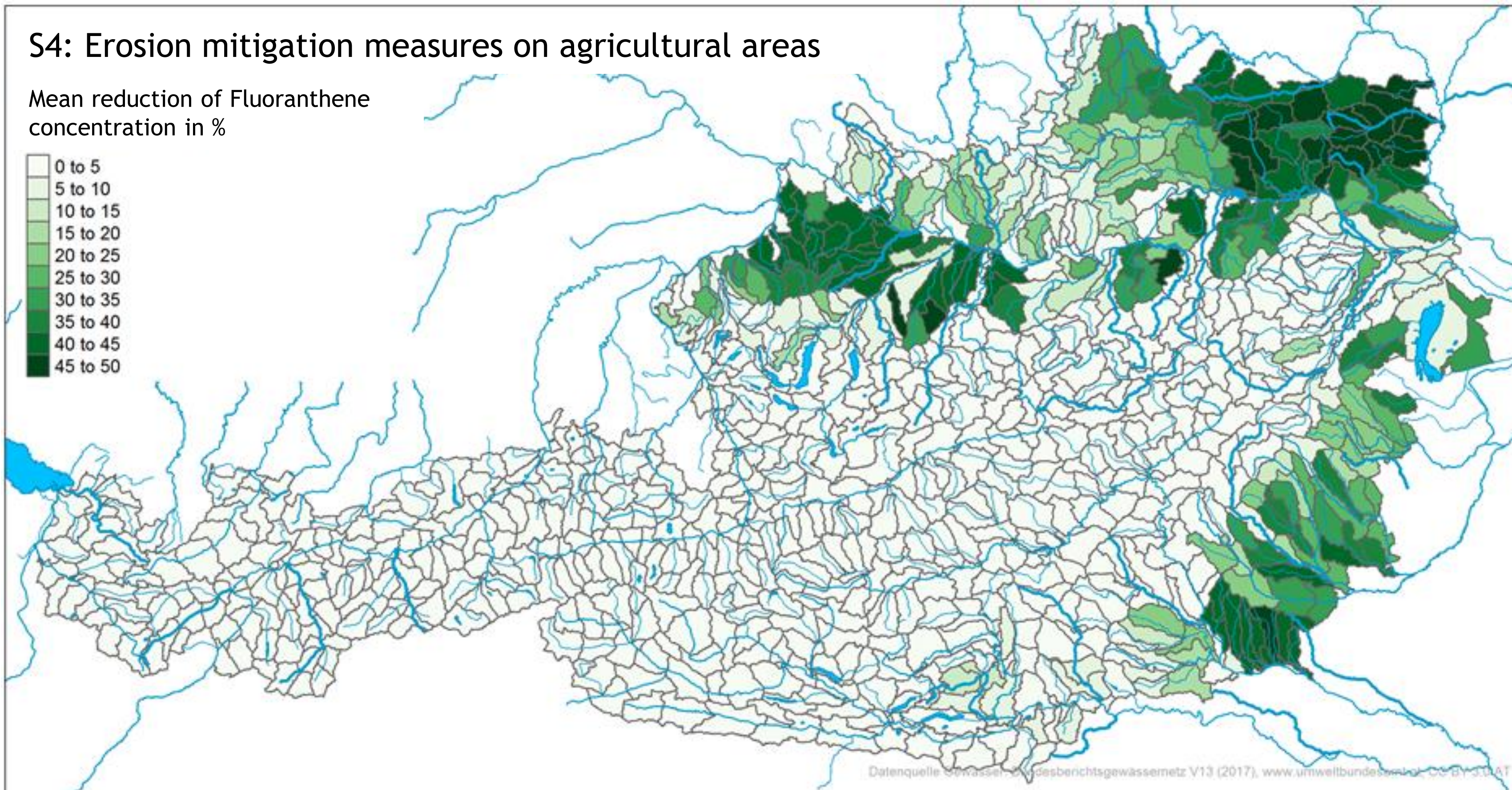
Topic 5: Modelling of Hazardous Substances- MoRE Emission model – results/mitigation measures

- Erosion mitigation measures and Fluoroanthene concentration in rivers



Topic 5: Modelling of Hazardous Substances- MoRE Emission model – results/mitigation measures

