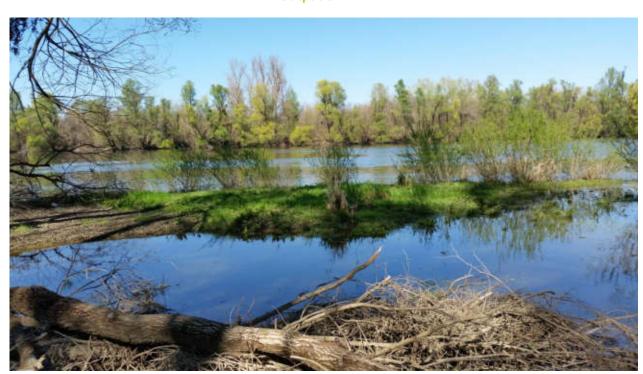




## **INVENTORY WORKSHOP – TRAINING OF 40 EXPERTS**

Output 3.2



Project title

Sediment-quality Information, Monitoring and Assessment System to support transnational cooperation for joint Danube Basin water management

Acronym

**SIMONA** 

Project duration

Date of preparation

1st June 2018 to 1st May 2021, 36 months 30/04/2019

Compiled by: Anca-Marina Vijdea

Responsible(s) of the deliverable: Anca-Marina Vijdea (RO-IGR) Co-responsible(s) of the deliverable: Gyozo Jordan (HU-SZIE)

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## 1. INTRODUCTION

The Inventory workshop was organized by the Geological Survey of Austria, at their headquarters in Vienna, Austria, on 10th April 2019.

42 participants from 12 DTP countries attended the workshop which was an open event to all stakeholders and beneficiaries of the SIMONA project.

The Inventory workshop was organized with the aims of describing the current status of the sediment sampling, laboratory and evaluation protocols of HSs in water, sediment and biota matrixes in project countries from DRB. Also, the international examples of good practices for sampling sediment in large and small rivers were presented. One of the important tasks was also interlinking the SIMONA project with DanubeSediment project by reviewing inventory questions related to sediment quantity dynamics.

This workshop is contributing to building the Specific Objective 'Common knowledge on current status of HSs' sediment monitoring in DRB' (SO1).

# 2. INVENTORY WORKSHOP AGENDA AND PRESENTATIONS

# I. WORKSHOP AGENDA

Wednesday, 10th April (open session for public)

12:00 – 12:30	Registration of participants and welcome coffee					
12:30 – 12:35	Welcome by Project Manager (SI-GeoZS) and Host institution AT - GBA					
12:35 – 12:50	Scientific Coordinator (HU-SZIE) presentation about status of the SIMONA tasks					
12:50 – 13:20	WP3 Leader (RO-IGR) presents the evaluation process of the Inventory Qs.					
13:20 – 15:00	Voluntary presentations on available (best) methods					
13:20 – 13:40	HU-NARIC/HU-SZIE (Evaluation WG leader presentation; CIS guidance, WFD					
framework)						
13:40 – 14:00	AT-GBA (sampling in small rivers)					
14:00 – 14:20	HU-BME (sampling in large rivers)					
<u> 14:20 – 14:40</u>	Coffee break					
14:40 – 15:00	ICPDR presentation (JDS4 plans, available data/support for SIMONA)					
15:00 – 16:40	Reviewed the current status by WP4 Activity 4.1.					
	Sampling WG leader presentation (status quo + future tasks/problems; CIS guidance,					
WFD framewoi	(K)					

15:40 – 16:20 Laboratory WG leader presentation (status quo + future tasks/problems; CIS guidance,

16:20 – 17:00 National Authorities – good practices and problems

<u>17:00 – 17:30</u> Open discussions

WFD framework)

# List of participants

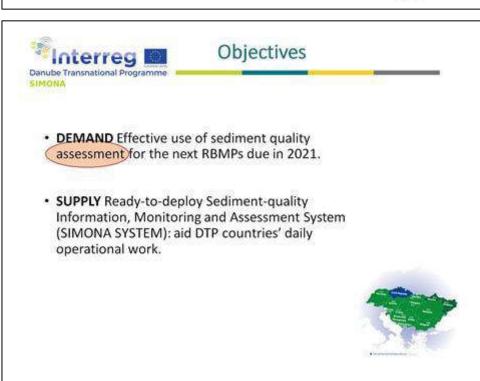
No.	Surname	Name	Institution
1	Alexe	Veronica	Geological Institute of Romania
2	Balan	Lidia	Geological Institute of Romania
3	Cerar	Sonja	Geological Survey of Slovenia
4	Čaić Janković	Ana	Croatian Geological Survey
5	Dević	Neda	Geological Survey of Montenegro
6	Erić	Suzana	University of Belgrade – Faculty of Mining and Geology
7	Fodor	Peter	Szent István University
8	Gheorghe	lepure	Tech.Uni. Of Cluj Napoca, North Uni. Center of Baia Mare
9	Ginin	Stela	Executive Environment Agency
10	Gyuris	Peter	Szent István University
11	Haslinger	Edith	Austrian Institute of Technology GmbH
12	Hiklová	Zuzana	Slovak Water Management Enterprise, state enterprise
13	Hikov	Atanas	Geological Institute of Bulgarian Academy of Sciences
14	Hucko	Pavel	Water research institute
15	Ivanišević	Danijel	Croatian Geological Survey
16	Jordán	Győző	Szent István University
17	Kamenova	Kalinka	Ministry of Environment and Water
18	Kéri	Barbara	Budapest University of Technology and Economics
19	Knoll	Tanja	Geological Survey of Austria
20	Kordik	Jozef	State Geological Institute of Dionyz Stur
21	Kovács	Zsofia	General directorate of water management in Hungary
22	Kovačević	Aleksandra	Public Institution "Waters of Srpska"
23	Liska	Igor	International Commission for the Protection of the Danube River
24	Mišur	Ivan	Croatian Geological Survey
25	Mitrović	Tatjana	Water Institute Jaroslav Černi
26	Mörtl	Mária	National Agricultural Research and Innovation Centre

27	Nasui	Daniel	Tech.Uni. Of Cluj Napoca, North Uni. Center of Baia Mare
28	Nováková	Jarmila	State Geological Institute of Dionyz Stur
29	Pfleiderer	Sebastian	Geological Survey of Austria
30	Roško	Vladimír	Water research institute
31	Simić	Barbara	Geological Survey of Slovenia
32	Stefan	Damian Gheorghe	Technical University of Cluj Napoca, North University Center of Baia Mare
33	Stríček	Igor	State Geological Institute of Dionyz Stur
34	Šarić	Kristina	University of Belgrade – Faculty of Mining and Geology
35	Šorša	Ajka	Croatian Geological Survey
36	Takács	Eszter	National Agricultural Research and Innovation Centre
37	Tokarčíková	Ľudmila	State Geological Institute of Dionyz Stur
38	Vetseva	Milena	Geological Institute of Bulgarian Academy of Science
39	Vićanović	Jelena	Public Institution "Waters of Srpska"
40	Vijdea	Anca-Marina	Geological Institute of Romania
41	Vulić	Dragica	Water Institute Jaroslav Černi
42	Zsolt	Szakacs Laszlo	Technical University of Cluj Napoca, North University Center of Baia Mare

## II. PRESENTATIONS

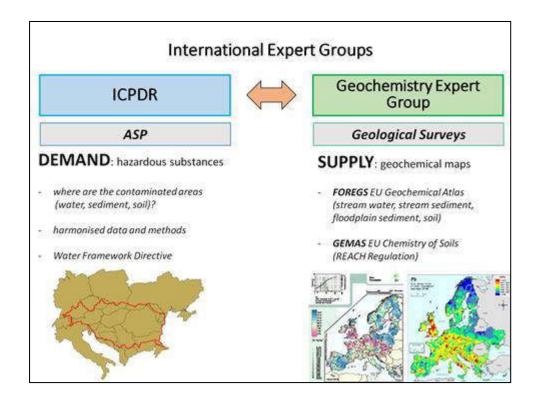
# II.1. General presentation of SIMONA project

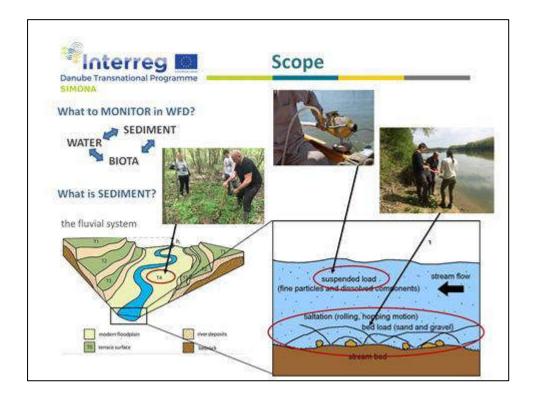


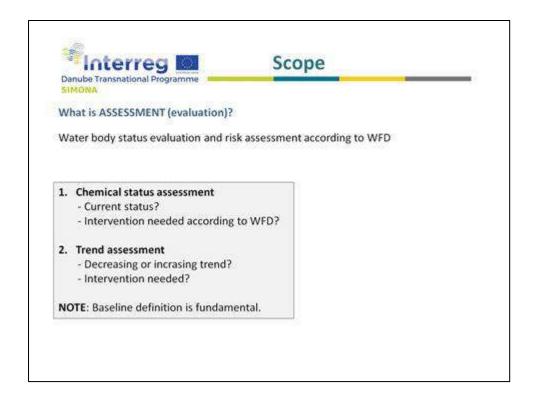


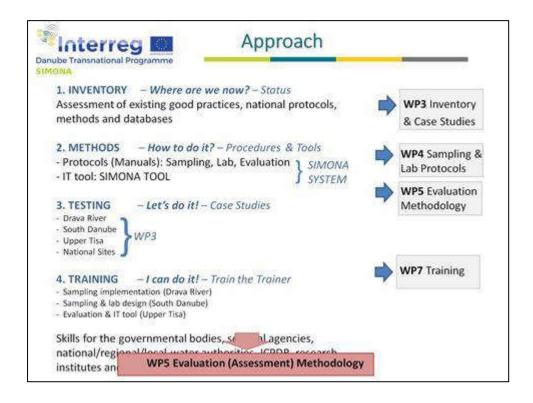


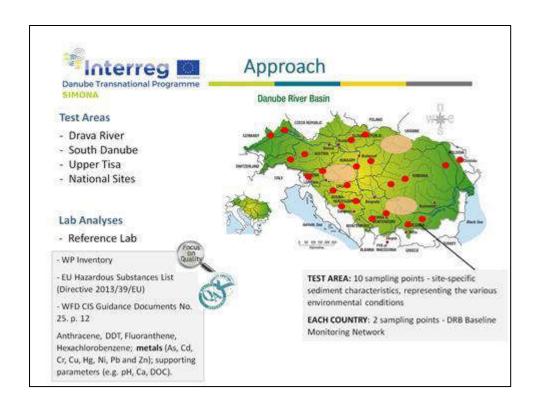






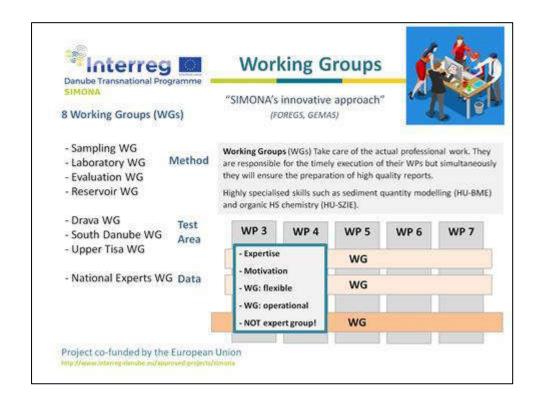


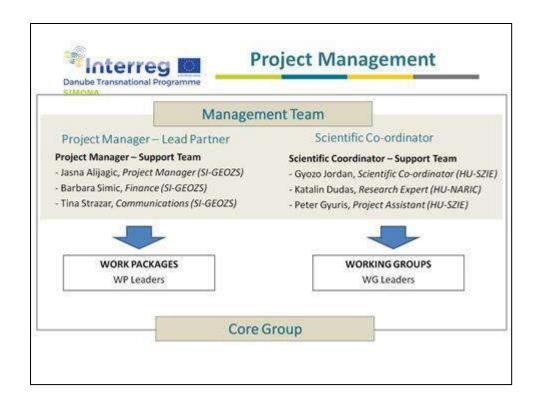


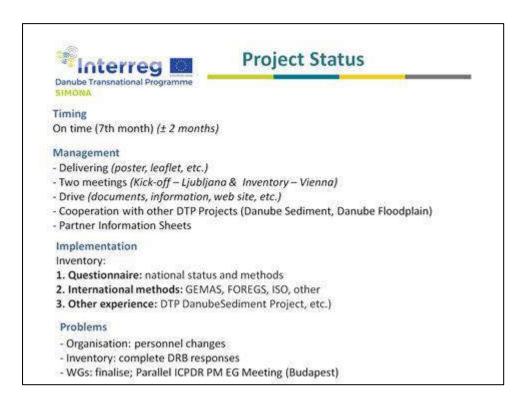














# **Inventory Workshop**

#### WP3 INVENTORY

### WP3 provides the essential frame for WP4 and WP5 protocol-developing

- Describes the current status of and common needs for sediment quality monitoring in the DRB countries by compiling an inventory of
  - national protocols
  - good practices
  - methods and databases
- 2. Verifies and demonstrates: Case Studies

Inventory, as a handbook tool, describes existing good practices and the available knowledge in the DRB counties, and presents international examples for sediment quality monitoring. The inventory also ensures that the protocols (WP4 and WP5) are based on the BEST AVAILABLE KNOWLEDGE.



# **Inventory Workshop**

### INVENTORY collects information in the DTP countries:

- legislative frameworks
- experiences
- > practices
- > technical procedures
- existing sampling, laboratory and evaluation methods
- existing water body monitoring and sampling sites
- existing methodologies of surface water chemical status assessment
- limit values: national, natural background levels
- metadata related to sediment quality monitoring, analysis and assessment

### **INVENTORY** uses:

- standardised questionnaire in order to ensure transparency and comparability of information among the countries
- Sampling, Laboratory and Evaluation WGs collect the information types for their protocol development, and deliver questions for the questionnaire
- National Experts WG collects the questionnaire answers and information from the water authorities



# **Inventory Workshop**

### WP3 INVENTORY

- > identification of problems of the current monitoring procedures in DRB
- review of the sediment monitoring network status, data and metadata availability
- inventory of sampling and laboratory methodologies

DELIVERABLE: 'Inventory of DRB sediment monitoring activity'



# **Inventory Workshop**

### WP3 INVENTORY - STATUS

### CANADIANG

'Complete' offer for sampling for sediment quality assessment methods on the table:

- 1. Large River suspended sediment: DTP DanubeSediment Guidance
- 2. Large River bottom sediment: DTP DanubeSediment Guidance
- 3. Small River suspended sediment: ???
- 4. Small River bottom sediment: FOREGS Field Manual
- 5. Floodplain sediments: FOREGS Field Manual (& Global Geochemical Mapping Manual)
- (+6). Other Standards: ISO Sediment Sampling Protocols (2017)

## LAB ANALYSIS

ISO Standard procedures



# **Inventory Workshop**

## **VIENNA WORKSHOP - TASKS**

- Identify gaps (missing information) in the Questionnaire (WP3 review, country reports), and fill the gaps (follow-up action)
- Review methods (sampling, lab, evaluation) and experience within the SIMONA Consortium Knowledge Base (GEMAS, FOREGS, DanubeSediment, etc)
- 3. Review methods in general (ISO, ICPDR, other)
- 4. Define action plans for the WGs



### After Vienna we have to

- Assess the Questionnaire information from the WFD viewpoint
- Based on the Inventory, WGs/WPs assess and start developing sampling, lab, evaluation methods & protocols



# Opportunity

### SIMONA

- Project: Develop future partnership
- Project: Develop cooperation with other DTP projects & network
- Country: Develop research organisation government links, domestic networks
- EU: Develop future EU projects
- Overall: Carrier development for YOUNG persons, PhD degrees, other
- Overall: Creat a sediment monitoring 'SIMONA' system that is used in the EU, Internationally (FOREGS, GEMAS)



# **Working Groups**

In the 18th month the Drava, South Danube and Upper Tisa working groups will

- design <u>sampling points</u> and
- the concrete measuring <u>components</u> (e.g. As(V) as an indicator component for arsenic and its compounds' contamination)

for the 3 test areas, using the already finalised SIMONA 'Transnationally harmonized sampling and laboratory protocols' (delivered in 17th month).

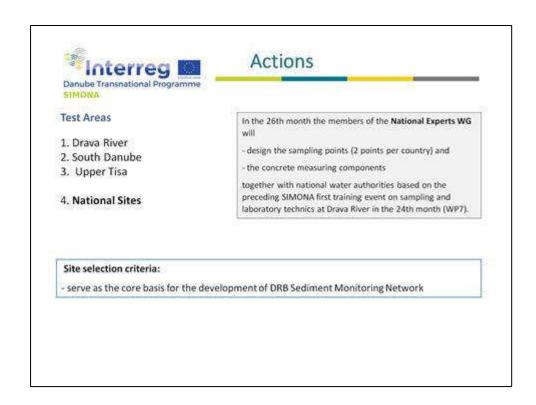
# 1. Drava River

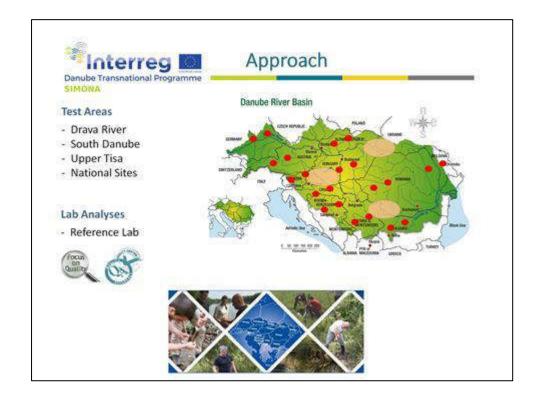
- I. Diava Mivel
- 2. South Danube
- 3. Upper Tisa
- 4. Reservoir

#### Site selection criteria:

- trans-national character
- existing national, ICPDR monitoring points
- existing supporting background data, information (former, on-going project)
- good access
- Representativity (sediment type, hydrology: small, rage river, etc)
- othor









# **Working Groups**

### WGs - Mehtod

### Sampling WG

Members: AT-GBA, BA-FZG, BG-GI-BAS, HR-HGI-CGS, MD-IGS-ASM, ME-GSM, RO-IGR, SI-GEOZS, SK-SGIDS and UA-UGC

NOTE: Responsible for testing with special regard to the sampling protocol

### Lab WG

Members: HR-HGI-CGS, SK-SGIDS, HU-SZIE, HU-NARIC, MD-IGS-ASM, ME-GSM and SI-GEOZS

NOTE: Responsible for testing with special regard to the laboratory analysis protocol

### **Evaluation WG**

Members: AT-AIT, HU-NARIC, HU-BME, HR-HGI-CGS, ME-GSM, RO-TUCN, SK-SGIDS and UA-UGC

NOTE: Responsible for testing with special regard to the evaluation protocol, and they test all the features of the SIMONA-tool with the 'DRB baseline network' real field measurement data



# **Working Groups**

### WGs - Mehtod

Sampling WG (National Geological Surveys, 2 DTP DanubeSediment partners)

- (1) undertakes sampling at the 3 test areas;
- (2) contributes to the development of sampling protocol, on the basis of their profound knowledge and experience obtained in the FOREGS and GEMAS projects; and experience in industrial pollution and pesticides measuring;
- (3) contributes to demonstration and organisation of exercises on sample collection.