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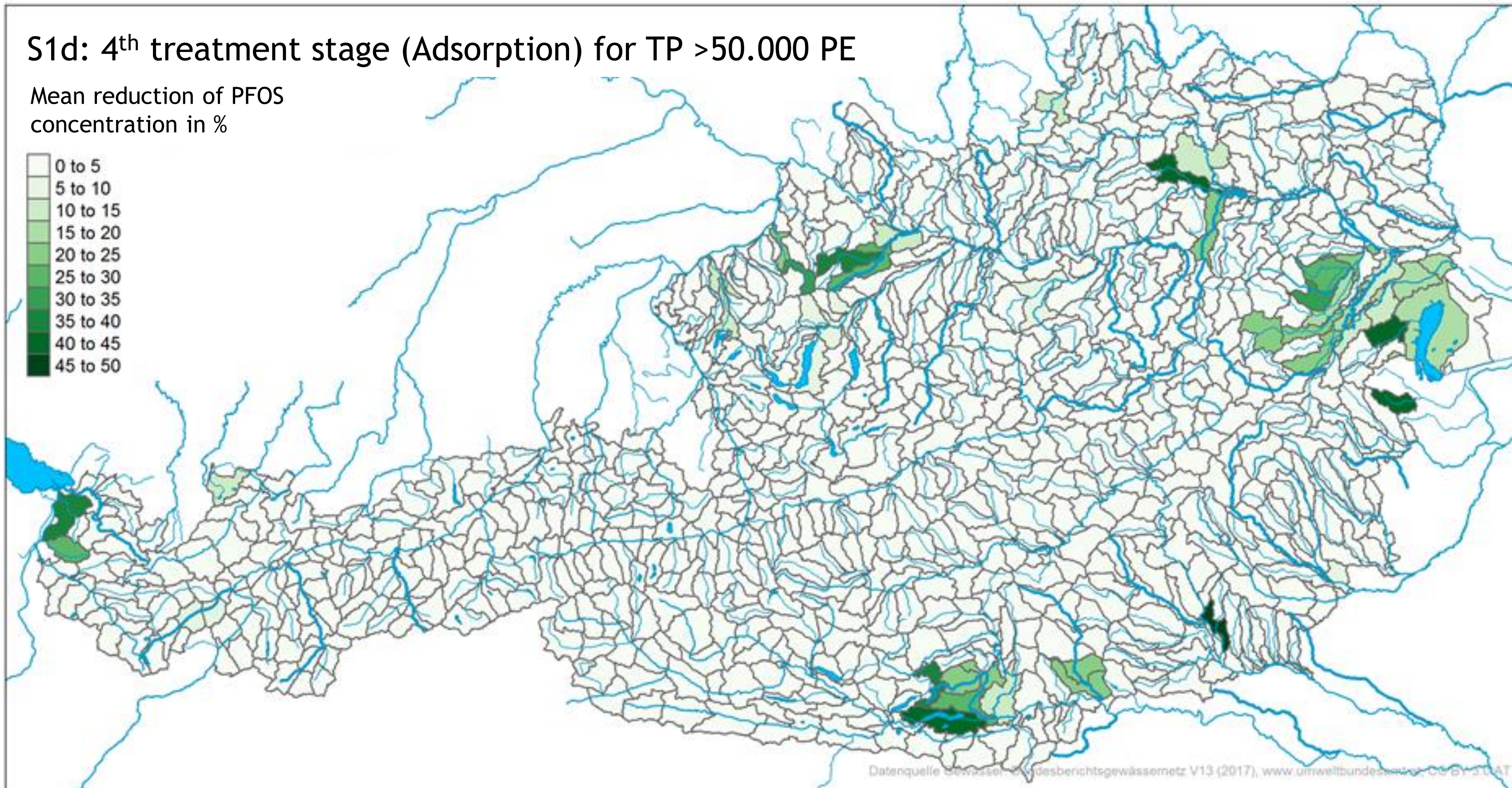
- 4th treatment stage (Adsorption) effect on PFOS concentrations in rivers



Topic 5: Modelling of Hazardous Substances – „Solutions“ model - general

- Source-oriented, conceptual model, originally developed in the solutions project
- Uses generic open-source water quality modelling software Delft3D (https://oss.deltares.nl/web/delft3d)
- Set up to model organic (emerging) contaminants, as many as possible, under conditions of data scarcity
- Set up to be used on large spatial scale (Europe)
- Built on top of the continental scale hydrology model E-Hype (https://hypeweb.smhi.se/about-us/about-the-model/)

Topic 5: Modelling of Hazardous Substances – „Solutions“ model - general

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- Spatial resolution determined by E-Hype: about 23,000 sub-catchments for the Europe-wide application, on average about 200 km2
- Set up to simulate acute and chronic exposure of aquatic ecosystems to chemicals: uses daily time step
- validated using 226 “substance + case study” combinations, among the case studies was the Joint Danube Survey 3
- Concepts and validation described by van Gils et al. (2020)
- Applicability described by van Gils et al. (2019)
- Mixture Risk Ass. for 1,785 simulated chemicals by Posthuma et al. (2019)
- Role as a stressor for EU ecosystems evaluated by Lemm et al. (2021)