### **Laboratory WG**

- manages protocol development, on the basis of their leading knowledge on laboratory analysis and outstanding experience with all kinds of sampling and laboratory work;
- (2) contributes to laboratory methods training, according to the developed protocols.

Evaluation WG (research-institutes, SIMONA-tool developing organisation)

- develops the evaluation protocol and the SIMONA-tool, on the basis of their experience with environmental risk assessment and developing methodologies;
- (2) evaluate the DR8 baseline network field data.



# **Working Groups**

SIMONA

#### WGs - Method

### The Sampling and the Laboratory WG

#### EXAMPLE

critically review the existing water and sediment national methods, the state-of-the-art knowledgebase, good practices and experiences in the DTP countries, including EU and non-EU countries.

Reviewing will be done against the following criteria: the developed protocols

- (1) should be acceptable in all DTP countries,
- (2) should be in-line with the ICPDR and the EU requirements,
- (3) use the lattest scientific knowledge, and
- (4) have to be sustainable.

The main steps of reviewing the sampling and laboratory methods are

- reviewing national spatial and temporal sampling and monitoring techniques and laboratory analysis
  procedures for sediment quality measurements of the water phase, biota, bottom sediment,
  suspended sediment, floodplain sediment with passive and other sampling technics under the WFD
  implementation requirements;
- (2) reviewing national uncertainty analysis techniques for sampling and laboratory analysis including representativity assessment; and (3) providing a critical summary and conclusions of the reviews.



# **Working Groups**

### WG - National Experts

Members: AT-GBA, BA-FZG, BG-GI-BAS, HR-HGI-CGI, HU-NARIC, MD-IGS-ASM, ME-GSM, RO-IGR, RS-JCI, SI-GEOZS, SK-SGIDS and UA-UGC

National Expert WG will collect the Inventory data, will directly approach the relevant national TGs and discuss the results of the evaluation protocol. With the above mentioned direct outreach for the national TGs and with the 30 days open commenting period, the Evaluation protocol will be finalized and approved by the TGs, and the protocol will be ready to be integrated into the national and transnational water management methodology and procedures

- WFD Experts
- Contact: TG & ASP

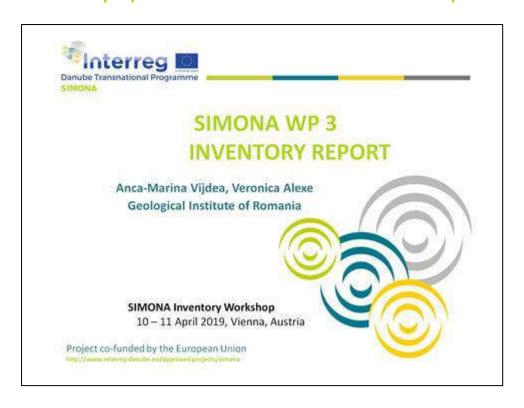


## SIMONA

- Action 1: WP Leaders contact WP members: establish network & communication
- Action 2: LP: Establish Project File Server (google drive; kick-off ppt's, etc.)
- Action 3: WP Leaders send out 'WP Activity Sheets' (what, when, who, how)
- Action 4: All project partners receive 'Partner Activity Template' & 'Partner Budget Table'
- Action 5: WGs start exchange of information
- Action 6: INVENTORY
  - design of questionnaire (sampling, lab, evaluation)
  - collecting information from DRB
  - collecting EU, International experience (e.g. UK, Sweden, NL, USA, Canada)



## II.2. WP3 Inventory report in DRB based on SIMONA countries questionnaires





## **WP3 Objectives**

- to describe the current status of and common needs for sediment quality monitoring in the DRB countries by compiling an inventory of good practices, national protocols, methods and databases related to sediment quality monitoring;
- to verify and demonstrate the integration and added value of surface water sediment quality monitoring by two pilot action for improving transnational water management.

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## INVENTORY QUESTIONNAIRE

# 5 parts:

- LEGISLATIVE FRAMEWORK
- II. PRACTICES, EXPERIENCES
- III. INVENTORY OF SAMPLING METHODOLOGIES
- IV. INVENTORY OF LABORATORY METHODOLOGIES
- V. INVENTORY OF EVALUATION METHODS

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Inventory workshop, 10-11.04.2019, Austria





- I.1. National or/and European legislation
- I.2. List of hazardous substances in waters, soils, sediments and biota
- 1.3. Quality objectives for hazardous substances
- 1.4. Listing of analytical standards
- 1.5. List of chronic or acute toxicity tests and biota
- I.6. List of national and international guides of techniques
- 1.7. Recommended remedy measures

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# II. PRACTICES, EXPERIENCES

- II.1. Significant projects
- II.2. Significant papers
- II.3. Sampling sites
- II.4. Polluters data availability
- II.5. Monitoring problems

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THE PROPERTY OF THE PROPERTY O	III INDUSTRIAL TO SERVE	1000000000		
III.1. Water	III.2. Sediments	III.3. Biota		
III.1.1.Design of sampling strategy	III.2.1. Type of sampled/measured sediment	III.3.1. Type of biota		
III.1.2.Parameters of water quality/quantity measured in situ	III.2.2. Design of sampling strategy	III.3.2. Design of sampling strategy		
III.1.3. Instruments for in situ measurements	III.2.3. Parameters of sediment quality/quantity measured in situ	III.3.3. Parameters of biota quality/quantity measured in situ		
III.1.4. Methodology for in situ measurements	III.2.4. Sampling devices for in situ measurements	III.3.4. Instruments for in situ measurements		
III.1.5. Tools for collecting samples for laboratory measurements	III.2.5. Methodology for in situ measurements	III.3.5. Methodology for in situ measurements		
III.1.6. Sample preservation	III.2.6. Tools for collecting samples for laboratory measurements	III.3.6. Tools for collecting samples for laboratory measurements		
III.1.7. Methodology for sample collecting	III.2.7. Methodology of sample collecting for laboratory measurements	III.3.7. Methodology of sample collecting for laboratory measurements		
	III.2.8. Transport methodology of samples for laboratory measurements	III.3.8. Transport methodology of samples for laboratory measurements		
	III.2.9. Sample archiving	III.3.9.Sample archiving		



## IV. INVENTORY OF LABORATORY METHODOLOGIES

### IV.1. Mechanical preparation of samples

IV.2. Chemical preparation of samples and laboratory analysis

IV.2.1. Procedure for organic matter

IV.2.2. ICP-MS, ICP-AES systems

IV.2.3. AAS systems

IV.2.4. XRF

IV.2.5. DC-arc - AES

IV.2.6. Radionuclides

IV.2.7. Organic compounds (HSs)

IV.2.8. XRD

IV.3. Inventory of national laboratories

### IV.4. Good practices

### IV.5. Protocols

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### V. INVENTORY OF EVALUATION METHODS

- V.1. Establishing threshold values for HSs
- V.2. Fixed or variable threshold values for HSs
- V.3. Corrections for threshold values
- V.4. Basis of the environment quality objectives
- V.5. "Bioaccumulation" in legislation
- V.6. Categories of environment quality in national legislations
- V.7. Number of media for defining the categories of environment quality
- V.8. Algorithm for defining the categories of environment quality
- V.9. Difference between contamination and pollution in national legislations
- V.10. Relations between specific HSs and the contamination and pollution sources
- V.11. Actions in case of contamination and pollution
- V.12. Representations of results, targeted audience and avilability
- V.13. Space-time risk assessment methods

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# I. 1 National or/and European Legislation

The legislation was classified according to topic:

- Drinking water
- Surface and groundwater
- Waste (sewage) water
- Air
- Soil
- Sediments

7 tables were made with the legislation in national language and English for the above topics.

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Inventory workshop, 10-11.04.2019. Austria



## I. 1 National or/and European Legislation

### CONCLUSIONS:

- Every country has national legislation related to water (drinking water, surface and groundwater, soils)
- EU water legislation is implemented in all countries, and the water bodies are monitored, in line with EU-WFD
- Few countries (Slovakia, Serbia) have specific legislation for sediments.
- Some countries (e.g. Romania, Slovenia) have some previsions related to sediments in the laws regarding water.
- In all countries there is additional legislation regarding environment protection (limiting, reducing or forbidding toxic emission and discharge).

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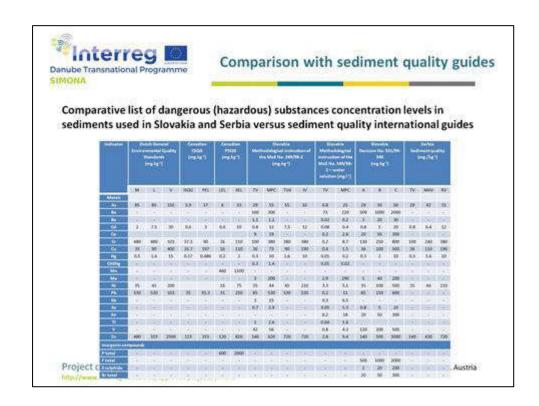


## I. 2 List of hazardous substances in waters, soils sediments and biota

Tables were made for all countries regarding:

- Maximum, respectively normal content of major elements and trace elements in river water
- Maximum, respectively normal content of major elements and trace elements in drinking water
- Definitions of maximum and minimum/normal content of elements in soils. Difficult issue, as some legislations foresee one set of values, while others foresee more classes of values, for different soil types (sandy, silty, clay soil etc.)
- Maximum, respectively normal content of major elements and trace elements in soils
- Maximum, respectively normal content of trace elements in river sediments
- Normal content of major elements in river sediments (only Slovakia)

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## Comparison with sediment quality guides

### **Explanations:**

- TV target value negligible risk, undisturbed natural environment, uncontaminated sediment and 100% survival of aquatic organisms, represents 1/100 MPCl:
- MPC maximum permissible concentration represents the maximum permissible risk, the level ensuring the survival of 95% of all species of organisms in the given ecosystem;
- TVd tested value the environmental risk is not expressed, the value lies in the interval between MPC and IV can be used for deciding on sediment management;
- IV intervention value represents a serious risk; the concentration of a substance in which only 50% of all species of the ecosystem are protected;
- A reference value,
- B indication value (if value exceeded, site monitoring is required),
- C intervention value (if value exceeded, remediation measures are required);
- · MAV-maximum allowed value;
- RV-remediation value(intervention value)

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### Comparison with sediment quality guides

# Explanations:

Canadian CSQG means Canadian Environmental Quality Guidelines

Canadian PSQG means Provincial Sediment Quality Guideline

Lowest Effect Level (LEL): indicates a level of contamination that can be tolerated by the majority of sediment dwelling organisms. Sediments meeting the LEL are considered clean to marginally polluted.

Severe Effect Level (SEL): indicates a level of contamination that is expected to be detrimental to the majority of sediment dwelling organisms. Sediments exceeding the SEL are considered heavily contaminated.

ISQG = interim sediment quality guideline.

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# I. 2 List of hazardous substances in waters, soils sediments and biota

#### CONCLUSIONS

- In the list of dangerous substances (molecular compounds) in soils, all partner countries took into
  account besides chemical elements (heavy metals, non-metals) and their molecular compounds that are
  known to be sometimes more toxic than the elements as such, but also other molecular organic
  compounds: polycyclic aromatic hydrocarbons PAHs, polychlorinated biphenyls PCBs, insecticides
  based on chlorinated hydrocarbon, herbicides or the particular values of each component. A large
  number of other parameters are laid down in legislation for both water and soils.
- A short list found in most of the lists (according to annexes 2-15) includes:
  - 16 PAHs mononuclear and polynuclear aromatic compounds (Benzen, Etil-benzen, Toluen, Xilen, Stiren, Fenol, Benz(a)piren, Naftalina, Antracen, Fenantren, Fluoranten, Benzo(a)antracen, Crisen, Benz(ghi)perilen, Indeno(1,2,3-cd)piren, Benz(k)fluoranten).
  - 7 PCBs Bifenilipoliclorurat (PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180)
  - 11 pesticides gamma-HCH (lindan); HCH (suma alfa-, beta-, delta-HCH); DDT/DDD/DDE (suma); Aldrin; Dieldrin; Endrin; Drinuri (as sum) Atrazin; Endosulfan; Heptaclor; organo-stanic coumpounds.
- For this minimal list, it is necessary to compare the maximum and normal values as set out in the national legislation, in the EU-WDF and in the Sediment Quality Guides.
- It is worth mentioning that in the aquatic environment the danger of chemical elements resulting from biochemical activity must be analyzed for establishing the list of hazardous substances.
- For drinking water or bathing water all countries have threshold limit values of microbiological indicators, such as Intestinal Enterococci [CFU/100 mi] and Escherichia coli [CFU/100 mi]. A series of aditional bacteria are foreseen in the list.

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Inventory workshop, 10-11.04.2019, Austria



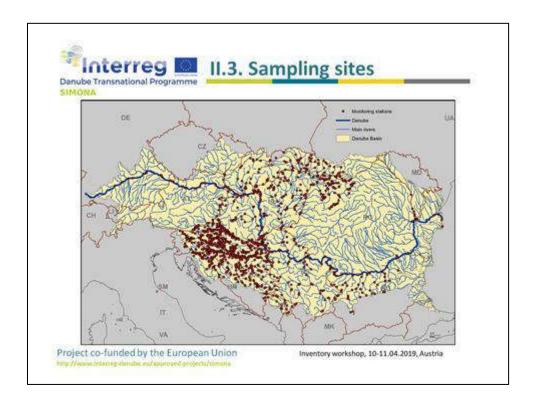
# Interreg II.3. Quality objectives for HSs

The surface or groundwater bodies' quality is established on the basis of the values of certain parameters and the classification is adopted by the majority of SIMONA countries.

Example of classifying a water body in four categories based on chemical and physical parameters - Yearly average threshold limit values for surface water and quality standards for water biota - Croatia

Indicator	very good	good	moderate	No.
Transparency [m]	> 10	< 10	<1.	a
Oxygen seturation [N]	80 - 120	surface layer: 120 – 170 bottom layer: 30 – 80	surface layer: > 170 bottom layer: 30 – 80	surface layer: > 170 bottom layer: 0 - 30
Dissolved enorganic retrogen (µmol/1)	42	< 10	< 20	>20
Onsolved phosphorous (umoVI)	< 0.3	<0.6	<13	>1.3
Chlorophyll a [µ/l]	<1	45	e 10	> 10
TRIX	2-4	4-5	5-6	6-8

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- Some countries listed the main economic polluters, indicating also the polluting activities and the associated HSs.
- · Some other countries gave a link to the pollutants.
- On the basis of these data (and of the list of big cities, legislation and literture data), which will be completed with relevant data by partner countries, the list of HSs for SIMONA project will be made.

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# II.5. Monitoring problems

 Procedures of monitoring in the past included the analysis of a smaller number of parameters and the sampling was done for more locations.

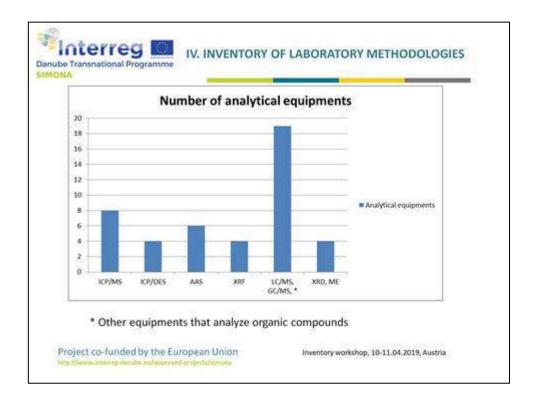
- The implementation of the WFD requests a bigger number of parameters, which leads to additional costs. Some countries face budget problems related to the analysis of so many parameters, therefore the sampling locations suffered a decline since 2011.
- We propose in SIMONA that a special attention to be paid to a realistic approach in the selection of relevant HSs, which will be analyzed in order to establish sediment quality.

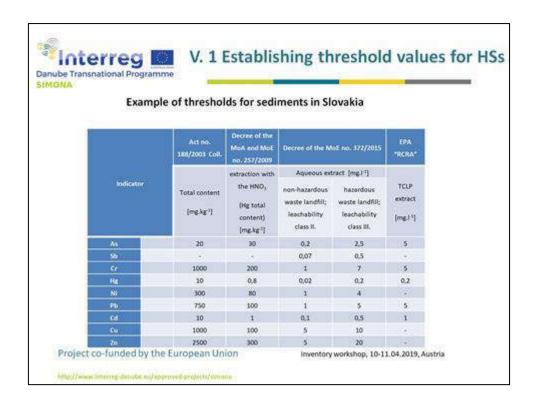
Interreg III. INVENTORY OF SAMPLING METHODOLOGIES Danube Transnational Programme

### Conclusions

- There is a lot of experience (obtained during projects work)
- Generally since 2010-2014 surface waters are monitored (annual public reports elaborated by national environmental agencies exist)
- EU-WDF is implemened and within this Directive sediments and biota are monitored in the majority of SIMONA countries.
- · The same parameters are analyzed in situ, with similar equipments
- ISO standards are used for sampling, transport, storage and preservation, which are found in the Inventory Report.

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# V. 8 Algorithm for defining the environment quality categories

In Ukraine:

Total pollution factor (Zc):

Zc=\(\sum\_ci/Cb-(n-1),

Ci - the content of the chemical element in the sample;

Cb - background content of the chemical element;

n- number of chemical elements in the sample with abnormal content (Ci/Cb>2).

Tentative scale of estimation of pollution of rivers by intensity of accumulation of chemical elements in bottom sediments.

	Zc	Level of technogenic pollution	Level of sanitary- toxicological danger	toxic elements concentration in river water	
	< 10	Weak	Allowable	Most elements within the background	
	10-30	Medium	Moderate	Most elements exceed the background, and some reach the level of MPC	
	30-100	High	Dangerous	Some elements exceed the MPC level	
Project co-fun	100-300	Very high	Very dangerous	Most items exceed the MPC level	.2019, Austria
Petp://www.hstameg-	>300	Extremely high	Extremely dangerous	Most elements consistently exceed the MPC level	

Interreg Danube Transnational Programme

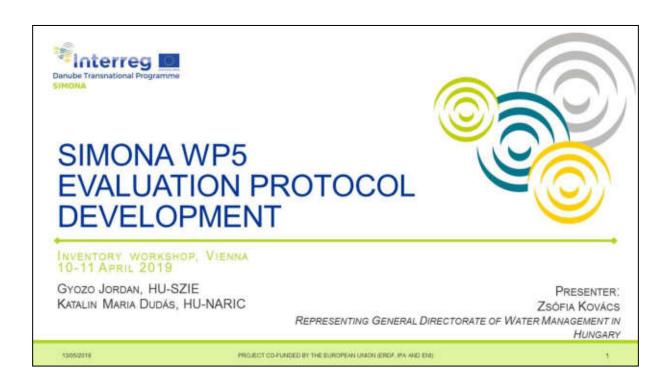
### V. INVENTORY OF EVALUATION METHODS

### CONCLUSIONS

- The quality standard values are established in legislative acts.
- Some legislations take into account the natural background concentrations of metals and their compounds, water hardness, pH, dissolved organic carbon for water, soil type (clay, sand, silt), the geological features of underground or surface waters.
- Some legislations take into account the fact that sometimes an metal is more toxic in some of its molecular compounds (especially in the aquatic environment). Therefore, besides "Total Metal Analysis", analyzes of metal compounds are also done.
- The legislations reflect to a small extent the phenomenon of selective bioaccumulation and traceability of metals (the accumulation of mercury in big fish or PAH in certain biota).
- Due to the general character of legislations, establishing a zonal bioconcentration factor associated with a certain type of biota can be done only with the help of a zonal guide. This will be the role of SIMONA project.
- Legislations generally do not specify exact methods for remedying pollution because the laws have a general character. When developing a zonal guide, dedicated to a certain ecosystem (e.g. the aquatic Danube ecosystem), these remediation methods must be reflected.
- There are differences regarding the establishment of ecological quality classes, although the classification criteria are generally the same.

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# II.3. Protocol development, CIS guidance, WFD framework





- WFD requirements, Monitoring of contaminants in sediment
- II. Hungarian chemical assessment methodology
- III.Future steps

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## LEGAL FRAMEWORK - EU LEGISLATION

### Water Framework Directive (WFD, 2000/60/EC)

The objective of the WFD is to achieve good ecological and chemical status in all bodies (2015, 2021, 2027).

## Environmental Quality Standards Directive (2008/105/EC)

- Objective: Setting forth the priority substances and corresponding environmental quality standards with the aim of achieving "good surface water chemical status" in EU member states
- Annex I: 33 priority substances and 8 other pollutants and corresponding environmental quality standards for water column Directive Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the field of water policy 2013/39/EU
  - Maximum and annual average environmental quality standards for 45 priority substances and 8 other pollutants in water column
  - Biota environmental quality standards for 11 priority substances

### The CIS Guidance Document 19 and 25

The objective of the WFD is to achieve good ecological and chemical status in all bodies of surface water, ground water and artificial water bodies and very modified water bodies by 2015, 2021 and 2027.

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# CONCEPT OF HAZARDOUS SUBSTANCES

HAZARDOUS SUBSTANCES IN WATER RESOURCES

# **EU WFD**

## **Priority Substances**

- Substances posing siginificant risk for water environment
- Determined by EU directives and elaborated on EU level

Reaching "good chemical status"

 Progressively reducing emissions, discharges and losses

### Specific Pollutants

- Substances posing risk on water resources due to significant amounts of discharge
- Determined by Member States
- Either national or river basin level
- Reaching Igood ecological status"

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# WAY TO CONTROL IN WATER - EQS

IMPLEMENTATION OF ENVIRONMENTAL QUALITY
STANDARDS (EQS) FOR MANAGEMENT OF PRIORITY
SUBSTANCES AND SPECIFIC POLLUTANTS!





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### **ENVIRONMENTAL QULITY STANDARDS - EQS**

- Not discharge standard
- Standard not to be exceeded in receiving bodies
- Derived for priority substances and specific pollutants
- · For the control of acute effects:
  - MAXIMUM ALLOWABLE STANDARDS (MAC-EQS)
- · For the control of chronic effets:
  - ANNUAL AVARAGE STANDARDS (AA-EQS)

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WFD requirements Interreg I **ENVIRONMENTAL QULITY STANDARDS - EQS** =(e)S SEDIMEN To protect benthic EQS species against pollutants BIOTA protect humans from the effects of foods contaminated with chemicals To protect predators against secondary poisoning risk PROJECT CO-FUNDED BY THE EUROPEAN UNION (EREIF, IPA AND ENI) 13/05/2018



# BACKGROUND INFORMATION, GUIDANCE DOCUMENTS

In addition to chemical and ecological status assessment, the prevention of further deterioration of the status of aquatic ecosystems is another important objective of the WFD.

Monitoring of contaminants in sediment and biota may be used to assess the longterm impacts of anthropogenic activity and thus, to assess the achievement of the above mentioned objective. It includes the determination of the extent and rate of changes in levels of environmental contamination.

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# Monitoring of contaminants in sediment

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# Monitoring of contaminants in sediment

### TO ASSESS THE LONG-TERM IMPACTS OF ANTHROPOGENIC ACTIVITY

Hydrophobic and lipophilic substances that tend to accumulate in sediment may be monitored in sediment for resource effective trend monitoring in order to:

- assess compliance with the no deterioration objective (concentrations of substances are below detection limits, declining or stable and there is no obvious risk of increase) of the WFD,
- assess long-term changes in natural conditions and those resulting from widespread anthropogenic activity,
- monitor the progressive reduction in the concentrations of priority substances (PS) and the phasing out of priority hazardous substances (PHS).

Source: CIS guidance No. 19. - 4.2.1.

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# Monitoring of contaminants in sediment

### OTHER REASONS TO MEASURE CONTAMINANTS IN SEDIMENT

Use of sediment in monitoring priority (hazardous) substances is important in other issues of WFD implementations, viz.:

- ·identify the fate and behaviour of pollutants,
- describe the general contaminant status and supply reference values for regional and local monitoring programmes,
- accumulating matrices (sediment or biota) give an integrated and less variable measure of the contaminant burden over a longer time period, and consequently, an improved statistical power for time series analysis

Source: CIS guidance No. 19 - 4.2.1.

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# Monitoring of contaminants in sediment

### LOCATIONS FOR SEDIMENT TREND MONITORING

### Sediment samples should be

- · collected from areas characterised by relatively low natural variability;
- A representative of a water body or a cluster of water bodies.
- · performed in non-erosion areas.

Representativeness is a key point, i.e. how well a sample reflects a given area or how much area the sample represents given a certain level of statistical significance.

 For example, it is essential to collect specimens for analysis well away from the mixing zones when the sampling point is downstream of a significant discharge.

Source: CIS guidance No. 19. - 4.2.1.

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# Monitoring of contaminants in sediment

### MONITORING FREQUENCIES

Typical sampling frequency will vary from

- once every 1 to 3 years for large rivers or estuaries that are characterized by high sedimentation rates, to
- once every 6 years for lakes or coastal areas with very low sedimentation rates.

### Sediment sampling appropriate frequency

•have to be defined on a local basis = taking into account the sedimentation rate and hydrological conditions (e.g., flood events).

Source: CIS guidance No. 19 - 4.4.

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# Monitoring of contaminants in sediment

### THE SELECTION OF THE SAMPLING FRACTION

- < 2 mm fraction of the sediment should be analyzed for organic contaminants</p>
- < 63 µm fraction should be analyzed for metals.</p>
- If the specific purpose of the monitoring requires analysis of the fine sediment fraction, the sample should be split using appropriate sieving techniques.



The degree of accumulation of a contaminant depends on the **sediment and suspended** particulate matter (SPM) characteristics (grain size, composition and surface properties).

- It is essential to compare analytical results from sediments and SPM with similar properties or to compare normalized results to assess the degree of contamination.
- Therefore, particle size analyses, measurements of organic carbon content or measurement of other common normalization parameters, such as Li and Al are advised. Detailed guidance for sediments on the use of normalizing parameters is given in Annex 5 of the Joint Assessment Monitoring Programme (JAMP) Guideline for Monitoring Contaminants in Sediments.

Source: CIS guidance No. 19 - 6.3

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# Monitoring of contaminants in sediment

### SELECTION OF COMPOUNDS TO BE MONITORED IN SEDIMENT

The more hydrophobic (water repulsing) a compound is, the less soluble it is in water, and therefore more likely to adsorb to sediment particles.

A simple measure of the hydrophobicity of an organic compound is the octanol—water partition coefficient
(K<sub>in</sub>), which is a good predictor of the partitioning potential of the contaminant in the organic fraction of the
sediment (K<sub>in</sub>).

As a rule of thumb,

- compounds with a log K<sub>e</sub>>5 should preferably be measured in sediments, or in suspended particulate matter (SPM), while
- · compounds with a log K < 3 should preferably be measured in water.

For compounds with a log K\_ between 3 and 5, the sediment matrix or suspended particulate matter is optional and will depend on the degree of contamination.

 If the degree of contamination for a hydrophobic compound is unknown or expected to be low, sediment should be an additional monitoring matrix (due to accumulation).
 Source: CIS guidance No. 25 – 3.3

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# Monitoring of contaminants in sediment

### PREDEFINE THE QUANTITATIVE OBJECTIVES

•The quantitative objectives of the trend monitoring are determined before any monitoring programme is started.

(For instance, the quantified objective could be to detect an annual change of 5 % within a time period of 10 years with a power of 90 % at a significance level of 5 % with a one-sided test.)

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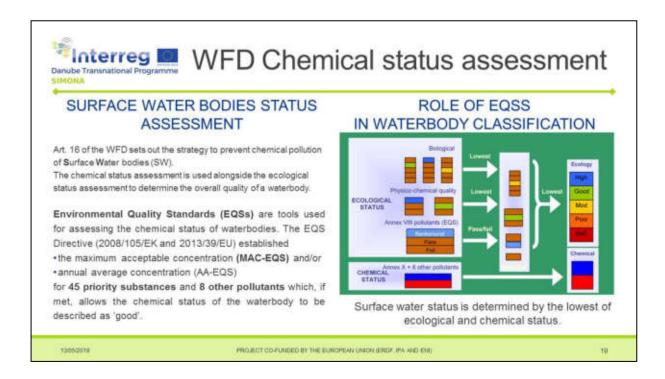
# II. WFD EVALUATION METHODOLOGY — HUNGARIAN BEST PRACTICE

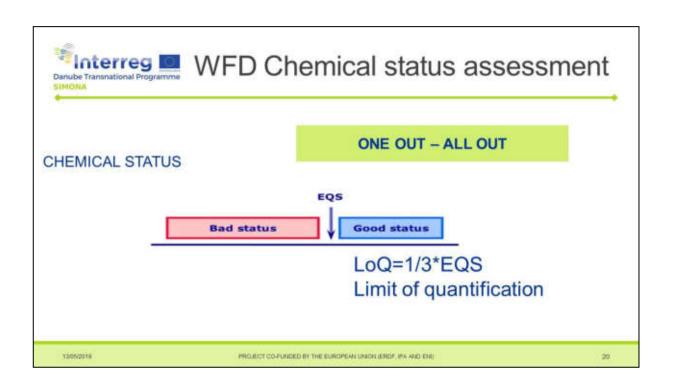


MONITORING PROGRAMS & CHEMICAL STATUS ASSESSMENT

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# WFD Chemical status assessment

### CRITERIA OF GOOD STATUS

# Annual avarage concentration < AA-EQS?

•Maximum concentration < MAC-EQS?</p>

### If not:

- •Is it possible to use EQS-corrections?
  - · bioavailabiltiy concentration of metals
  - natural background concentration of metals
  - local EQSs in mixing zones

### CRITERIA OF HIGH CONFIDENT

### Do we analyse

- all of PSs identified as being discharged into the body of water; and
- all relevant PSs min. 12 times (1/month) during 1 year; and
- all of other substances identified as being discharged in significant quantities into the body of water; and
- all relevant other substances min. 4 times (each 3 months) during 1year?
- And all LOQs ≤ 0.3 · EQSs?

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# EQSS FOR DIFFERENT MATRICES EQSS FOR DIFFERENT SPATIAL SCALES

- Water samples
  - whole
- dissolved (0.45 µm glass-fibre filters)
- bioavailable
- Sediment
  - · bottom
  - · suspended particular matter (SPM)

### Biota

· fish, mussels or seabird eggs

EU level - EQS<sub>generic</sub>

protect min. 90% of EU waterbodies

National/regional level - EQS<sub>regional</sub>

protect min. 90% of the WBs in the region

Local level - EQS<sub>local</sub>

protect one waterbody or one group of waterbodies

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# WFD Monitoring Programs

# 1) GENERAL - SURVEILLANCE MONITORING PROGRAM

According to WFD Annex V1.3.1 the objectives of surveillance monitoring of surface waters are to provide information for:

- supplementing and validating the impact assessment procedure (WFD Annex II);
- the efficient and effective design of future monitoring programmes;
- the assessment of long-term changes
  - · in natural conditions; and
  - resulting from widespread anthropogenic activity.

# 2) OPERATIVE MONITORING PROGRAM

Operational monitoring shall be undertaken (Annex V.1.3.2) in order to:

- establish the status of those bodies identified as being at risk of failing to meet their environmental objectives, and
- assess any changes in the status of such bodies resulting from the programmes of measures.

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# WFD Monitoring Programs

# 3) INVESTIGATE MONITORING PROGRAM

Investigative monitoring may be required in specified cases (Annex V.1.3.3). These are given as:

- where the reason for any exceedance (of environmental objectives) is unknown,
- where surveillance monitoring indicates that the objectives for a body of water are not likely to be achieved and operational monitoring has not already been established.
- in order to ascertain the causes of a water body or water bodies failing to achieve the environmental objectives.
- •to ascertain the magnitude and impacts of accidental pollution.

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# Sampling frequency for water

### GENERALLY FOR WATER

According to WFD, Annex V 1.3.4:

- once-a-month for priority substances and
- once-per-three-months for other pollutants will result in a certain confidence and precision.

Take samples in equidistant time intervals over a year, e.g., every four weeks resulting in 13 samples.

### MORE FREQUENT SAMPLING

More frequent sampling may be necessary

- ·to detect long-term changes,
- ·to estimate pollution loads and
- to achieve acceptable levels of confidence and precision in assessing the status of water bodies

Remember: Sediment sampling frequency will vary from once every 1 to 3 years for large rivers to once every 6 years for lakes.

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# Sampling frequency

### SEASONALLY VARIABLE SUBSTANCES

TO ACHIEVE ACCEPTABLE LEVELS OF CONFIDENCE AND PRECISION IN ASSESSING E.G. SEASONAL PRESSURE FROM TOURISM, SEASONAL INDUSTRIAL ACTIVITIES, PESTICIDES

Seasonally variable substances can show peak concentrations within short time periods

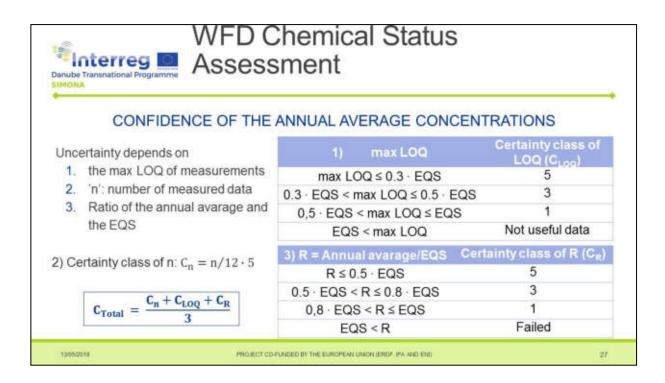
- -> enhanced sampling frequency may be necessary in these periods.
- -> The results should be compared with the MAC-EQS (based on acute toxicity).

For example the best sampling time for detecting concentration peaks of pesticides

- due to inappropriate application is after heavy rainfall within or just after the application period.
- failure to comply with good agricultural practice, e.g., inappropriate cleaning of equipment during or at the end of the season before winter.
- Collecting composite samples (24h to one week) might be another option to detect peak concentrations of seasonally variable compounds.

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- . How many monitoring sites were identify all partners?
- What kind of samples should be taken (water/sed/biota)?
- What do you think do you have enought measurements to well-descibe the chemical status of the water bodies?
- What sampling frequency is your country's practice (b and d column), and what do you think what is the ideal sampling frequency (c and e column) based on your experties, for the following sampling matrices?
- Using the Biotic Ligandum Model (BLMs)
  - -other corrections
  - -define local EQSs?
- Useing total toxicity tests?
- Apply the grouping techniques?
- Classification means: Make a decision, that the water body is good or bad (the avarage concentration is bigger or lower then the AA-EQS)?
- Does your national legislative find categories of environment quality based on deviations from threshold values?

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# THANK YOU FOR ATTENTION!

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# II.4. Sampling of stream bed sediments

This presentation is annexed (Annex 1) to this output at the following link and it is also in SIMONA web site Library:

https://www.dropbox.com/s/p44km0fv257ht3j/T1.2 Annex1 Sampling%20of%20stream%20bed%2 0sediment.pdf?dl=0

# II.5. Sediment sampling in large rivers

This presentation is annexed (Annex 2) to this output at the following link and it is also in SIMONA web site Library:

https://www.dropbox.com/s/i87dio682tnnfr9/T1.2 Annex2 Sediment%20sampling%20in%20large% 20rivers.pdf?dl=0

# **II.6. ICPDR Monitoring**

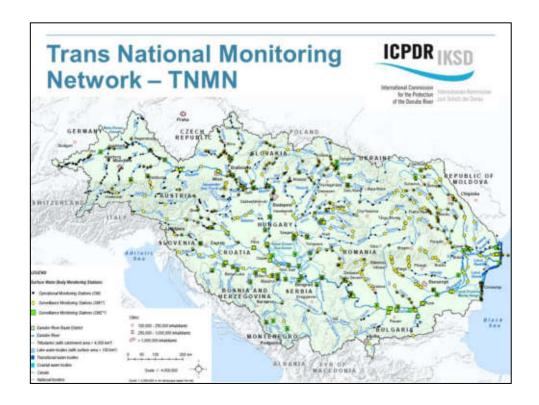


# Water quality monitoring: Major drivers

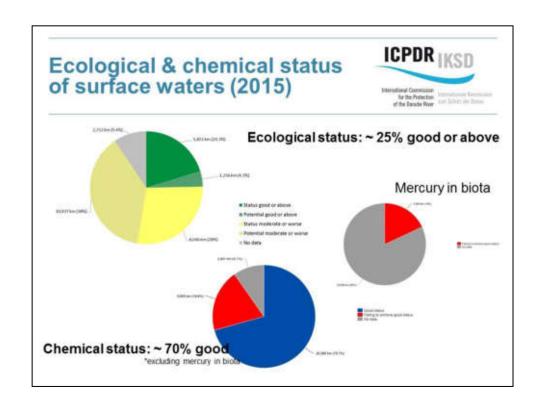


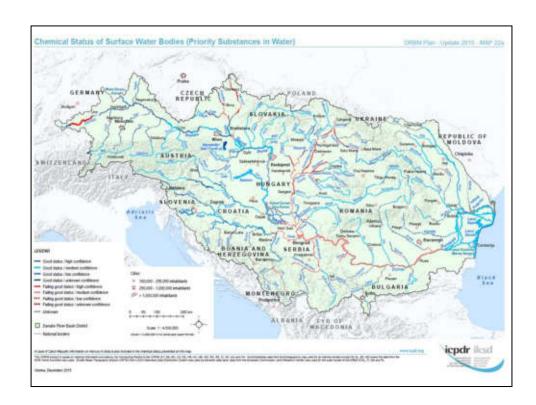
⇒ DRPC (According to the Article 9 of the DRPC the Contracting Parties to DRPC have agreed to cooperate in the field of monitoring and assessment of the water resources)

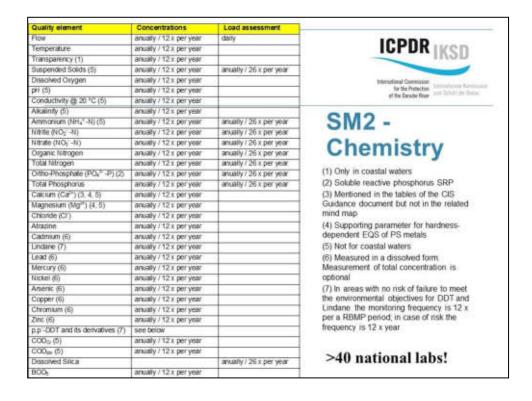
⇒ EU WFD (establishing of WFD compliant monitoring networks by 22 December 2006)



TNMN	ICPDR IKSD  International Commission for the Proportion of the Bander filter	
Monitoring activity	Data collection	Final product
Surveillance Monitoring 1	Aggregated data	Status assessment in DRBMP
Operational monitoring	Aggregated data	Status assessment in DRBMP
Surveillance Monitoring 2	Raw data	TNMN Yearbooks & reporting to BSC
Investigative monitoring	Raw data	Joint Danube Survey reports







# WFD Investigative monitoring: Joint Danube Surveys



⇒Producing comparable & reliable information on selected water quality elements for the whole Danube River including the major tributaries on a short-term basis;

- Providing an opportunity for harmonization & training in WFD related monitoring;
- Addressing information gaps from standard monitoring activities





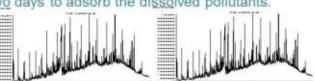
# Large number of emerging polar organic substances detected at very small concentrations; Concentrations in 2013 mostly lower compared to JDS2 in 2007; Pharmaceuticals mostly < 40 ng/l; Elevated concentrations: metamizol metabolites FAA and AAA, artificial sweeteners acesulfame, cyclamate and

metabolites FAA and AAA, artificial sweeteners acesulfame, cyclamate and sucralose, metformin, enalapril, triphenylphosphinoxide, 2-benzothiazolesulfonic acid, benzotriazoles, iodinated X-ray contrast media and the stimulant caffeine.