Topic 5. Schematization / Case Studies

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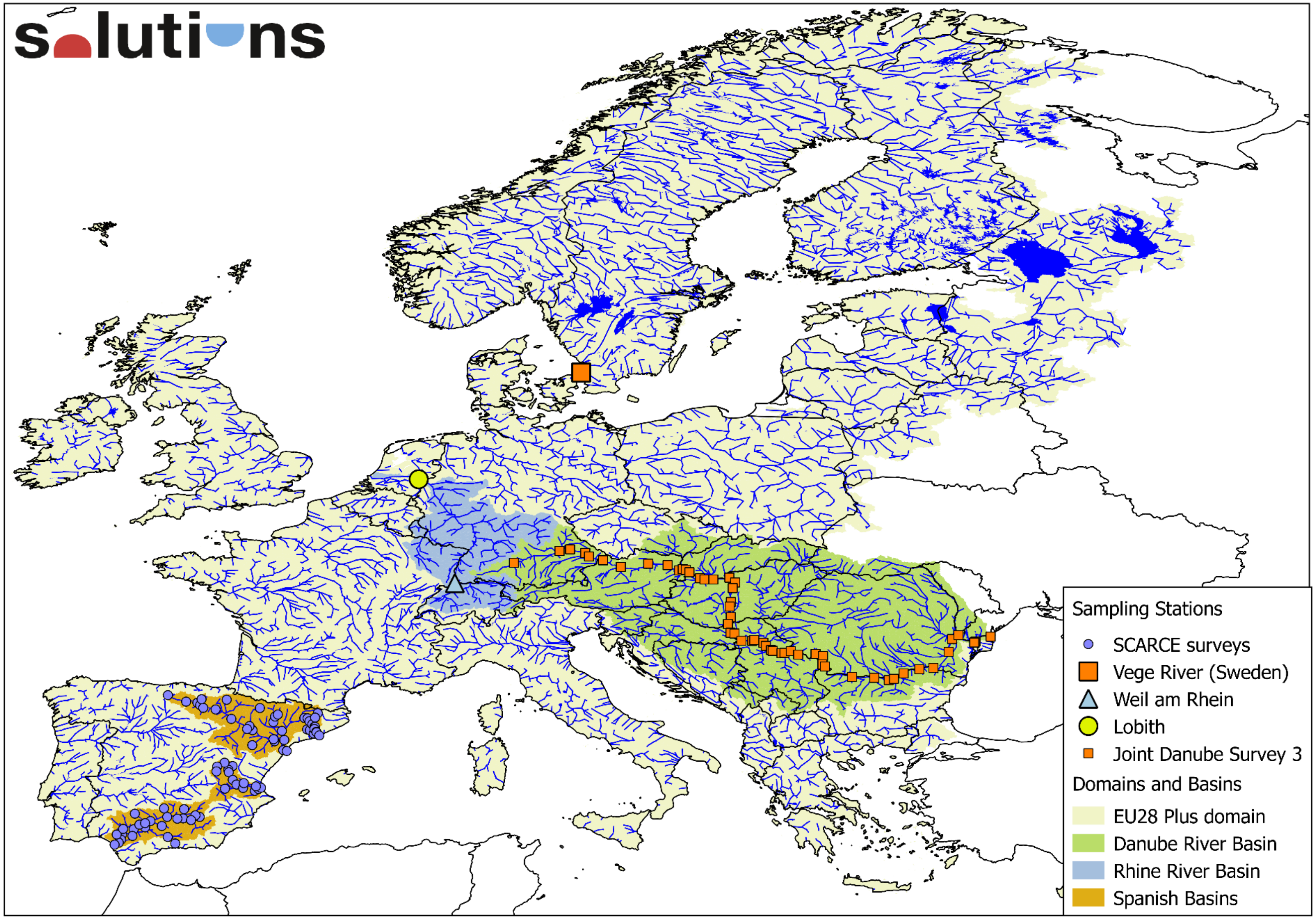

Topic 5. Simulated mixture risk

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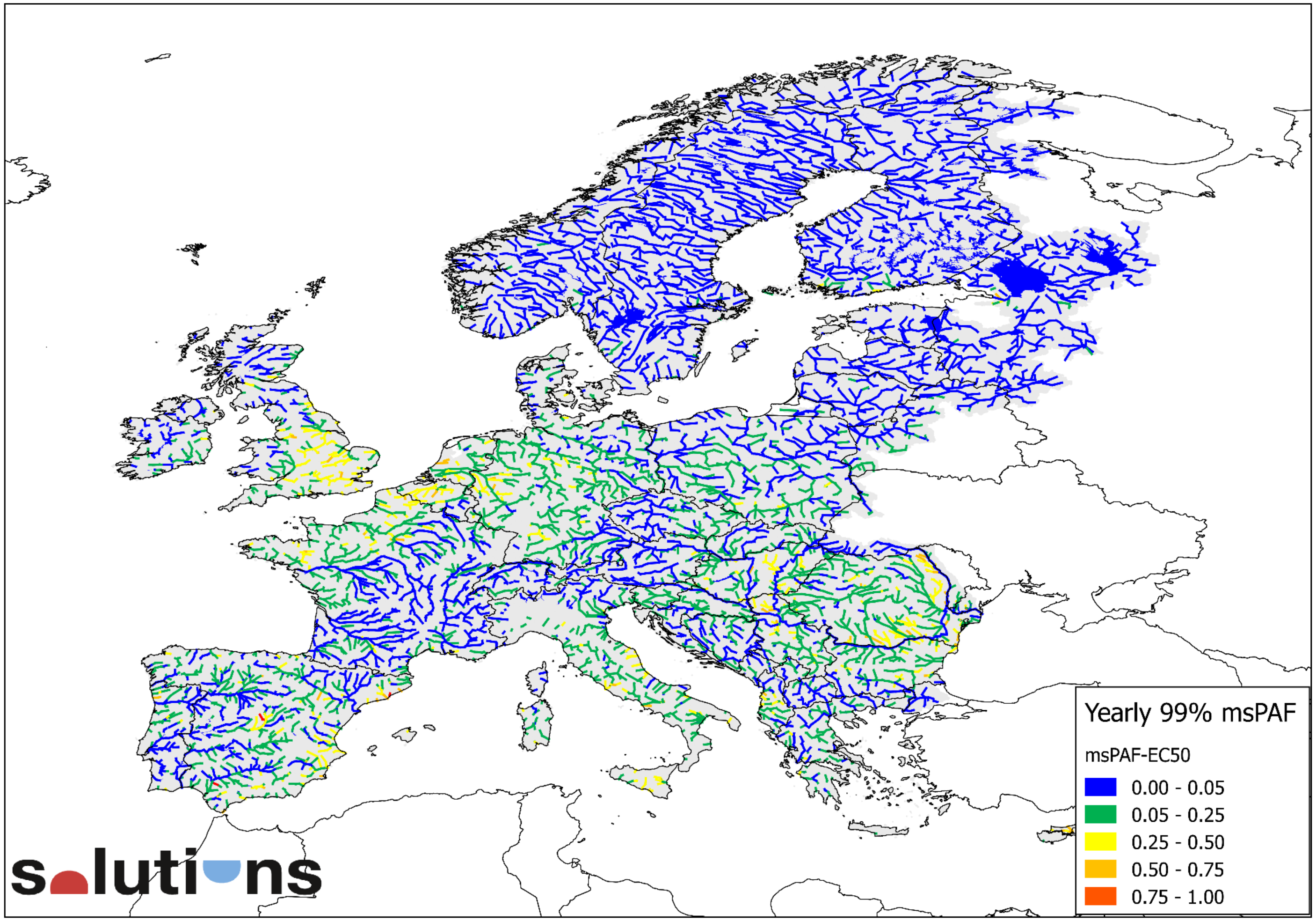
Metric:

fraction of aquatic species expected to suffer from acute toxic effects



Topic 5: Modelling of Hazardous Substances – „Solutions“ model – role in DanubeHazard m3c

- Most important: as a vehicle for upscaling emission inventories to the DRB as a whole
- Adaptations of the original model:
  - metals were added
  - more elaborate formulations were added (in anticipation of better data availability)
  - the Danube River Basin was cut out of the original model
- Status: preliminary version available, final version under development

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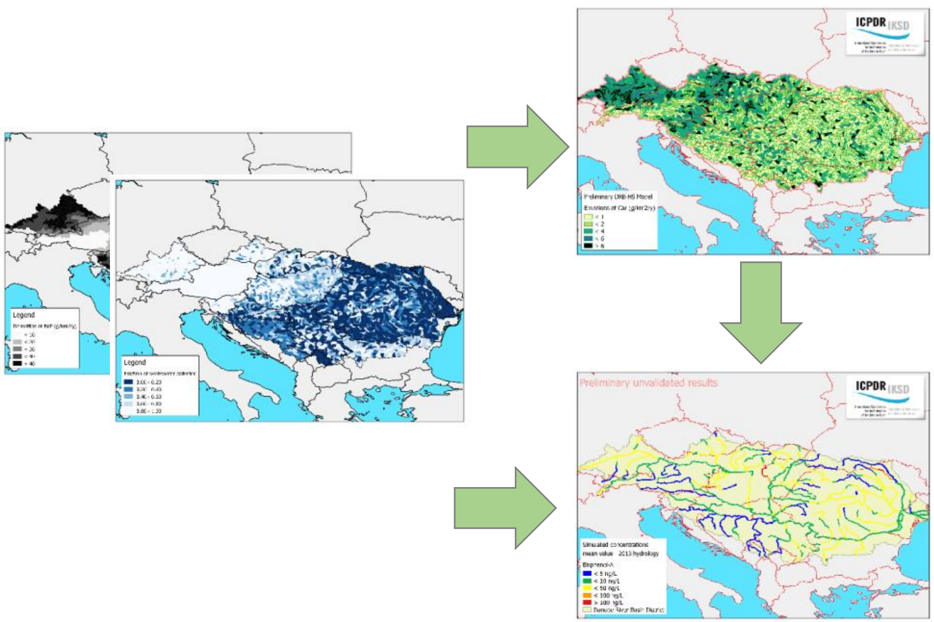
Topic 5: Modelling of Hazardous Substances – „Solutions“ model – set up

input:

- spatial data
- emission factors
- substance properties
- hydrology
- sediment

emission model



water quality model

output:

- emissions, subdivided over sources, pathways
- concentrations in water bodies (for validation)

Topic 5: Modelling of Hazardous Substances – „Solutions“ model – sources and pathways

- Source oriented method relies on Substance Flow Analysis (SFA)
  (for man-made chemicals)
- The Substance Flow starts with “use volume”
  (= production + imports – exports)

Topic 5. Use of chemicals

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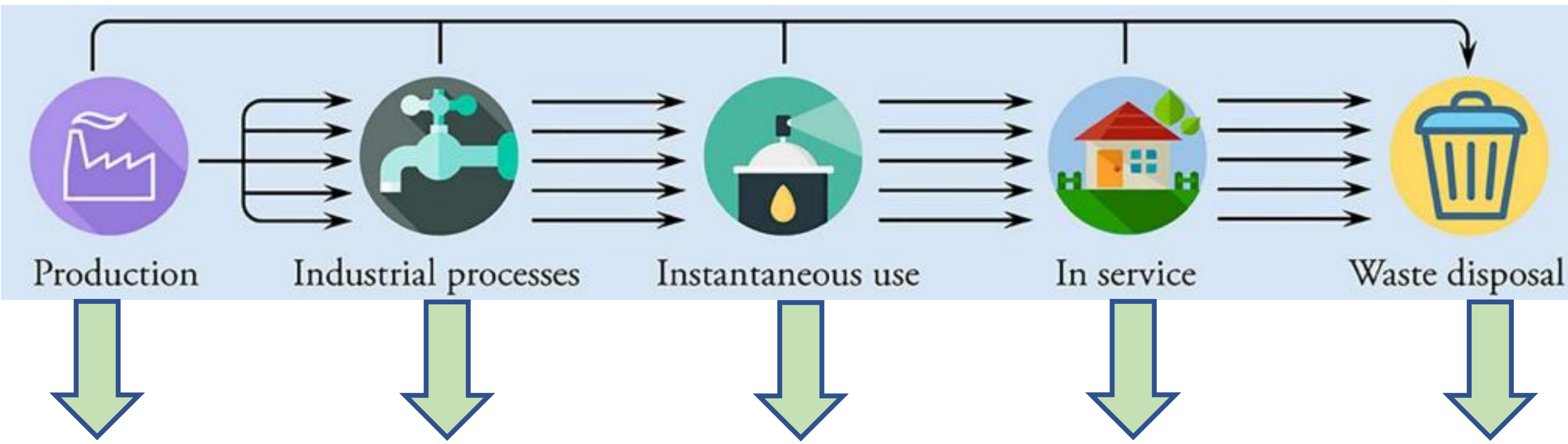
Chemicals in the anthroposphere / technosphere