# Organics - new technics



- Effect-based screening used large-volume extraction (1000 I water) and analysis of 264 substances using LC-HRMS followed by a set of in vitro and in vivo bioassays;
- Non-target screening was based on UHPLC-QTOF-MS and LC-HR-MS to search for as many compounds as possible; > 3370 different organic compounds found;
- An alternative passive sampling approach to detect the trace concentrations of organics was tested - samplers were exposed to water for up to two days to adsorb the dissolved pollutants.

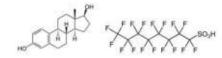


# **RBSP** prioritization

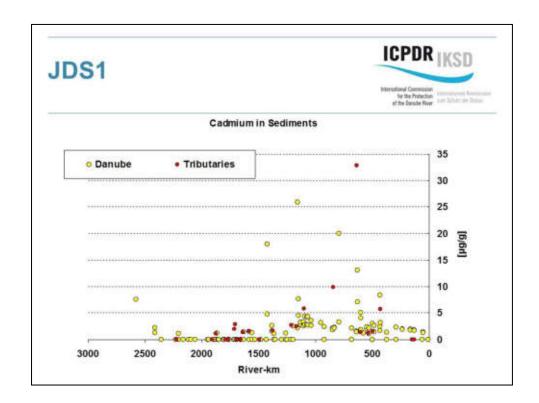


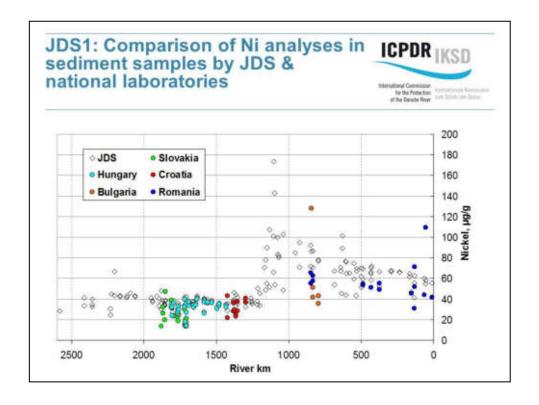
 Prioritization methodology developed by NORMAN network produced a list of 22 substances suggested as relevant for the DRB based on the results of the JDS3 target screening of 654 substances in the Danube water samples by 13 laboratories;

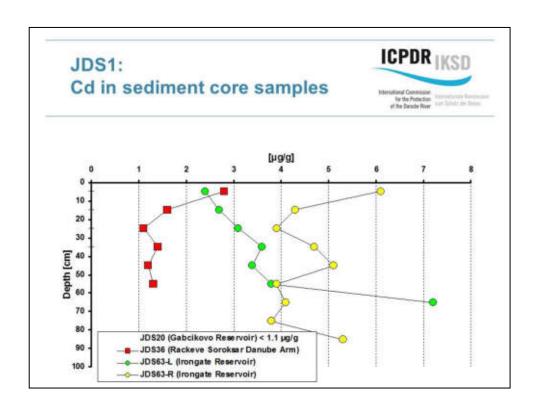
- PNEC values were available for 189 out of 277 JDS3 substances actually determined in the samples;
- The list contains five WFD priority substances (three PAHs, fluoranthene and PFOS) and two EU Watch List candidate compounds (17beta-estradiol, diclofenac).

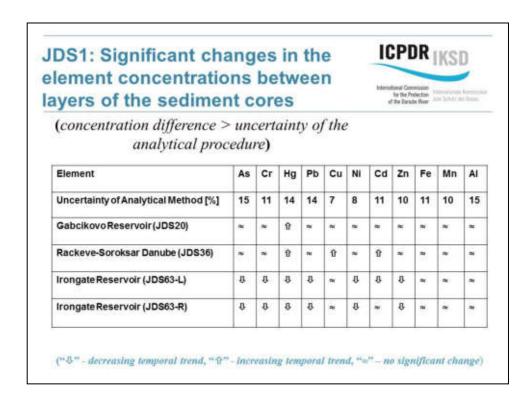


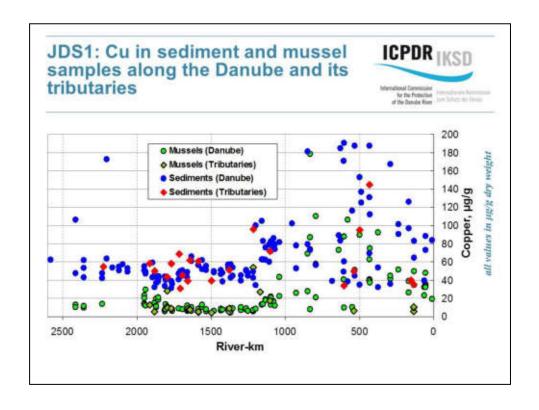


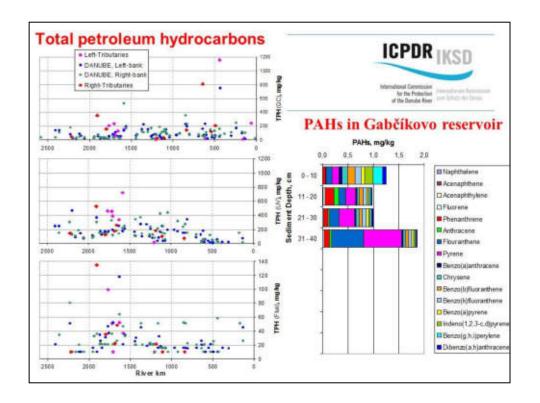


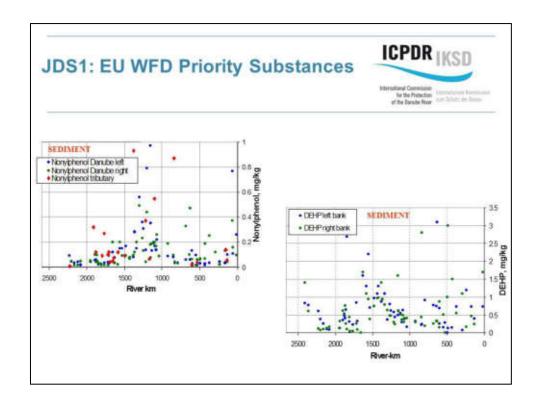










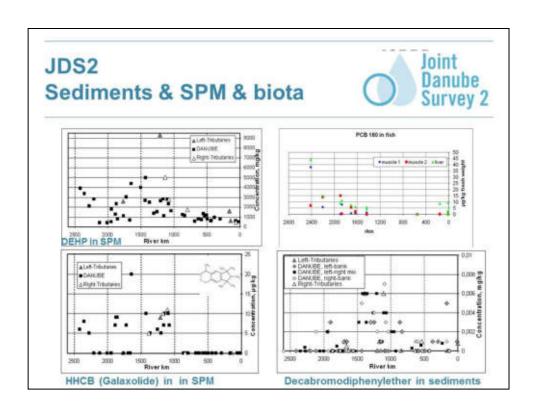


# JDS2 Sediments & SPM



The results for organochlorine compounds do not indicate that these substances are relevant pollutants in the Danube, which is an improvement of the past situation as described in the Danube Roof Report 2004.

- PAH values in sediments were about one order of magnitude lower than those typically found in the Elbe.
- Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like PCBs were more than one order of magnitude lower when compared to the Elbe and only one site slightly exceeded the "safe sediment value" for PCDD/Fs. EC-6 PCBs did not exceed the German quality standards in sediment.
- The results of the ecotoxicological analysis of the Danube sediments showed no significant toxic effects.

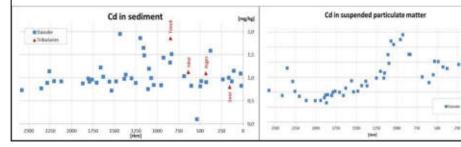


# JDS3: Metals



 Contents of metals in water, SPM and bottom sediments were similar to those observed during JDS1 and JDS2;

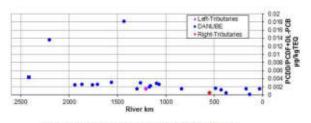
- In sediment the DE targets for metals were with one exception (Cu at JDS48) met at all sites for all elements;
- Concentrations of Hg in all analyzed fish samples exceeded the EQS significantly.



# JDS3: Organics in sediment



- Concentrations for PAH in SPM and sediments were comparable to JDS2 results;
- For PCDD/F and PCBs none of the existing EQS values for aquatic biota and SPM/sediments, and none of the EU food limits concerned were exceeded.

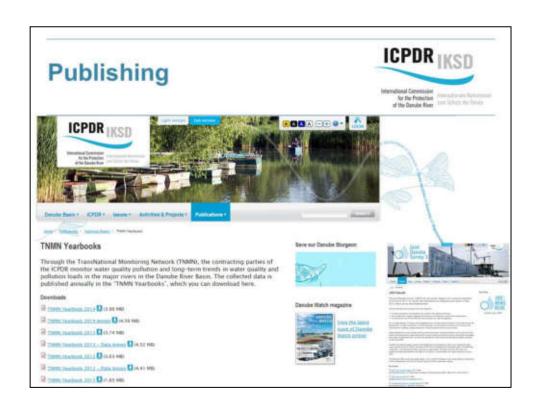


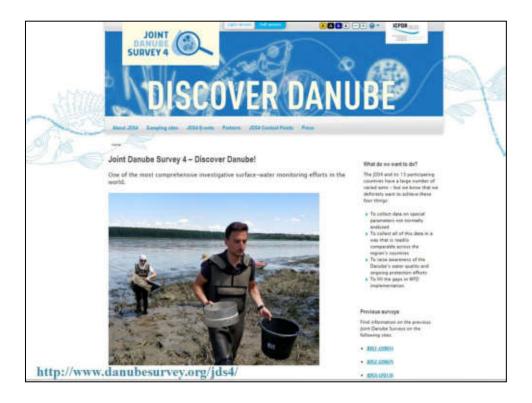
Dioxins and dioxin-like compounds in sediment

# **JDS4** sediments



- Sediment data from JDS1-JDS3 are available;
- Directive 2013/39/EU again is not setting EQS for sediments;
- Sediment analysis for trend monitoring requires more than one sampling per year and should take place every three years, thus results from JDS1 – JDS4 would not be a reliable base for trend monitoring. On the other hand there are national data available e.g. for metals and PAH;
- JDS4: No target analysis of sediments;
- Wide-scope target and suspect (DSFP) screening of sediment by LC-HR-MS and GC-HR-EI-MS (UFZ) and LC-HR-MS and GC-HR-APCI-MS (UoA/EI).





# **II.7. SIMONA Sampling Work Group**

This presentation is annexed (Annex 3) to this output at the following link and it is also in SIMONA web site Library:

https://www.dropbox.com/s/e9isuvzyzy7y38j/T1.2 Annex3 SIMONA WG Sampling WP4.pdf?dl=0

# **II.8. SIMONA Sediment Sampling Protocols**

This presentation is annexed (Annex 4) to this output at the following link and it is also in SIMONA web site Library:

https://www.dropbox.com/s/cud6ekn1lhcy2o5/T1.2 Annex4 SIMONA%20Sediment%20sampling%2 Oprotocols.pdf?dl=0

# II.9. SIMONA Laboratory WG - Harmonization of analytical methods

This presentation is annexed (Annex 5) to this output at the following link and it is also in SIMONA web site Library:

https://www.dropbox.com/s/lrwzy7wo1sw9mh4/T1.2 Annex5 Harmonisation%20of%20analytical% 20methods.pdf?dl=0

### III. WORKSHOP MINUTES

The Inventory workshop was an open event to all stakeholders and beneficiaries of the SIMONA project. In the first part, the partners were invited to give presentations on (best) methods. While the second part was devoted to review the current status of activity WP 4.1 Reviewing current sampling and laboratory methods of HSs in water, sediment and biota matrixes. This presentation was followed by two presentations of the working groups Sampling and Laboratory.

At the open discussion the challenge of harmonizing with existing project DanubeSediment emerged. The DanubeSediment will set up monitoring network with several extra monitoring points with the purpose to evaluate sediment balance. This network will serve as a baseline for SIMONA project, whose aim is mainly the evaluation of the quality of sediments. Regarding the harmonized procedures within the SIMONA project, the guidelines or rules given from the European Commission are not satisfactory. SIMONA project will provide joint monitoring exercises, respecting in the same time the national legislations.

Through the discussions, the partnership decided to start the harmonization at the starting point – inventorying and reviewing the existing ISO standards and guidelines. Some partners are not familiar with the international standards, so the mutual decision was made that partners will review and study the existing literature (there is budgetary line for this).

Based on the project results the main points and recommendations in relation to sediment monitoring were pointed out:

- The sampling and laboratory analysis protocols for sediment monitoring should be developed
  on the legal basis of the WFD and the knowledge base of the projects: FOREGS, GEMAS and
  DanubeSediment taking in account the current status in the WFD countries according to the
  questionnaires.
- Most of DTB countries face serious challenges of the implementation of the HSs concentrations
  monitoring in the surface water sediments required by the WFD, therefore the harmonized
  international sediment quality monitoring protocols and procedures it is essential to be
  developed. The chemical analysis of HSs in sediment should be performed in accredited
  laboratory.
- The challenge of harmonization SIMONA with DanubeSediment project, which is in a more advance state, emerged.

Additional recommendations from the Inventory workshop will be given in a SIMONA project report as well as in sampling and laboratory protocols.

Working groups (WG) were established at the Kick-off meeting in September 2018 in Ljubljana. Due to some changes in the project teams within partnership, the WGs were also finalized during Vienna meeting. The challenge of the working groups is to clearly define appropriate procedures for monitoring stream sediments. For the field work, common field sheets should be designed.

# 3. COUNTRIES FEEDBACK

### **AUSTRIA**

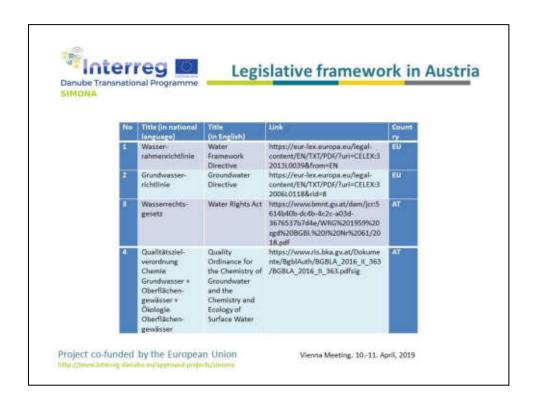


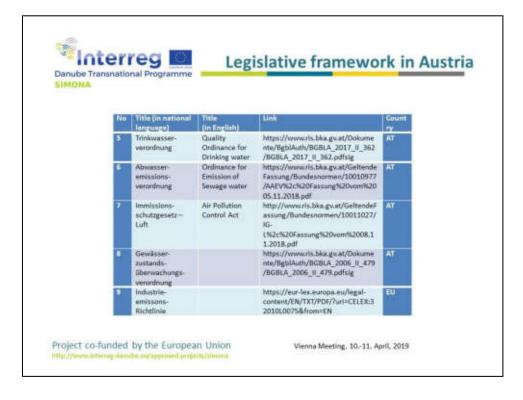


- Geological Survey of Austria
- · AIT Austrian Institute of Technology
- Federal Environment Agency (consulted on 28<sup>th</sup> Jan. 2019)

Project co-funded by the European Union

Vienna Meeting, 10.-11. April, 2019





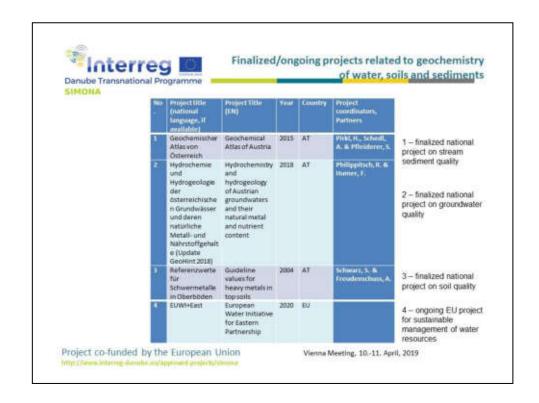


# Sampling by institutions

- Geological Survey of Austria
  - Stream bed and floodplain sediments (project-related)
- · AIT Austrian Institute of Technology
  - Thermal/mineral water (customer or research projects)
- Federal Environment Agency
  - National chemical monitoring of water (groundwater, surface water bodies); special monitoring in special projects, e.g. for pesticides
  - Sediment sampling (bottom, suspended) only in framework of projects

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### Water:

- Water sampling, transport and conservation are standardized by the Austrian norm ÖNORM EN ISO 5667.
- Sampling by the Federal Environment Agency Austria (UBA) follows a fixed design of location and number of sampling sites. Sampling frequency of groundwater at risk is 3 -4 times per year. Surface water sampling frequency is 1 time per month, additional sampling is carried out sporadically depending on governmental contract or running projects.

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### Sediments:

- Sampling of stream sediments is standardized by the Austrian norm ÖNORM G 1031.
- Geological Survey of Austria: bottom and floodplain.
- Environment Agency Austria: bottom, floodplain and suspended
- One sampling site per 10 km², at least on site per catchment (up to highest order) no mayor rivers except downstream of emitters (settlements, industrial sites, treatment plants etc.), only sites with active sediment (for river beds), double sampling for quality control every 50th sample

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# Biota:

- Biota are not sampled by the Geological Survey of Austria. The Environment Agency Austria collects biota samples according to the National chemical monitoring of water-monitoring network.
- Detailed information on sampling/measuring/analysing is not available.