DOI: 10.1289/EHP9372



losses to the environment can be caused by all life-cycle stages:

1. losses from industry
2. losses associated to comsumptive use
3. losses from wear or aging of products and materials
4. losses from waste management

Topic 5. Chemicals “stocks”

- In the technoshere: products, buildings, infrastructure, waste
- Losses to the environment from these stocks
- Consequences:
  - today’s use volume not representative for today’s emissions
  - longer time scales: today’s emissions dependent on use volumes from past years, decades (depends on product and construction life time, wear and release rates of the chemical)
- Similar issue with stocks in soils
- Solution: use the stock as a source (replace the source by a pathway)
- (also atmospheric deposition is actually a pathway)

Topic 5. Sources and pathways

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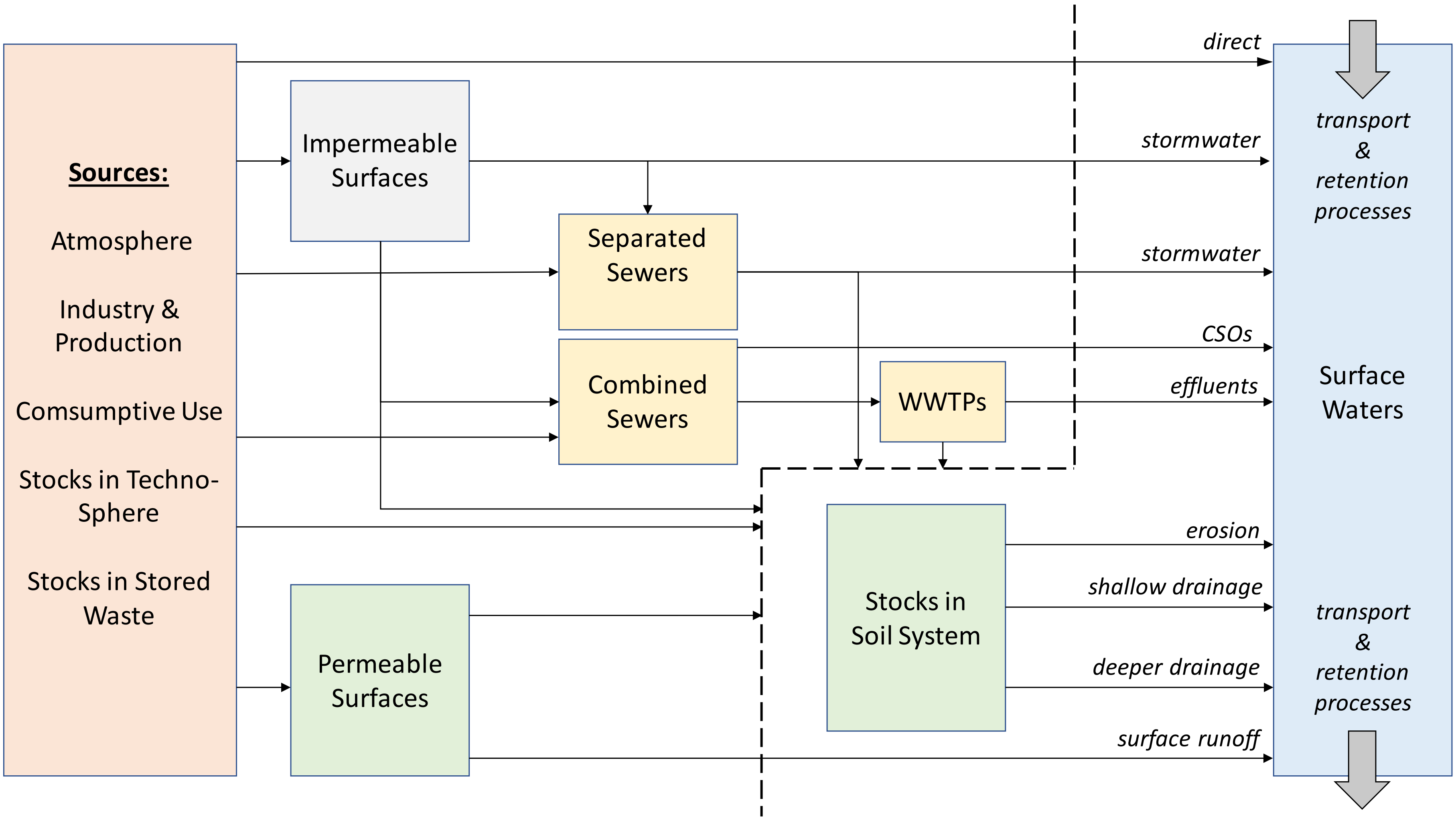

Topic 5. In prelimary version

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- The 2021 RBMP Update provides a table of sources included and reliability of (preliminary) data (Annex 6)