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# **BOSNIA and HERZEGOVINA (Republic of Srpska)**







1.2 List of dangerous (hazardous) substances

I.2 List of dangerous (hazardous) substances (metals, non-metals, PAHs, PCBs) concentration levels, their significance in waters, solids or blots, in accordance with the national legislative framework

 $Standard\ quality\ concentrations\ for\ surface\ water\ in\ Republika\ Srpska\ (from\ Directive\ 2008/105/EC)$ 

Name of substance	Annual average for inland surface waters EQS (µg/L)	Name of substance	Annual average for inland surface waters EQS (µg/L)
Alachilor	0.3	Hexachiorbenzene	10.0
Anthracene	0.1	Hexachlorbutadiene	0.1
Atraine	0.6	Hesachiorocyclohexane	0.02
Benzene	10.	gamma isomer, Lindane	
Cadmium and its compounds	± 0.08 (category 1)	troproturon	0.3
	0.08 (category 2)	Load	7.2
	0.09 (rategory 5)	Mercury	0.05
	0.15 (category 4)	Naphtalene	2.4
	0.25 (category 5)	Nickel	20
Chlorfensinghos	0.1	Noniphenois	0.3
Chlorpyritos	0.03	Octylphenol	0.1
Aldrin	V 0-25 0-44	Pentachkorobergene	0.07
Dieldrin	2=0.005	Pentachlorophenol	Ω4
Endrin		PAIts	1 0535
DDT total	0.025	Benzočajpyrene	0.05
Para para-DDT	0.01	Benzo(b)fluoranthene	20.08
1,2-dichloroethane	10	Benzo(g, h, ilperylene	20.002
Dichloromethane	20	BenzoBöffuoranthene	20.08
Di(2- ethylhexyl) phthaiate	13	Indexo(1,2,3-CD)pyrene	50.002
Diuron	0.2	Simurine	1
Endosullan	0.005	Trichloromethane	2.5
fluoranthene	0.1	Trifforalin	0.03

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#### III.INVENTORY OF SAMPLING METHODOLOGIES

#### III.1. Water

#### III.1.2. Parameters of water quality/quantity measured in situ

Temperature, dissolved oxygen, pH and electroconductivity.

III.1.3. Instruments used for in situ measurements

#### III.1.4. Methodology for in situ measurements

Temperature- Standard Methods 2550 APHA-AWWA-WEF, 2005 Dissolved oxygen- EN ISO 25814:2014 pH- BAS ISO 10523:2013

Electroconductivity- EN 27888:2002.

- III.1.5. Tools used for collecting samples for laboratory measurements
- III.1.6. Sample preservation
- III.1.7. Methodology for collecting samples and further procedures ISO 5667

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#### III.INVENTORY OF SAMPLING METHODOLOGIES

# IV.3 Inventory of national laboratories

Analytical control of all parameters according to ISO 17 025. Laboratory checked according to EN ISO/IEC 17043.

V.1. Setting threshold values for HSs in each type of media (sediment, water, biota)

Threshold values for HSs are set only for water samples in Regulation on water classification and categorization of water courses (Official Gazette of Republika Srpska 41/01) which is available at <a href="http://www.vaders.org/propisi-i-obrasci/pravna-regulativa/">http://www.vaders.org/propisi-i-obrasci/pravna-regulativa/</a>.

V.2. Threshold values for HSs are fixed.

All the answers are supported with references (national legislative documents and/or web links)

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#### II PRACTICES, EXPERIENCES

#### Instead conclusions

#### II.5. Problems of current monitoring procedures

- The lack of financial resources, inadequate laboratory capacities and lack of appropriate laboratory equipment and devices.
- Republika Srpska does not have regulations or criteria for including/excluding parameters from monitoring programme for priority substances, which would allow more efficient way to use budget resources.
- There are no systematic investigations of priority substances concentrations in samples of biota and sediment.

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#### **BULGARIA**





# **HSs Monitoring in Bulgaria** Responsible Institutions

1. Responsible National Institutions for the monitoring of HSs in river sediments in Bulgaria

#### 1.1 Ministry of Environment and Waters through Directorate of Water Management

# Functions: responsible for the policy on water management on national level

MoEW develops and implements the state policy on environmental protection: establishes and develops a legal and strategic framework, EU objectives and national environmental priorities; implements the environmental sectoral policies; monitors the current state of ecosystems; provides access to up-to-date information on the state of the environment and the ongoing environmental policy

# 1.2 Danube Region Basin Directorate

#### Functions: performs management, regulatory, information and control functions

The management functions of the Directorate consist mainly of the elaboration of a River Basin Management Plan and a Plan for the management of flood risks

#### 1.3 Executive Environment Agency

#### Functions: management, coordination and information functions

designs and manages the National System for Environmental Monitoring and information on the state of environmental components and factors on the complete territory of the country; National Reference Centre within the European Environment Agency (EEA)



# **HSs Monitoring in Bulgaria** Responsible Institutions

### Ministry of Regional Development and Public Works

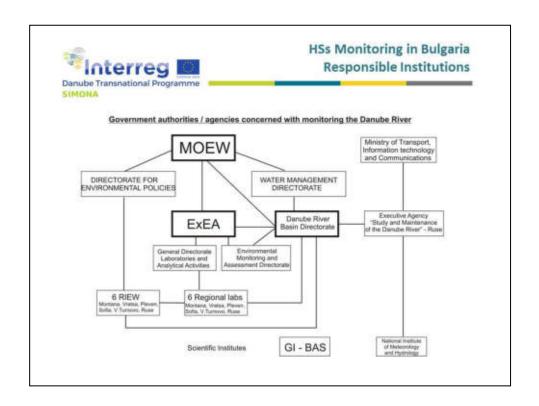
MRDPW through the Territorial Cooperation Management Directorate is the National Authority and National Contact Point for the INTERREG DTP.

# National Institute of Meteorology and Hydrology

NIMH at Bulgarian Academy of Sciences - participates in Action 2.1 with two projects: Danube River Basin Enhanced Flood Forecasting Cooperation (DAREFFORT) and Danube Sediment Management -Restoration of the Sediment Balance in the Danube River (DANUBE SEDIMENT).

# National Institute of Geophysics, Geodesy and Geography

NIGGG - partner of GI-BAS in the RoBuHaz project ("Romanian-Bulgarian cross-border joint natural and technological hazards assessment in the Danube floodplain. The Calafat-Vidin - Turnu Mägurele-Nikopole sector") finalized in 2013.







# HSs Monitoring in Bulgaria Current Status

- Type of sediments sampled for measuring HSs in surface waters sediments
- -> bottom sediments only
- 4. Sediment Sampling Strategy
- → River Basin Management Plans (2016-2021)
- → Monitoring locations 35 sites for the Danube River Basin in Bulgaria
- -> Frequency of sediment sampling 1 per 3 years









# HSs Monitoring in Bulgaria HSs measured in sediments

#### 5. Analyzed hazardous substances in sediments from surface waters in Bulgaria

→ No.2, 5, 6, 7, 12, 15, 16, 17, 18, 20, 21, 26, 28 x 30 from the priority substances list of the WFD

- EU2 Anthracene
- EU5 Brominated diphenylethers
- EU6 Cadmium and its compounds
- EU7 C10-13 Chloroalkanes
- EU12 Di(2-ethylhexyl)- Phthalate (DEHP)
- EU15 Fluoranthene
- EU16 Hexachloro-benzene
- EU17 Hexachloro-butadiene
- EU18 Hexachloro-cyclohexane
- EU20 Lead and its compounds
   EU21 Mercury and its compounds
- EU26 Pentachlorobenzene
- . EU28 Polyaromatic hydrocarbons (PAH)
- EU30 Tributyltin compounds (Tributyltin cation)
- → No 34, 35, 36, 37, 43 and 44 added from 2019
- + TOC content; 0,063 mm grain fraction content
- Quality Standards for hazardous and/or priority substances in sediments from surface waters – not regulated in Bulgaria



# HSs Monitoring in River Sediments Current Status in Bulgaria

- National and international guides of techniques on the design of sampling, transport, storage, and sample preparation
- БДС ISO 5667-12:2017 Water quality. Sampling bottom sediments from rivers, lakes, and estuary zones
- БДС EN ISO 15009:2016—Soil quality. Gas-chromatographic determination of volatile aromatic HCs, naphtalene and volatile halogenated HCs
- > БДС EN 16171:2016—Sediments, processed bio-wastes, and soils. ICP-MS elements determinations
- ISO 18287:2006 Soil quality. Determination of polycyclic aromatic hydrocarbons (PAH).
   Gas chromatographic method with mass spectrometric detection (GC-MS);
- ISO 11277:2009 Soil quality. Determination of particle size distribution in mineral soil material. Method by sieving and sedimentation;
- BAC ISO 14235:2002—Soil quality. Organic carbon determination by sulphochromic oxidation;
- ILM 4006/2010 Organochlorine pesticides and polychlorinated biphenyls determination in soils, sediments, and sludge;



#### Positive Practices and Problems

- Positive practices and problems in the HSs monitoring in surface waters sediments in Bulgaria
- Lack of participation by national responsible or academic institutions in previous European projects with similar objectives
- Minor experience in surface waters sediment sampling and monitoring
- Minor contact of national authorities to geological institutions traditionally surface water problems are studied by other institutions unfortanately with minor experience in sediments, missing Geological Survey in flutgaria
- National institutions willing to collaborate and interested in the Simona Project and its results:
- > Generally well-developed and continuously updating national monitoring regulation;
- Following WFD and relevant documents recommendations and guidelines;
- Using standardized documents for sampling, transport, storage, and laboratory analysis;
- Assigning projects related to HSs monitoring to specialized subcontractors aiming improved and effective environmental monitoring providing reliable results;
- National experts with long term experince in einvironmental monitoring willing to participate the trainings and workshops of the SIMONA project, etc.

## **CROATIA**







- follow EU legislation -> EU WFD (translated documents)
- · still no law on sediment quality analysis

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# Inventory - Croatia

- EU legislation
  - WFD and other directives
  - sediment monitoring not yet implemented, but it is planned to be soon
  - water and biota monitoring are ongoing according to the guidelines of the WFD
- HS -> as prescribed by WFD (incl. thresholds)
- methodology follows ISO norms
- geology

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- EU legislation
  - WFD
  - water and biota monitoring is ongoing (but not sediment)
- HS -> as prescribed by WFD (incl. thresholds)
- · methodology follows ISO and EPA norms
- problems -> lack of financial resources, inadequate laboratory capacities and lack of appropriate laboratory equipment and devices

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# **HUNGARY**





# SIMONA - HU

INVENTORY WORKSHOP, VIENNA 10-11 APRIL 2019

GYOZO JORDAN, HU-SZIE KATALIN MARIA DUDÁS, HU-NARIC

PRESENTER: Zsófia Kovács

REPRESENTING GENERAL DIRECTORATE OF WATER MANAGEMENT IN HUNGARY

13/05/2018

PROJECT CO-PUNDED BY THE EUROPEAN UNION (EREF, IPA AND EN)

4



# HU - QUESTIONNAIRE FOR EXISTING SAMPLING, LABORATORY AND EVALUATION METHODS

OVF (General Directorate of Water Management), and Kata Dud

The main (related) EU directives, what we adapted: 2000/60/EC, 2008/105/EC and 2013/39/EU and 2009/90/EC

- Hungary Law: 10/2010. (VIII. 18.) Environmental quality standards and other thresholds for Surface waters and the usage of these limit values)
- We use EQSs for waters, 2013/39/EU, we use these limit values- EQS (We have a methodological document with 250 pages, in Hungarian. So many specific problem has to be solve, grouping of parameters, bioavailability, LOQ is higher then EQS/3, data aggregation in time and space.)
- Analytical standard: ISO 5667-12:1995, MSZ 21470-1:1998, MSZ EN 14899:2006

SEDIMENT: We have no official, accredited sediment monitoring yet.

•ISO 5667-12:1995 standard: The main flow line of the river and in sediment deposits along vertical sections at 10 cm intervals

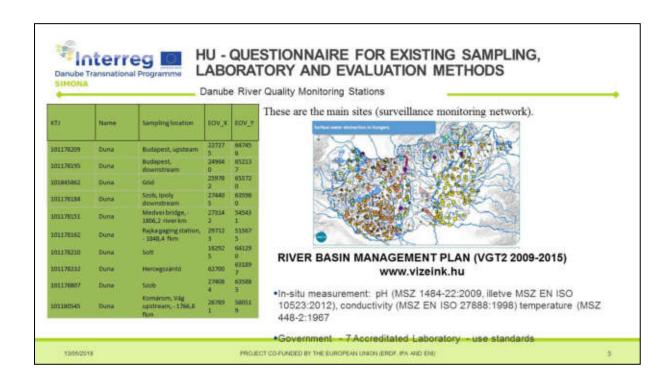
# BIOTA:

fish -We are investigating monitoring program now, to find the best sampling sites for long-term biota monitoring

13/05/2018

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2





- How many monitoring sites were identify all partners?
- Apply the grouping techniques?
- What kind of samples should be taken (water/sed/biota)?
- What do you think do you have enought measurements to well-descibe the chemical status of the water bodies?
- •What sampling frequency is your country's practice (b and d column), and what do you think what is the ideal sampling frequency (c and e column) based on your experties, for the following sampling matrices?
- Using the Biotic Ligandum Model (BLMs)
  - -other corrections
  - -define local EQSs?
- Useing total toxicity tests?
- Classification means: Make a decision, that the water body is good or bad (the avarage concentration is bigger or lower then the AA-EQS)?
- Does your national legislative find categories of environment quality based on deviations from threshold values?

13/05/2018

PROJECT CO-PUNDED BY THE EUROPEAN UNION (EREF, IPA AND ENI)

12

#### **MONTENEGRO**





# Inventory\_Country reports for GSM-ME

- I.LEGISLATIVE FRAMEWORK
- The Montenegro has legislation (laws, governmental orders, emergency ordinances) that regulates the concentrations of dangerous substances posing a risk to the health of the population or aquatic life, in soils, surface waters and drinking water.
- A regulation for the maximum allowable concentration of pollutants in sediment in Montenegro does not exist. Also does not have laws, regulation or any other official directives for mentioned sample media, except the obligation to implement EU WFD in the next years.
- II PRACTICES, EXPERIENCES
- Research of mineral resources in Montenegro\_1976\_UN&GSM
- Basic geochemical map of Montenegro\_2009\_GSM
- Strengthening Capacities for Implementation of the EU Water Framework Directive in Montenegro on going Water Directorate of Montenegro, Ministry of agriculture and Rural Development.

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# Inventory\_Country reports for GSM-ME

II.3 Existent waterbodies (rivers in Montenegro) and sampling sites/Ramsar,Natura2000 etc.) and current quality monitoring stations of the Danube River Danube River Quality Monitoring Stations (site on rivers) 22 places.

- **III.INVENTORY OF SAMPLING METHODOLOGIES**
- III.1.Water\_Institute of Hydrometerology and seismology of Montenegro
- Collection of geochemical samples and their systematization
- All samples are taken from those streams that are visible on the topographic map 1: 200 000. The samples were taken from the smallest fractions of the coating, cleansed of large pieces and organic matter. The sample is packed in plastic bags with the inscription of the sample. The data on the sample were recorded in a form containing: sample mark, line III, stream name, topographic sheet 1:25 000, petrographic composition of the sample, the edges of the surrounding rocks.
- Table for samples of stream sediments has 9 columns:
- 1. regular sample number
- 2. sample designation
- 3. name of the stream from which it was taken
- 4. x coordinates
- 5. y coordinate
- s. y coordinate
  6. angle [read from topographic map 1:25 000]
  7. macroscopic provision of currencies
  8. possible origin of the material
  9. Possible polluters

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#### Inventory\_Country reports for ME-GSM

- III.3. Biota\_Expert staff of the Agency for the Protection of Nature and Environment implements a biodiversity monitoring program from 2013, the locations of the monitoring program are different each year.
- · Important laboratory
- Institute of Hydrometerology seismology of and Montenegro, http://www.meteo.co.me/ekologija/Akreditacija.pdf
- 2. Institute for Public Health from Podgorica,
- 3. Center for Eco-Toxicology Research from Podgorica, http://eng.ceti.me/?page\_id=3610

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Inventory Workshop, 11/04/2019, Wien

# **ROMANIA**







# Inventory Workshop of the SIMONA Project

# Romanian partners progress of activities

10-11.04.2019, Vienna, Austria







# I. LEGISLATIVE FRAMEWORK

- I.1 finalized
- 1.2 soil data completed (4 quality classes depending on soil type use), for drinking water there's only
  one set of values (maximum admissible concentrations) for sediments there's also only one set of
  values (there is no specific legislation, but there are included in environment protection legislation),
  biota (there is no specific legislation, only in the fishing legislation, and it's monitored in the case of
  water quality assessment)
- I.3 finalized. Regarding river water 4 quality classes exist.
- I.4 For all parameters included in the national legislation regarding pollution (air, river waters, drinking water, soils, sediments and biota) there are ISO or EPA analytical standards. Those are listed in the final version of the national questionnaire.
- 1.5 The national legislation does not include toxicity tests, only in the case of aquatic environments, but within various projects, those tests are being performed in biology institutes laboratories.
- I.6 completed (ISO standards)







# II. PRACTICES, EXPERIENCES

- II.1 28 national and international projects on Danube River and tributaries.
- II.2 137 papers (we included a selected list of 137 papers some of them in English language – regarding hazardous substances, from a database of over 5.000 scientific works regarding Danube River).
- · II.3 finalized for Upper Tisa Catchment and Danube River
- II.4 only EEA data and metadata; complete list for Tisa Catchment economic agents.
  The list with all the Romanian economic agents is publicly available. Further more, The
  National Water Administration publishes (since 2010) annual reports regarding the
  main river polluters and water bodies quality.
- II.5 imposed by legislation, but not specific measures indicated.

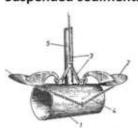






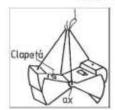
# III. INVENTORY OF SAMPLING METHODOLOGIES

# Suspended sediments



Rapid collector Nansen bottle (cylinder with flaps). The cylinder (1) is inserted at the point of collection with the flaps (2) raised and reinforced by a simple arming-tripping system (3). By the trigger, the flaps close suddenly, pulled by the springs (4).

#### River bed sediments





Sampling from the river bed (under water) is done with GRAIFER, CAROTIER.

From the floodplain (dry sampling) sediments are collected with an ordinary shovel.







# IV. INVENTORY OF LABORATORY METHODOLOGIES

- There is a list with analytical equipment regarding metals, ions, organic molecular compounds analysis, together with corresponding analytical standards (ISO and EPA), detection limit and methods accuracy.
- There are national accredited laboratories which perform all these analyses. In RO-IGR and RO-TUCN only metals are analyzed, including new and very new generation equipment, but the laboratories are not certified. Those labs work under ISO standards and can participate to laboratories comparison (especially for Total Hg analysis).