Table 12: Summary overview of quality of emission source quantification per substances group

Substance	Atmospheric deposition	Agriculture	Road traffic	Built environment	Households	Industry	Mining	Navigation	Natural background
Metals	x	x	xx	x	xx	xx	-	x	x
Benzo[*a*]pyrene (PAH)	xx		xx	-	xx	-		x	
PFAS	-		-	-	xx	-			
Industrial chemicals	-		xx	-	xx	x			
Pesticides		x		-	x				
Pharmaceuticals		-			x				

xx: quantification is considered adequate

x: quantification is considered preliminary

- : quantification is lacking

Grey cells are considered irrelevant

Topic 5: Modelling of Hazardous Substances – „Solutions“ model – Input Overview

Category	Examples	Sources
Hydrology Data	Rainfall, Run-off, water volumes and fluxes	E-Hype model (2003-2013)
Release of chemicals	Atmospheric deposition, Point Sources, Chemicals Use, Chemicals Stocks, emission factors, wear rates	Various, including ICPDR
Wastewater management	Collection rates, treatment levels	ICPDR
Substance properties	Partition coefficients, degradation rates	Various
Sediment Data	Concentrations of SPM, POC, DOC, soil erosion, settling of SPM	SOLUTIONS project

Topic 5: Modelling of Hazardous Substances – „Solutions“ model – results / validation

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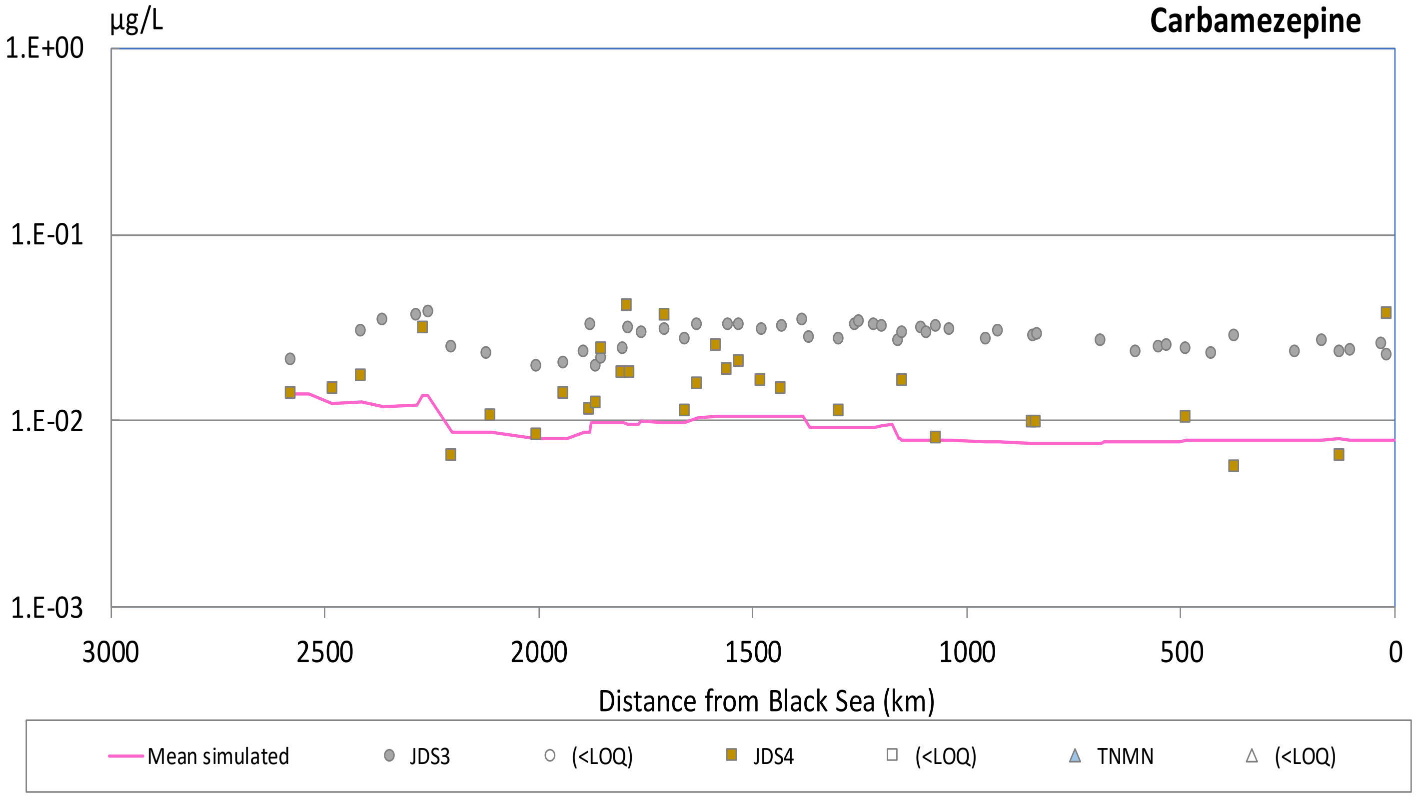
- Simulated water concentrations compared to observed concentrations (TNMN, JDS3 and JDS4)
- Example (prelimnary):



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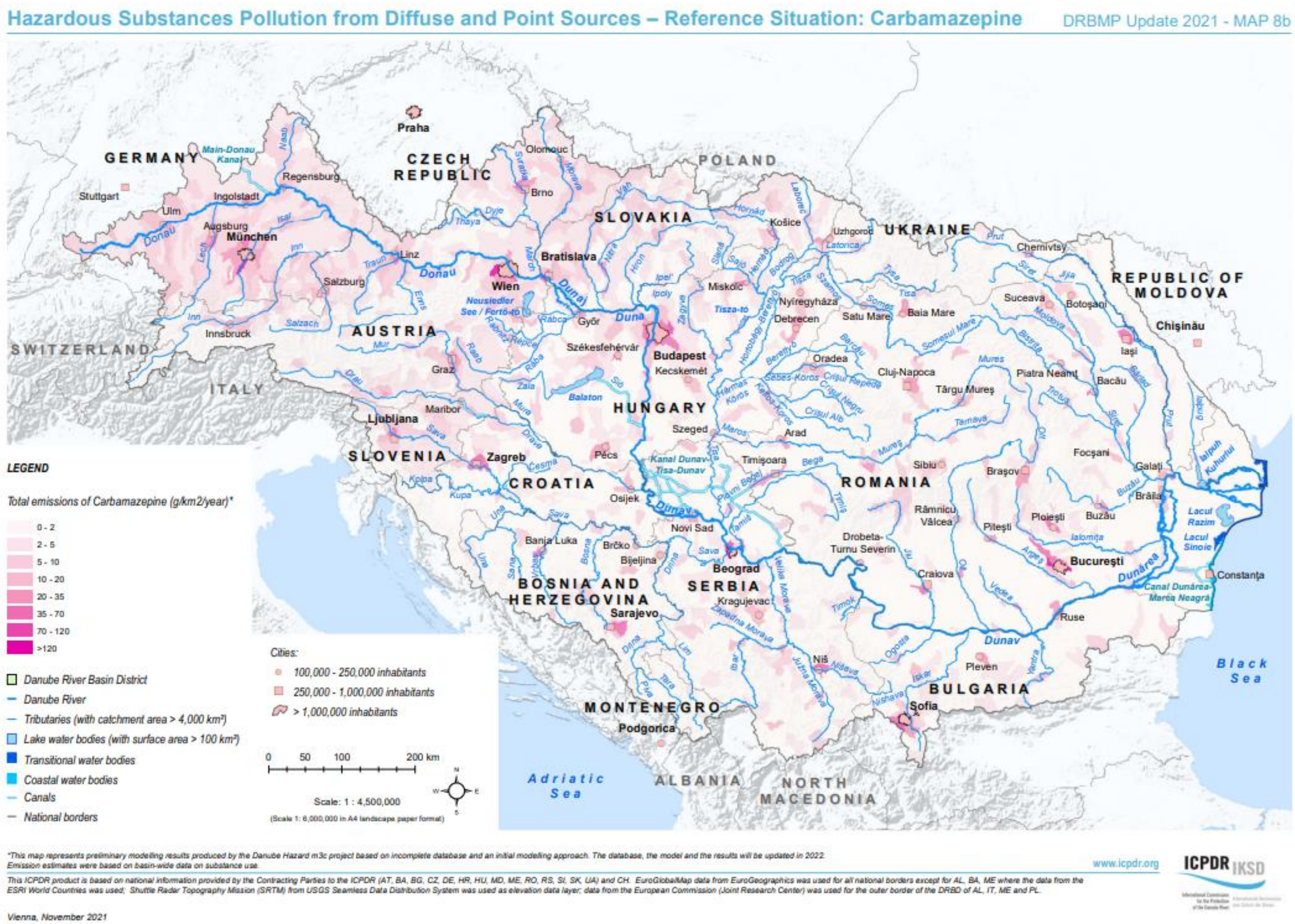
Topic 5: Modelling of Hazardous Substances – „Solutions“ model – Emissions to surface waters



Topic 5: Modelling of Hazardous Substances – „Solutions“ model – Emissions: sources and pathways

Table 13: Long-term average, basin-wide surface water emissions of selected hazardous substances according to pathways (in kg/year)

Compound	Symbol	Atmosphere	Agriculture	Households	Industry	Navigation	Runoff	Mixed sewers	Urban runoff	Soils	Total
Cadmium	Cd	251.8	0.0	22.2	1,210.1	0.0	321.2	825.9	44.0	23,312.4	**25,987.6**
Lead	Pb	6,373.7	0.0	407.1	14,064.0	0.0	6,469.1	9,777.0	2,688.9	1,160,873.9	**1,200,653.7**
Copper	Cu	15,945.0	0.0	2,819.0	74,855.0	0.0	26,401.0	75,160.6	8,179.9	1,182,312.0	**1,385,672.5**
Arsenic	As	2,093.1	0.0	121.9	2,696.3	0.0	1,441.1	5,823.9	262.3	464,101.3	**476,539.9**
Nickel	Ni	3,744.8	0.0	301.3	21,305.0	0.0	4,094.3	15,754.3	1,603.2	1,222,800.0	**1,269,602.9**
Mercury	Hg	150.8	0.0	17.8	343.7	0.0	151.5	543.8	15.9	4,707.0	**5,930.5**
Zinc	Zn	118,880.0	0.0	9,624.5	216,600.0	6,873.7	139,160.0	594,363.0	253,321.5	2,396,827.0	**3,735,649.7**
Benzo[a]pyrene	BaP	296.8	0.0	2.5	0.0	182.6	156.5	82.9	96.6	1,287.4	**2,105.2**
PFOS	PFOS	0.0	0.0	1.2	0.0	0.0	0.0	102.4	0.0	0.0	**103.6**
PFOA	PFOA	0.0	0.0	3.6	0.0	0.0	0.0	302.0	0.0	0.0	**305.6**
Bisphenol A	BPA	0.0	0.0	43.3	0.0	0.0	0.0	2,490.3	0.0	0.0	**2,533.5**
Metolachlor	Met	0.0	78.3	1.4	0.0	0.0	19.4	119.8	0.0	20.5	**239.5**
Tebuconazole	Teb	0.0	1,855.5	0.2	0.0	0.0	100.4	17.8	0.0	0.0	**1,973.9**
Carbamezepine	Car	0.0	0.0	26.8	0.0	0.0	0.0	2,247.1	0.0	0.0	**2,273.8**
Diclofenac	Dic	0.0	0.0	107.0	0.0	0.0	0.0	5,160.0	0.0	0.0	**5,267.0**
Nonylphenol	NP	0.0	0.0	17.7	130.3	0.0	0.0	371.2	167.3	0.0	**686.4**
4-tert-octylphenol	4tO	0.0	0.0	5.8	3.4	0.0	0.0	486.9	0.0	0.0	**496.0**