# V. INVENTORY OF EVALUATION METHODS

- The quality standard values are established in the national legislation.
- The natural environment and water hardness are not taken into account when establishing pollution thresholds.
- · The national legislation includes the monitoring of metals and their toxic compounds
- · Bioconcentration is not included in the national legislation
- The national legislation does not include remedial measures.

# **SLOVAKIA**





- SLOVAK QUESTIONNAIRE FOR EXISTING SAMPLING, LABORATORY AND EVALUATION METHODS
  - State geological institute of Dionýz Štúr
  - Water research institute
  - Slovak water enterprise

Project co-funded by the European Union

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Danube Transnational Programme									
Indicate	Methodological instruction of the MoE No. 549/98-2 (mg.kg <sup>-1</sup> )				Methodological instruction of the MoE No. 549/98-2 - water solution (mg.2-1)		Decision No. 531/94-540 (mg.kg <sup>2</sup> )		
	TV	MPC	TVA	IV	TV	MPC	A	В	C
ansenic	29	55	55	55	0,8	25	29	30	50
barriers	160	300	-	-	23	220	500	1000	2000
berylians	1.1	1,2		- 6	0.02	0.2	- )	20	30
cadexan	0,8	12	7.5	12	0,08	0,4	0,8	3.	20
cobalt	9	19	1.00	- +/	0,2	2,8	20	38	300
chromium	100	380	380	385	0,2	8,7	130	250	900
coppet	36	73	90	190	0,4	1,5	36	100	500
minute	0,3	- 10	1,6	10	9,01	0,2	0,3	2	10
methyl mercury	0.3	1,4	-		0,01	0,02			
manganése									
molybdeman	3	200	-		2,9	290	- 1	45	200
micket	35	44	43	-210	3,3	3,1	35	100	.500
lead	85	530	.530	538	0,2	11	85	150	.600
untinony.	3	15	-		0,3	6,5			
referrium	0,7	2.9			0,05	53	0,5	1.	30
tin	- 5	1.4.	- 54	. 100	0,2	. 18	20	50.	-300
thakum	1	2,6	-		0,04	1,6			
vanadium	42	.56	1.41	1.90	0,8	4,3	120	200	500
me	140	620	720	720	2,8	9,4	140	500	3000
P total									
F total							500	1000	2000
5 sulphide							. 2	20	300
Br MADJECT CO-TUNG	led by the	Luropear	Union		Inventory	Workshop , Vienne	Acretria.	10 - 16 Apri	2019a



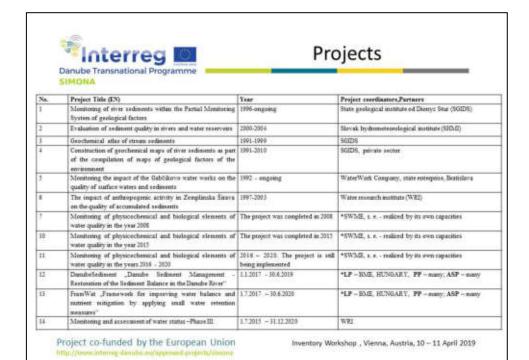
# Analytical standards

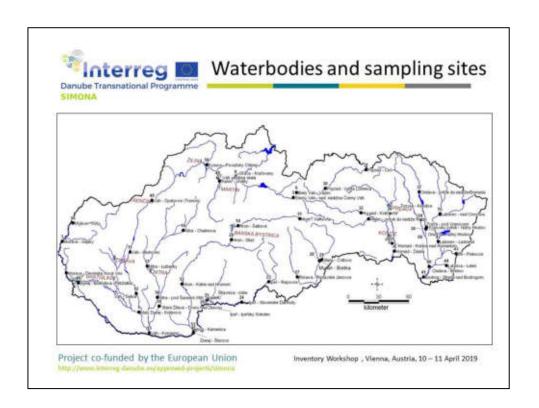
#### · Most accessible methods

- Atomic Absorption Spectrometry (AAS),
- Inductively Coupled Plasma Atomic Emission Spectrometry (ICP - AES),
- Inductively Coupled Plasma Mass Spectrometry (ICP MS),
- X-ray Fluorescence Spectrometry (XRF)
- Identification of minerals in sediments
  - electron microscopy (SEM, transmisive TEM) and electron microanalysis or X-ray powder diffraction analysis
- · Mobility of the elements
  - colony or batch experiments, one-step extraction methods and sequential extraction methods

Project co-funded by the European Union

Inventory Workshop , Vienna, Austria, 10-11 April 2019







- · Geochemical Atlas of Europe FOREGS
  - Surface water
  - Stream and bottom sediments
  - Floodplain sediments
- Water Research Institute
  - Bottom sediments
- SGIDS
  - Stream sediments

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# Laboratory methodologies

- SGIDS (Spišská Nová Ves)
  - acredited
  - sediments, water, soils, rock environment

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# Future tasks

- Some information in the questionnaire missing – fill in soon (biota, inventory of evaluation methods)
- Ready for discussion to finalize protocols, sampling and laboratory methodology (location, measuring compounds and matrices...)

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#### **SLOVENIA**





# **REGULATIONS and MONITORING**

- In Slovenia, monitoring of water, sediments and biota is carried out in accordance with the WFD.
- Monitoring and assessment of water status are regulated by the Rules on the monitoring of surface waters (Official Gazette of the RS, 10/2009, 81/2011)
- The criteria and method of water status assessment are determined by the Decree on the Status of Surface Waters (Official Gazette of the RS, 14/2009, 98/2010, 96/2013, 24/2016)
- Programs for monitoring are prepared by the Slovenian Environment Agency, which is also responsible for their implementation, data control and assessment.

Project co-funded by the European Union

Inventory Workshop, Austria, 10-11 April 2019

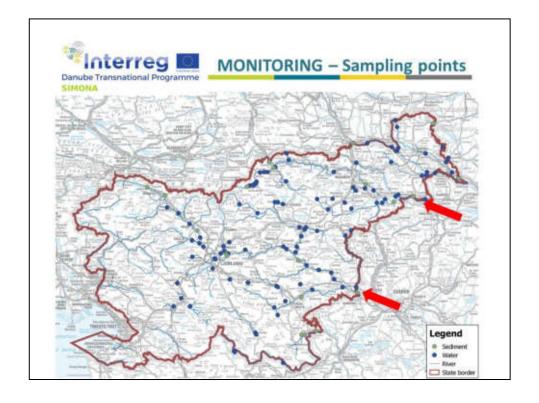
http://www.listoneg.dom/die.eu/approved-projects/simona



- The monitoring program of the water chemical status for the period 2016 - 2021 has been prepared in accordance with national and European legislations (WFD) and in accordance with international conventions and interstate agreements with neighboring countries.
- Slovenia is involved in the Transnational Monitoring Network
  (TNMN) on the Danube tributaries, on the Sava and the Drava
  Rivers. These are the locations on the border profiles with Croatia,
  which are also included in the national program and in the
  bilateral monitoring with Croatia.

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# MONITORING – chemical parameters - water

 Surface water monitoring includes 45 priority substances of which 21 are priority hazardous substances (eg. cadmium, mercury, endosulfan, nonylphenol, etc.)

- For these substances a uniform Environmental quality standards (EQS) are set up for water and organizms (fish).
- Monitoring of water in performed at least monthly and for organizms yearly.

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# MONITORING – chemical parameters - sediment

- For long-term trend assessment of chemical parameters in waters, monitoring of sediments in fraction < 63 μm is also carried out.</li>
- · Chemical parameters for sediments are:

Anthracene, Cadmium and its compounds, Brominated diphenyl ether, Chloroalkanes C10-C13, DEHP, Fluoranthene, Hexachloro-benzene, Hexachloro-butadiene, Hexachloro-cyclohexane, Lead and its compounds, Mercury and its compounds, Pentachloro-benzene, PAH, Tributyltin compounds, Dicofol, PFOS, Quinoxyfen, Dioxins and dioxin-like compounds, HBCDD, Heptachlor and heptachlor epoxide

· Sediments are monitored due to trends every 3 years

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# MONITORING – sampling and transport

#### WATER:

<u>Sampling:</u> SIST ISO 5667-6: 2015; Water quality - Sampling - Part 6: Guidance on sampling of rivers and streams

<u>Transport and storage:</u> SIST EN ISO 5667-3: 2013; Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3:2012)

#### SEDIMENT:

<u>Sampling:</u> SIST ISO 5667 – 12:1996; Water quality -- Sampling -- Part 12: Guidance on sampling of bottom sediment

<u>Transport and storage:</u> SIST ISO 5667 – 15: 2010; Water quality - Sampling - Part 15: Guidance on the preservation and handling of sludge and sediment samples (ISO 5667-15:2009)

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# MONITORING – chemical analysis

- Sampling and most of the analyzes are performed by external laboratory, the Slovenian Environment Agency (ARSO) only carries out analyzes of metals in water.
- External laboratory has accreditation for sampling and most of the analytical methods, all in accordance with ISO 17025.
- ARSO has ISO 17025 accreditation to analyse metals in water.
- Analytical methods:
  - Metals = ICP-MS
  - Organic compounds = LC-MS, GC-MS, HPCC, etc.

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- . EQS are defined for water and biota in accordance with WFD
- EQS are generally fixed. Some metals also consider the natural background (Cd, B, Hg, Cu, Zn, Co, Sb) and bioaccumulation (Ni and Pb).
- For some elements such as Cd, Cu, Zn EQS vary depending on the water hardness.
- Evaluation of the ecological status and definition of categories is done according to WFD and Decree on the status of surface waters.
- The results of monitoring are available in the web site of Slovenian Environment Agency <a href="http://www.arso.gov.si/en/">http://www.arso.gov.si/en/</a>. The original data (concentrations) are available in MS Excel files also in the web site: <a href="http://www.arso.gov.si/vode/podatki/arhiv/kakovost arhiv2018.html">http://www.arso.gov.si/vode/podatki/arhiv/kakovost arhiv2018.html</a>

Project co-funded by the European Union

Inventory Workshop, Austria, 10 - 11 April 2019

# Inventory workshop of the SIMONA Project 10 April 2019 Vienna, Austria





Sebastian Pfleiderer Geological Survey of Austria

Gamma Geologische Bundesanstalt

# Introduction

- 1. Choice of sampling sites
- 2. Sampling equipment
- 3. Sampling procedure
- 4. Sample preparation in the field
- 5. Sampling documentation

# Past experiences:

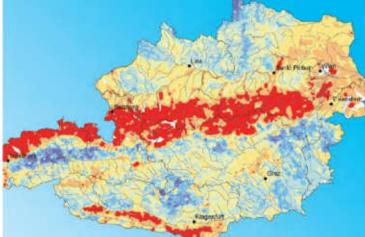
- Austrian Standard (ÖNORM G 1031) for geochemical sampling (1979)
- Geochemical Atlas of Austria (1989) (Bohemian Massif and Central Alps) http://opac.geologie.ac.at/ais312 /dokumente/AL0028 Gesamt.pdf (29,690 stream sediment samples)
- FOREGS (Salminen et al., 1998) http://tupa.gtk.fi/julkaisu /opas/op 047.pdf (19 floodplain, 12 humus, 18 topsoil 15 subsoil, 20 stream sediment and 20 stream water samples in Austria)
- Geochemical Atlas of Austria (2015) http://opac.geologie.ac.at/ais312 /dokumente/AL0028 Gesamt.pdf (36,162 stream sediment samples)

# BUNDESWEITE UND FLUSSSEDIMENTGEOCHEMIE (1978-2010)

# ARCHIV LÄGERSTÄTTEN **FORSCHUNG**

BAND 28







Geologische Bundesanstalt

# 1. Choice of sampling sites

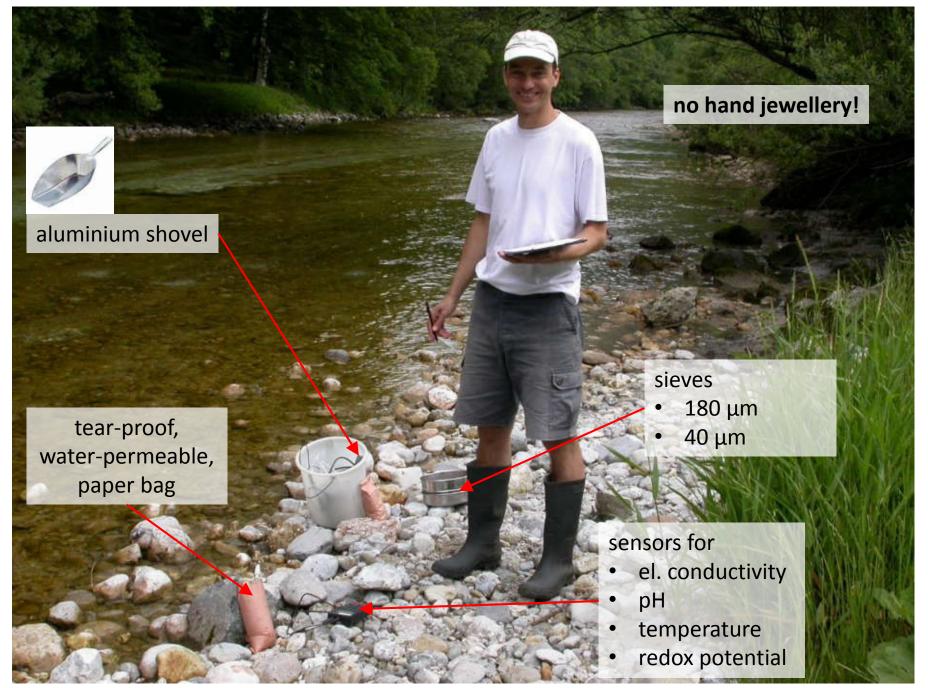
- for mineral exploration in alpine regions
- for environmental monitoring in populated / industrial regions

# **Possible problems**

- boulders
- river construction
- agriculture
- large, deep rivers
- slope failures
- adapt sampling sites



# 2. Sampling equipment



# 3. Sampling procedure

- 1 1.5 kg of active sediment (fine- to medium grained bed load material transported by running water)
- if necessary collect material over a stretch of 50 m up-/downstream of sampling point
- 2 grain size fractions:
  - sand/silt (180 μm)
  - silt/clay (40 μm)
- if necessary wet sieving
- in situ measurements of
  - air temperature
  - in stream water: temperature, electrical conductivity, pH, Eh
  - in sediment (in bag before decanting): temperature, el. conductivity, pH, Eh (comparison allows to test if sediment is active)
- not during / after heavy rain events or high floods!
- duplicate sampling for quality control every 50th sample

# 4. Sample preparation in the field

dewatering in dry storage rooms

# in the field lab / at home:

- weighing of total sample
- drying in oven at < 110°C → water content (Austrian Standard ÖNORM B 4410)</li>
- sieving < 180 μm (German Standard DIN 4188)</li>
- weighing of samples after drying & sieving

# 5. Sampling documentation

- General data: person, sample number, location (name of village / area on topographical map), coordinates, coordinate system, altitude, date & time, weather, name of river, reasons for sampling site adaptation, duplicate sample for quality control (y/n)
- Outcrop description: sketch, photo, dry river bed (y/n), river constructions, dams, influence of industrial /residential sites, traffic routes, mining activities, waste, sewage etc.
- **Sample description**: grain size fraction, in-situ measurements, measurement devices, visible iron or manganese oxide precipitations
- Description of in situ sample preparation: drying, weighing, sieving;
   total sample weight, water content, sample weight after drying and sieving



# Sediment sampling in large rivers DanubeSediment project

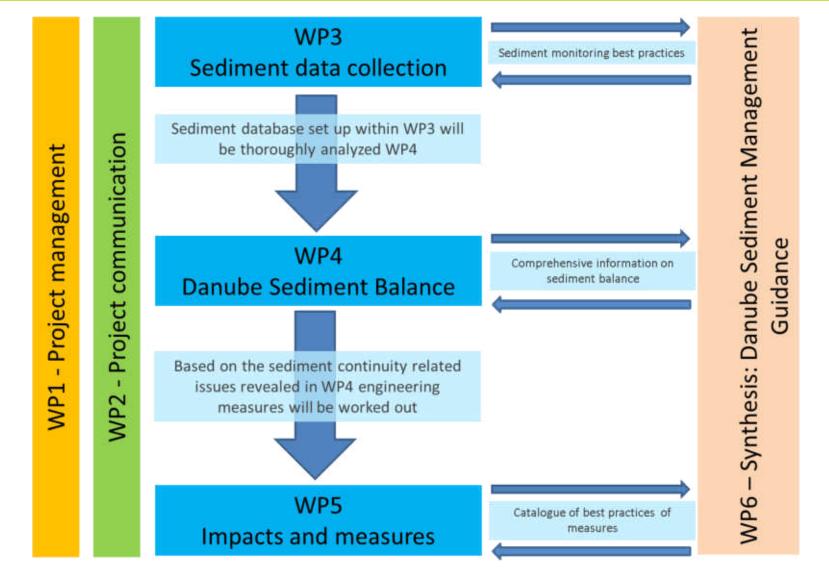
Introduction of applied sediment monitoring methods along the Danube

Barbara Kéri and Sándor Baranya, BME

Vienna, 10.04.2019

# **Project methodology**





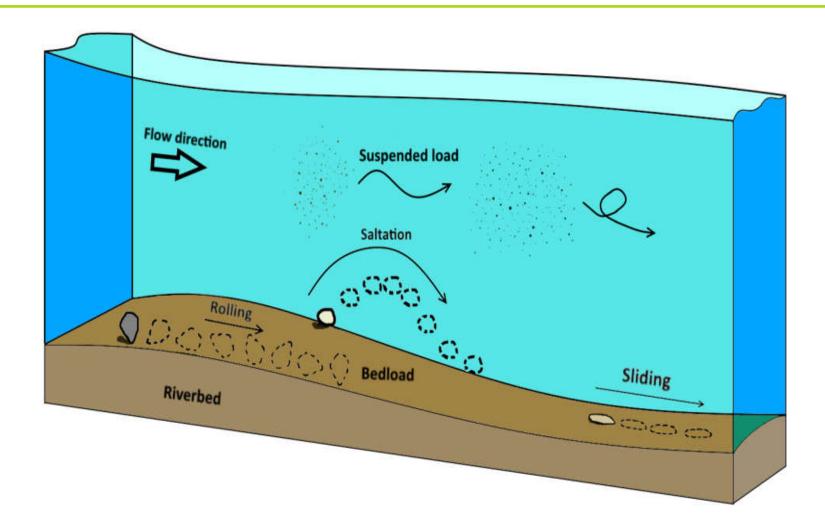


### **Objectives**

- Reveal all available sediment data for the Danube and the major selected tributaries at the confluence
- Permanent interaction with the data owner stakeholders (water directorates, private companies, Project Partners)
- Limited sediment transport monitoring at short reaches with significant data gaps
- Comparative analysis and intercalibration of different sediment monitoring techniques
- Recommendations for the good practices of sediment monitoring techniques
- Training of sediment experts on an international workshop