Topic 5: Modelling of Hazardous Substances – „Solutions“ model – Scenario Simulations (older)

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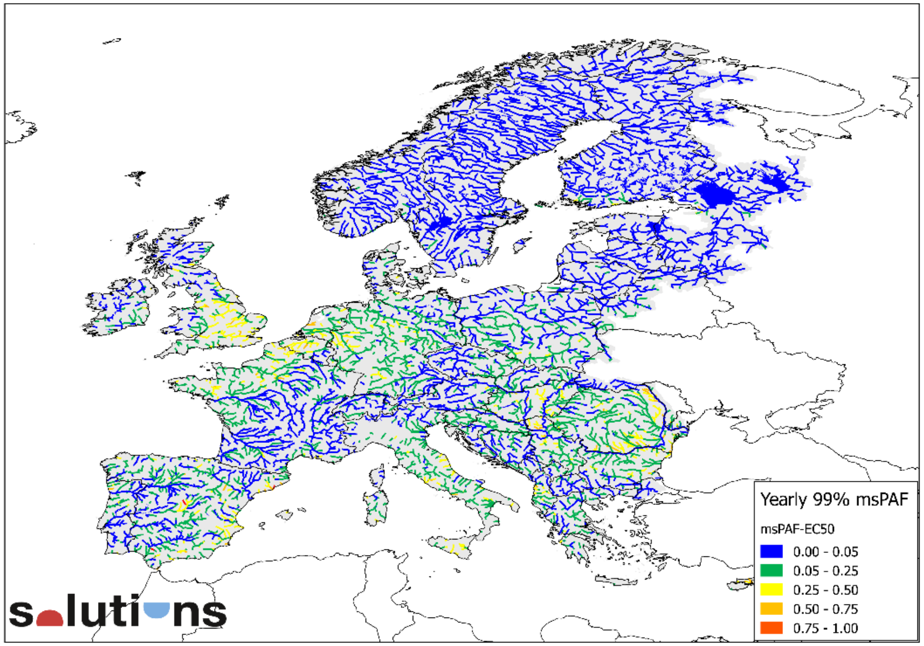
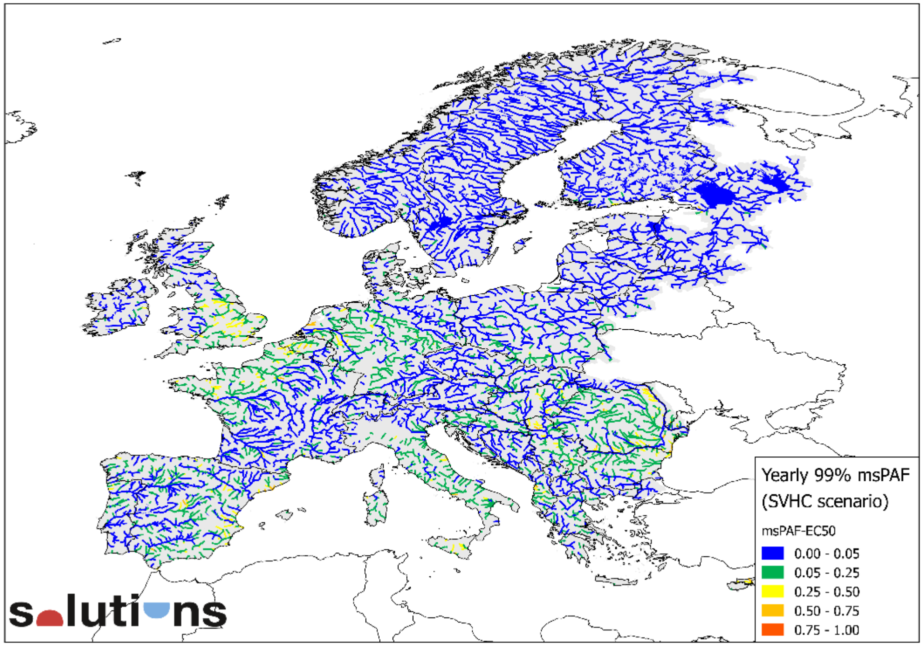
- Effect of banning 26 Substances of Very High Concern (SVHC - REACH) out of a simulated cocktail of 1357 industrial chemicals
- Metric shown: fraction of aquatic species expected to suffer from acute toxic effects






THANK YOU