## Transport modes of sediments in rivers

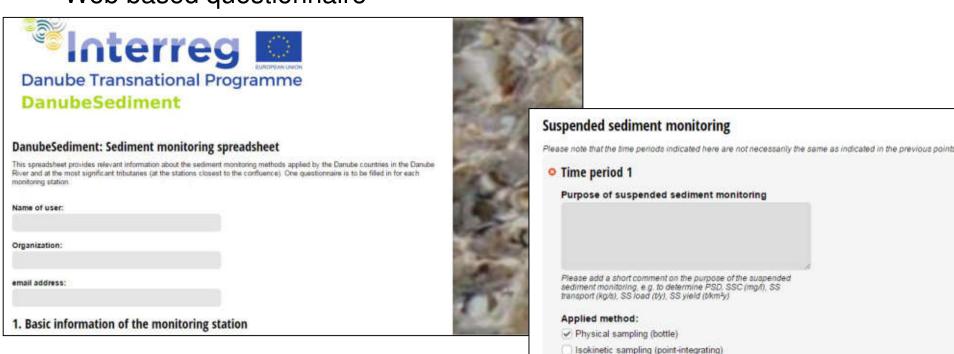


# Sediment monitoring system along the Danube and at the most important tributaries



#### Collection of metadata

Web based questionnaire



Isokinetic sampling (depth-integrating)

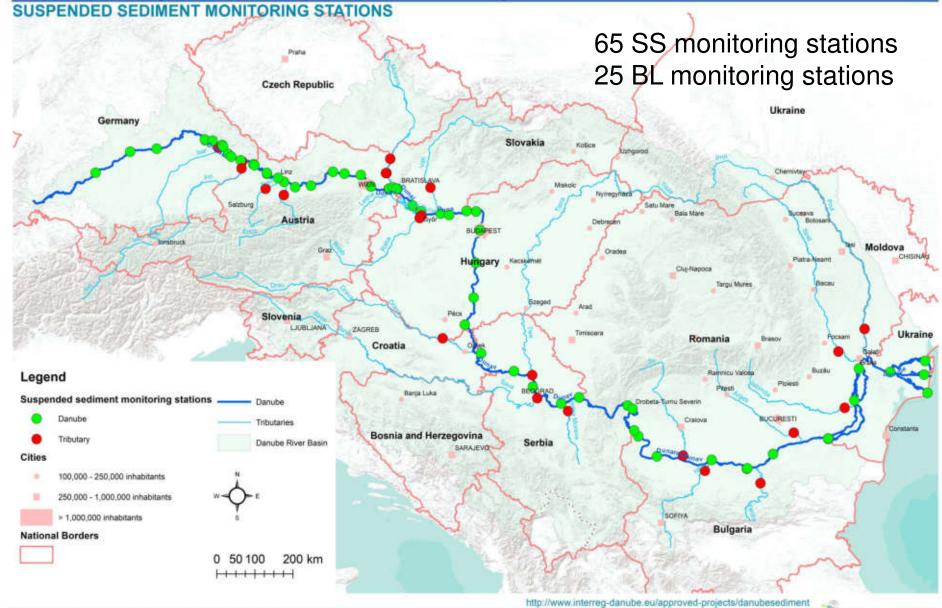
Automatized bottle sampling

Optical backscatter point sensor

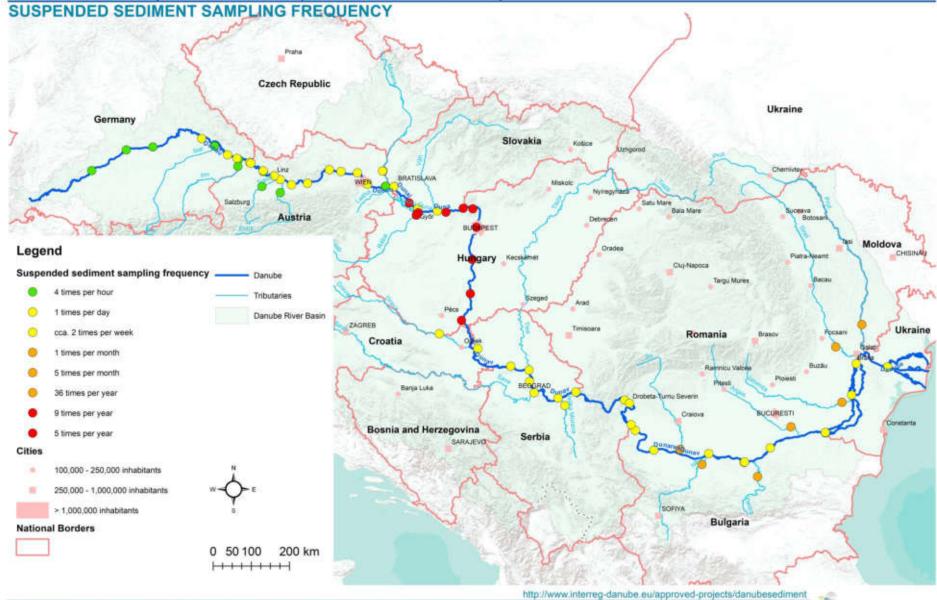
Optical Laser diffraction point sensor

Pump sampling

Acoustic devices







This map was produced in the frame of the EU funded project DanubeSediment, and is based on national information provided by Contracting Parties (AT, BG, DE, HR, HU, RO, RS, SK). Budapest, April 2018

Interreg Danube Transnational Programme

## Suspended sediment monitoring in Germany



 Responsible institute: Bavarian Environment Agency (LfU), Bavarian Hydrological Service (GKD), Federal Waterways and Shipping Administration (WSV)

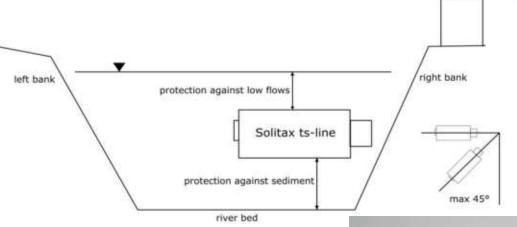
Automatized monitoring using Optical Backscatter Sensors (OBS), physical sampling

housing

(bottle)

Sampling frequency: 15 min

Nr. of stations: 9 (2 trib.)





Solitax ts-line



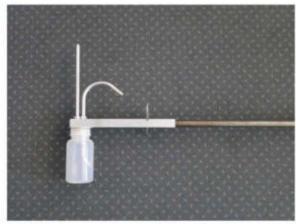


## Suspended sediment monitoring in Germany

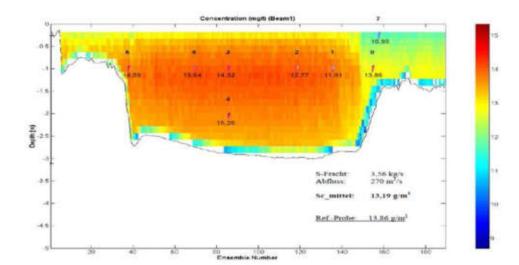


Calibration of OBS – point sampling at the sensor





- Multipoint sampling and
- Acoustic profiling:
  - StreamPro ADCP + ViSea
- SSC analysis method: filtering





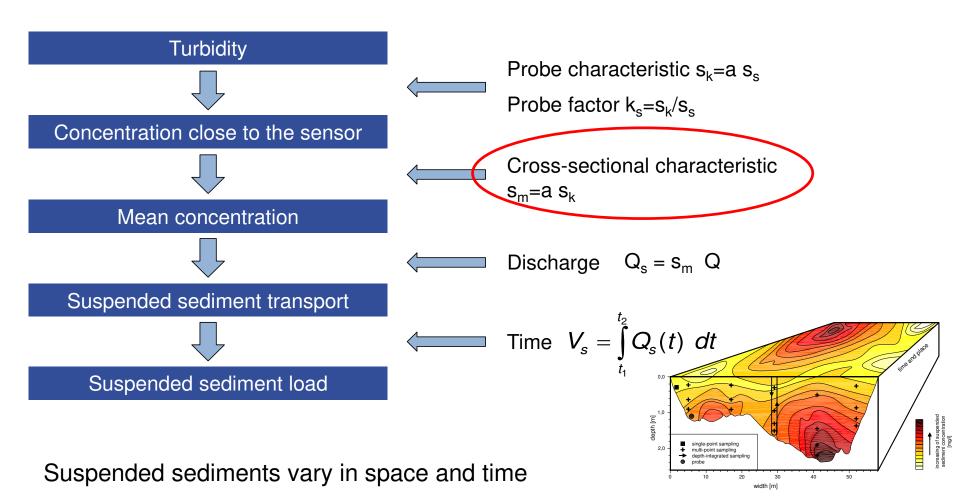
- Responsible institute: ViaDonau, Verbund Hydro Power
- Automatized monitoring using Optical Backscatter Sensors (OBS), pump sampling, automatized bottle sampling
- Sampling frequency: 15 min
- Nr. of stations: 11 (4 trib.)







Estimation of sediment load (Habersack et al., 2013):





• Cross-sectional calibration – multipoint sampling









- Laboratory analysis of water samples
- SSC  $\rightarrow$  vacuum filtration (0.45 µm filter), drying (2 hours on 105° C), weighing
- PSD → sieving instrument and sedimentation instrument



## Suspended sediment monitoring in Slovakia



- Responsible institute: SHMU, VUVH
- Typical frequency: 3 to 20 times/week
- Depth-integrated sampling at representative verticals
- Nr. of stations: 5 (1 trib.)



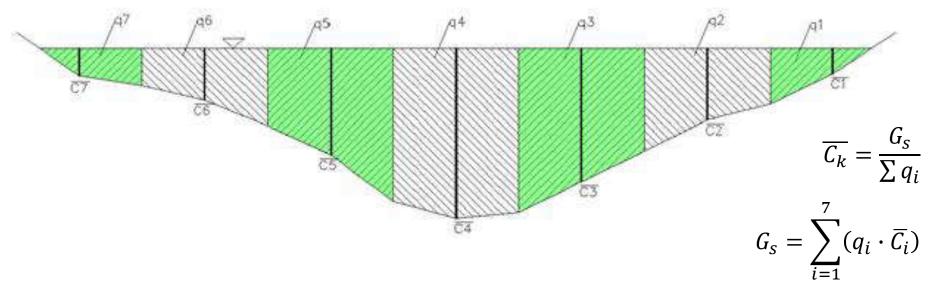


SSC → filtration of 0.2 I (0.45 µm filter), drying (24 hours on 105° C), weighing

## Suspended sediment monitoring in Hungary



- Expeditionary multipoint measurements
- Typical frequency: 5 times/year
- 7 verticals, 10 points/vertical, 1 liter/point using pump
- 10x1 liter samples are integrated → sedimentation → extraction of 9 liters → remaining 1 liter is analysed → drying, weighing
- PSD → sedimentation instrument
- Nr. of stations: 7 (1 trib.)



## Suspended sediment monitoring in Hungary



Pump sampler





• Estimation of SSL using sediment rating curves and actual discharge

## Suspended sediment monitoring in Croatia



- Daily physical sampling in one point at the water surface using bucket sampler→ filtration (0.45 µm filter) → filters to laboratory, drying (on 105° C), weighing
- Multipoint measurements 6 times/year with pump
- Nr. of stations: 1 trib.









- Daily physical sampling in one point at the water surface using bucket sampler (10 liters) → filtration (0.45 µm filter) → filters to laboratory, drying (on 105° C), weighing
- Multipoint measurements 1-3 times/year with vacuum bathometer in 7-10 verticals, 5 points/vertical, ~40 liter sample/point
- Estimation of SSL → Correlation between surface concentration and mean concentration along the cross-section
- Sedimentation of samples for days → 1-1.5 liter of concentrated sample is extracted → repeated settling for a day → 0.1 liter of concentrated sample is extracted → drying, weighing
- Nr. of stations: 7 (3 trib.)



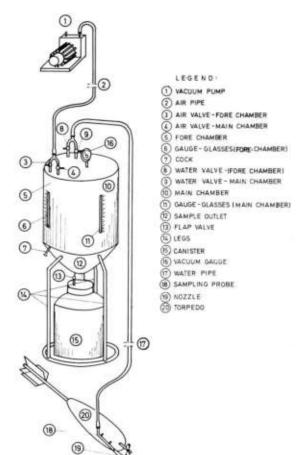
Daily physical sampling

Multipoint measurements 4-6 times/year with bathometer in 5-9

verticals

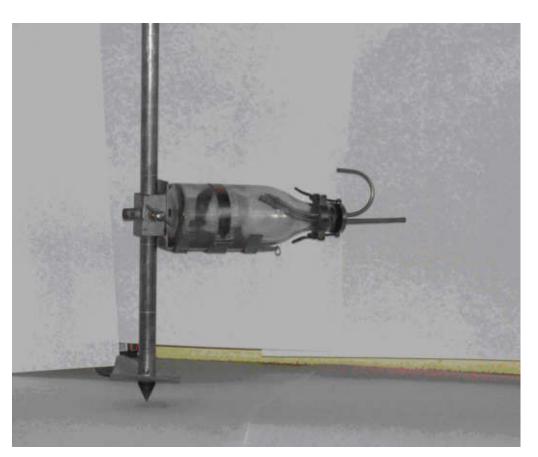
 Correction of point samples with cross-section calibration

→ daily sediment discharge





- Daily physical sampling with bottle sampler at the river bank
- Mean concentration in the cross-section is assumed to be the measured one at the river bank
  - → daily sediment discharge
- Nr. of stations: 6 (2 trib.)



## Suspended sediment monitoring in Romania



- Daily physical sampling with bottle sampler at the river bank
- Multipoint measurements 4-6 times/year with bathometer in 5-9 verticals
- SSC is determined using a portable turbidity sensor
- Nr. of stations: 19 (5 trib.)







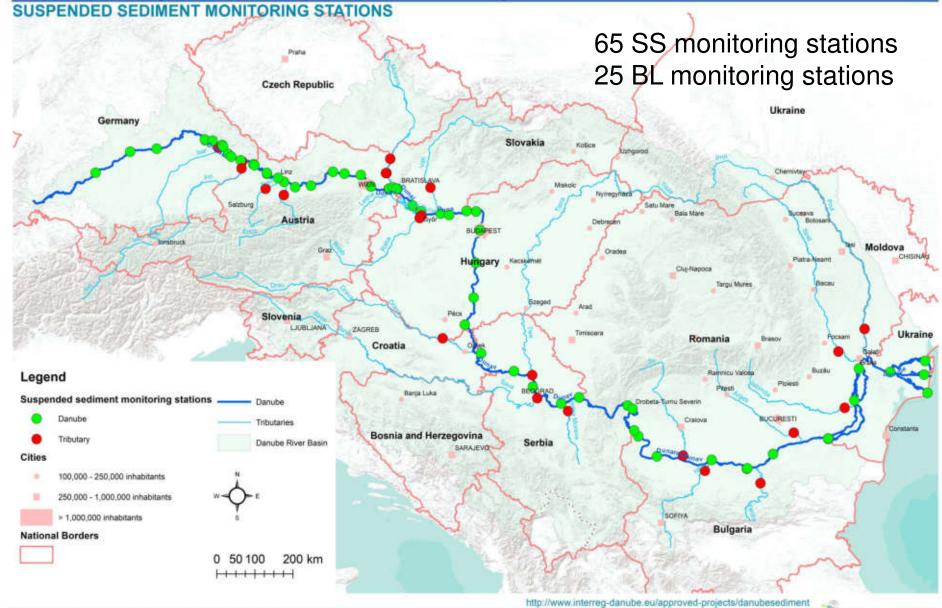




This map was produced in the frame of the EU funded project DanubeSediment, and is based on national information provided by Contracting Parties (AT, BG, DE, HR, HU, RO, RS, SK).

Danube Transmittional Progr

Interreg







This map was produced in the frame of the EU funded project DanubeSediment, and is based on national information provided by Contracting Parties (AT, BG, DE, HR, HU, RO, RS, SK). Budapest, April 2018

Danube Transnational Programme
Banutie Sediment



- Germany: expeditionary monitoring campaigns at 9 sites
  - BfG sampler
  - Sampling from ship
  - Rating curves
- Austria (1 station):
  - BfG sampler (monitoring at Bad-Deutsch Altenburg)
  - Mesh size: 1 mm
  - Sampling from bridge or from ship
  - 8-15 verticals, 3x5 minute long samplings
  - 3 times/year
  - Drying, sieving







- Slovakia (2+1 stations):
  - intensive measurement campaigns in 1997-1998 and 2002-2003
  - Swiss-type sampler, 5-6 verticals
  - 2-5 min long samplings
  - Drying, sieving of the samples
  - Rating curves have been set up







### • Hungary (1 station):

- continuous monitoring since 1998 at Vámosszabadi (Medvedov)
- 4-6 times/year using the modified Károlyi-sampler at 7 verticals
- 15 min long samplings
- Drying, sieving of samples



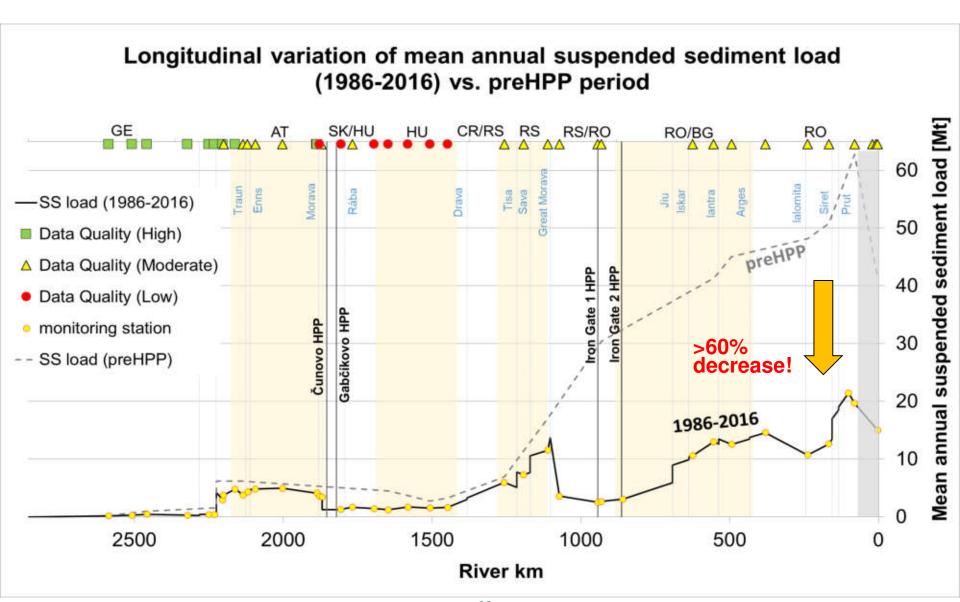


- Romania (11 stations):
  - 4-6 times/year at 11 monitoring stations, 5-9 verticals
  - ~10 min long samplings
  - Drying, sieving (0.063-50 mm)



## Longitudinal variation of long-term (1986-2016) mean annual suspended sediment load along the Danube River







## Thank you for your attention!

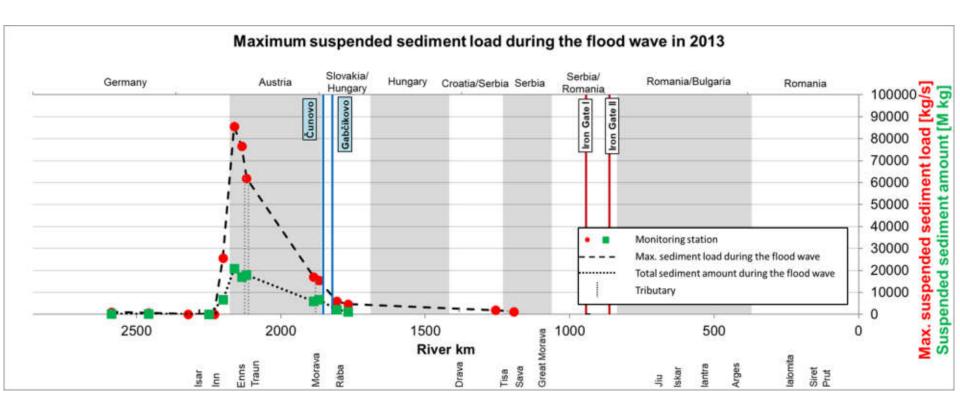
- Barbara Kéri
- keri.barbara@epito.bme.hu
- +36 30 275 2655





### Activity 3.3 – Assessment of sediment data

Influence of floods on SS transport

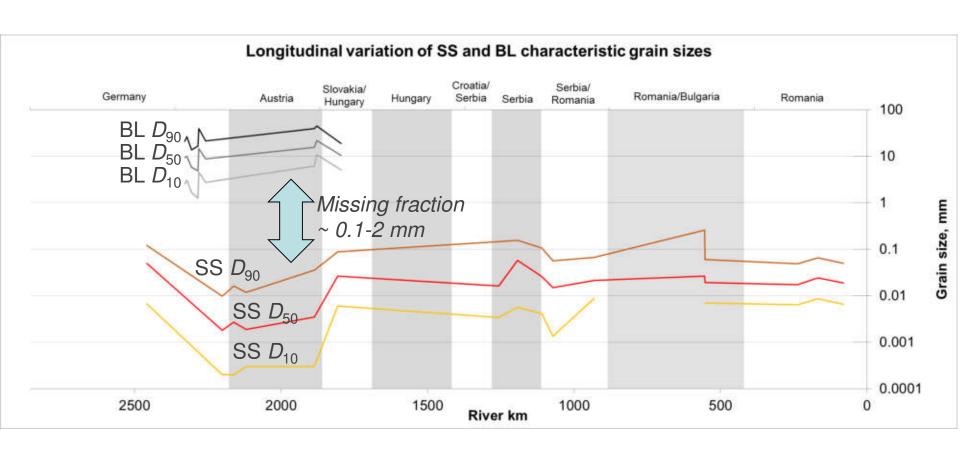


20M tons mobilized in AT (mean annual around 5Mt)



### Activity 3.3 – Assessment of sediment data

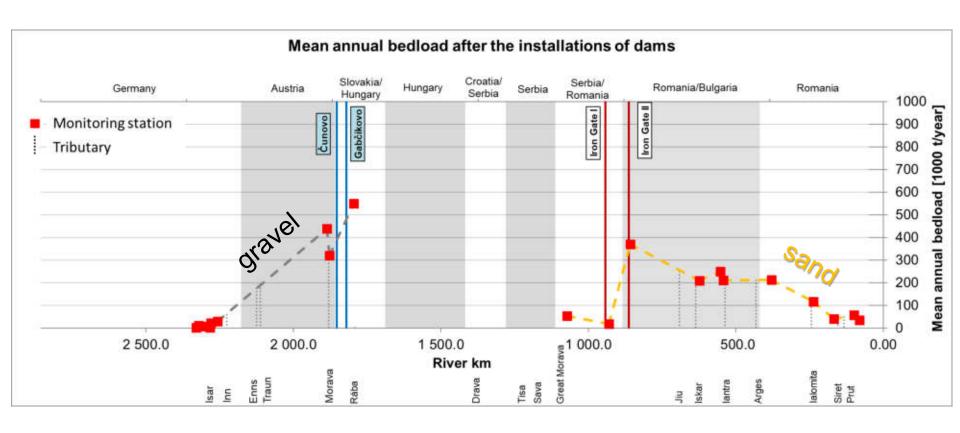
Longitudinal variation of characteristic sediment grain sizes





### Activity 3.3 – Assessment of sediment data

### Bedload transport

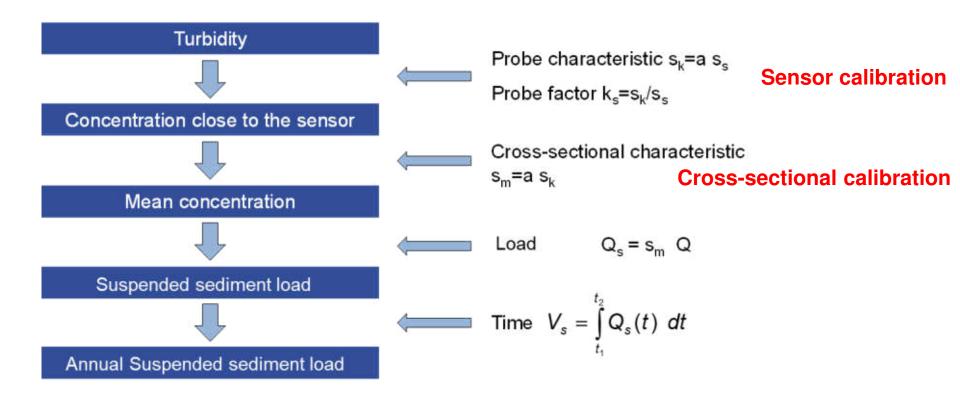




### **Activity 3.2 – Comparative analysis**

Good practices in SS monitoring

### Methodology

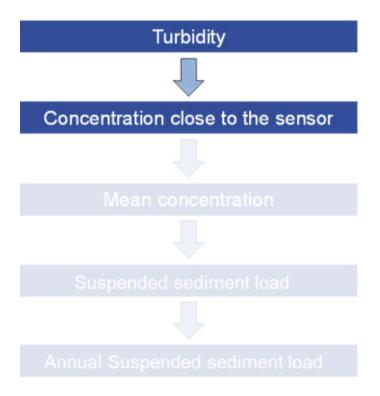


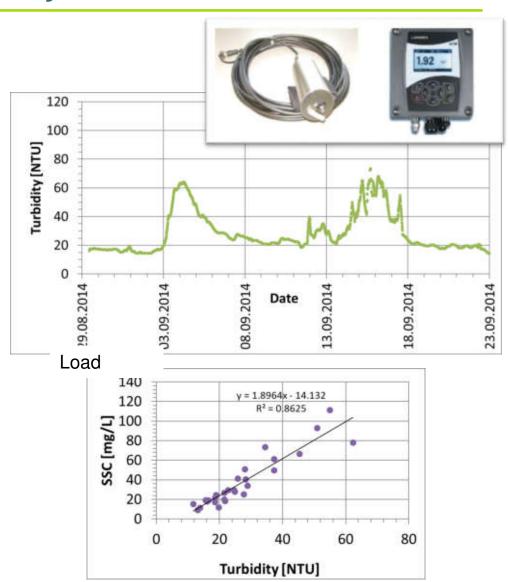


### **Activity 3.2 – Comparative analysis**

Good practices in SS monitoring

Sensor calibration



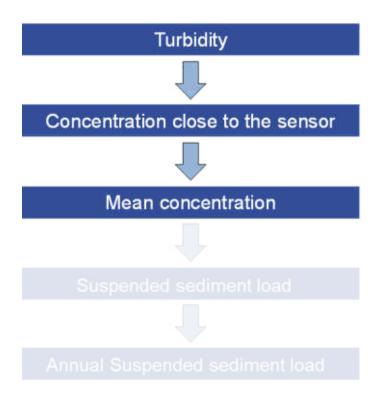


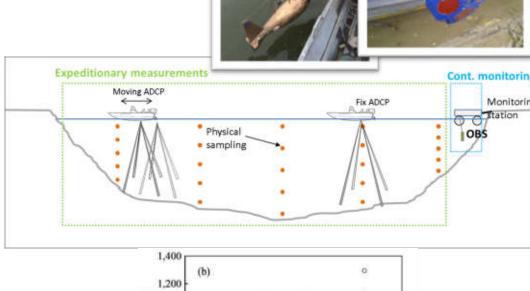


### **Activity 3.2 – Comparative analysis**

Good practices in SS monitoring

Cross-sectional calibration (isokinetic sampling!)





y = 3.58x - 634.67

Haimann et al. (2014)

Concentration close to the sensor (mg 1-1)

 $R^2 = 0.36$ 

y = 1.52x

 $R^2 = 0.99$ 

Mean concentration (mg 1-1)

1,000

800

600

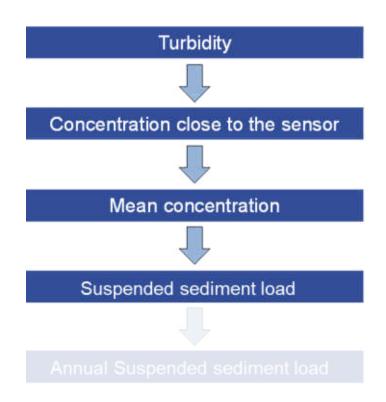
200

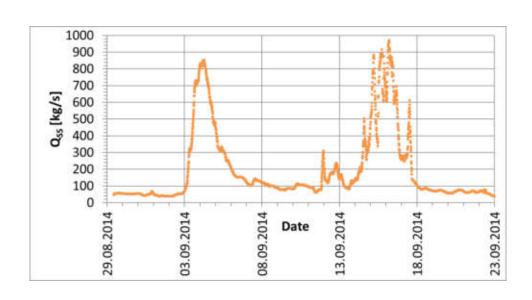


### **Activity 3.2 – Comparative analysis**

Good practices in SS monitoring

Temporal variation of SS load



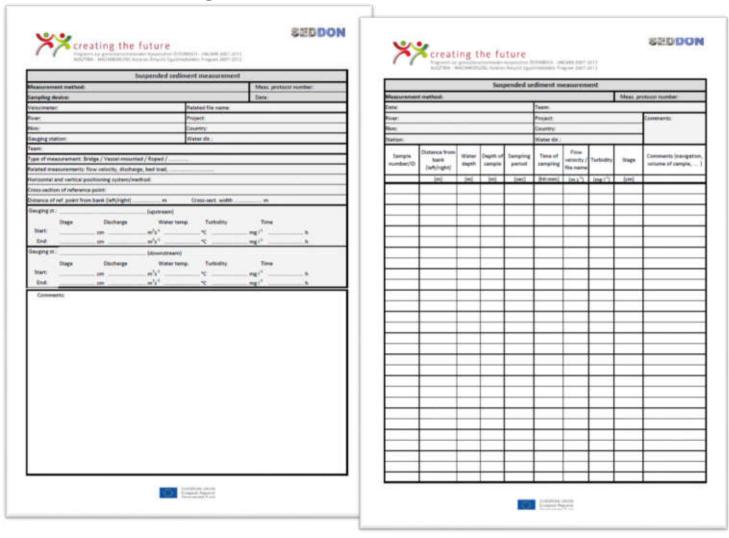




### **Activity 3.2 – Comparative analysis**

Good practices in SS monitoring

**Protocols** 



### **WP3: Sediment Data Collection**



### **Activity 3.2 – Comparative analysis**

Good practices in SS monitoring Laboratory analysis after BMLFUW (2008, 2017)

### Main steps:

- Drying of membrane filter (of 0.45 µm pores) at 105° C until constant weight, after the drying the filter is placed in a desiccator, to let the filter cool down
- Mass of the plate and filter is measured  $(m_a)$
- Membrane filter is placed into the filtering device.
- Sample is poured into the filtering device and its volume is measured precisely  $(V_p)$ .
- After filtering, the membrane filter is dried at 105° C until constant weight, after the drying the filter is placed in a desiccator, to let the filter cool down
- Plate and membrane filter is weighted again  $(m_b)$ .
- Dry matter content is:  $m_T = m_b m_a$  [mg].
- SSC =  $m_T/V_p$  [mg/l].





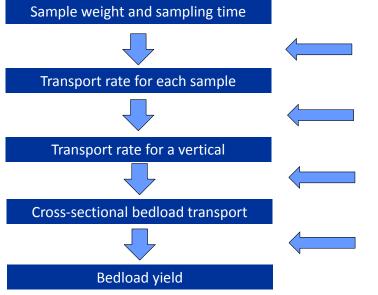
### **WP3: Sediment Data Collection**



# **Activity 3.2 – Comparative analysis**

Good practices in BL monitoring

### Methodology



Calibration coefficient
Sampler width

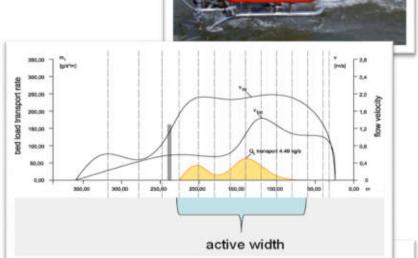
Average samples of one vertical

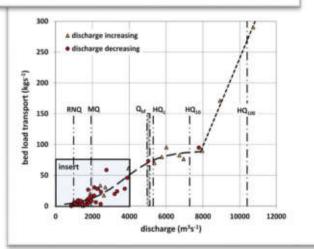
Integrate over the active width

Integrate over time:

Bed load – discharge relation (rating curve)

And Discharge







# **SIMONA Sampling WG presentation**



Inventory Workshop of the SIMONA Project

10<sup>th</sup> – 11<sup>th</sup> April, 2019, Vienna

Project co-funded by the European Union

http://www.interreg-danube.eu/approved-projects/simona



### WGs

**Dr. sc. Gyozo Jordan**, Szent Istvan University, Hungary, **Scientific Coordinator**:

#### The Sampling and the Laboratory WG

#### **EXAMPLE**

<u>critically review</u> the existing water and sediment national methods, <u>the state-of-the-art</u> knowledgebase, good <u>practices and experiences</u> in the DTP countries, including EU and non-EU countries.

Reviewing will be done against the following criteria: the developed protocols

- (1) should be <u>acceptable</u> in all DTP countries,
- (2) should be in-line with the ICPDR and the <u>EU requirements</u>,
- (3) use the latest scientific knowledge, and
- (4) have to be <u>sustainable</u>.

The main steps of reviewing the sampling and laboratory methods are

- (1) <u>reviewing national</u> spatial and temporal sampling and monitoring techniques and laboratory analysis procedures for sediment quality measurements of the water phase, biota, bottom sediment, suspended sediment, floodplain sediment with passive and other sampling technics under the WFD implementation requirements;
- (2) <u>reviewing national</u> uncertainty analysis techniques for sampling and laboratory analysis including representativity assessment; and (3) <u>providing a critical summary and conclusions of the reviews</u>.



# Sampling WG

### Based on WP3 Questionnaires - Danijel's WORK PLAN for WP4 - Activity 4.1

**Activity 1 – Review** 

**February 2019 - March 2019** 

#### Sampling

**HR-HGI-CGS** (Croatian Geological Survey) - sampling strategy;

**RS-JCI** (Institute for Development of Water Resources "Jaroslav Černi") - bottom sediment sampling procedures;

AT-GBA (Geological Survey of Austria) - suspended sediment sampling procedures;

SI-GEOZS (Geological Survey of Slovenia) - floodplain sediment sampling procedures;



# Sampling WG

### Danijel's WORK PLAN for WP4 - Activity 4.1

### Sampling

**BA-FZG** (Geological Survey of Federation of Bosnia and Herzegovina) - transport and storage of sediment samples;

**HU-BME** (Budapest University of Technology and Economics) - sediment sampling methods related to DTP DanubeSediment project on sediment quantity;

**MD-IGS-ASM** (Institute of Ecology and geography of the Academy of Sciences of Moldova) - specific sampling procedures related to physiographic and climatic conditions in partner countries across the DRB; **UA-UGC** (State Enterprise "Ukrainian Geological Company") - problems regarding HSs monitoring across partner countries;

**BG-GI-BAS** (Geological Institute, Bulgarian Academy of Sciences) - will review HSs measured in sediment across partner countries.



### AT-GBA (Geological Survey of Austria), Sebastian Pfleiderer

- suspended sediment sampling procedures. The review includes methodology for suspended sediment sampling. That means position in the stream (for example in the middle of the river, closer to river banks,...), sample volume/mass, tools and procedure including time needed to collect specific volume/mass.

- in the national questionnaires only the Geological Institute of Romania describes the method they use for suspended sediment sampling;
- articles, Edwards & Glysson (1999) and Lalk et al. (2017) provide the most detailed descriptions.



### SI-GEOZS (Geological Survey of Slovenia), Jasminka Alijagić

- floodplain sediment sampling procedures. The review includes methodology for floodplain sediment sampling. That means sampling location (for example how far from the stream,...), sample volume/mass, tools and procedure.
- Austria, Moldova, Croatia they sample the floodplain sediment;
- Romania, Slovakia, Slovenia, Ukraine they do not sample floodplain sediment;
- Bulgaria, Bosnia, Republic of Srpska, Hungary, Montenegro no data.
- Sampling location: no data.
- Sample volume/mass: different mass, but mostly no data.
- Tools: various (stainless steel shovels, PVC or ceramic spoons, scoops, ...)
- Procedures: different.



**BA-FZG** (Geological Survey of Federation of Bosnia and Herzegovina), Ismir Hajdarević transport and storage of sediment samples. Transport and storage equipment (bags, boxes,...). For how long are samples archived, special conditions for storage,...

#### **Transport:**

Austria, Bosnia and Herzegovina (Federation of B&H) - no specific methodology;

Bosnia and Herzegovina (Republic of Srpska), Bulgaria, Hungary, Montenegro – no data;

Croatia, Moldova, Slovakia - use refrigerators; Germany - in brown glass bottles;

Romania - suspended sediment on filters; Ukraine - dried and sieved;

Slovenia - ISO 5667 - 15: 2010 Water quality - Sampling.

#### **Archive:**

Austria, Bosnia and Herzegovina (Federation of B&H) - samples keep until project completion;

Bosnia and Herzegovina (Republic of Srpska), Bulgaria, Hungary, Montenegro, Slovakia - no data;

Croatia, Slovenia - samples are not archived; **Germany, Moldova, Romania, Ukraine – archived.** 

Project co-funded by the European Union

Inventory Workshop 10th – 11th April, 2019, Vienna



**UA-UGC (State Enterprise "Ukrainian Geological Company"),** Volodymyr Klos - problems regarding HSs monitoring across partner countries.

### **Summary:**

- in all countries the level of surface water at the hydrological stations is monitored;
- use of different coordinate systems;
- frequency of monitoring is not always indicated (with the exception of Bulgaria);
- maximum experience in sediment monitoring in Slovakia;
- in the questionnaires no information on the analysis of suspended substances in the water flow.



### **Conclusions:**

- the use of an unified coordinate system;
- before the Vienna meeting or before adopting the final field research methodology - a short report of Slovakia about experiences in monitoring;
- similar reports from Hungary, Austria, Romania, Bulgaria project
   DanubeSediment;
- Croatia the results of the project Monitoring of Drava alluvial sediments;
- the **source** of geochemical anomalies in bottom sediments **scientific** research;
- no information about the analysis of suspended solids in the water flow poor knowledge about it - it is possible that this type of monitoring should not be included in the SIMONA project – the need of more detailed scientific research.



**BG-GI-BAS** (Geological Institute, Bulgarian Academy of Sciences), Millena Vetseva review HSs measured in sediment across partner countries. (Within this review, we should also check if there are some HSs which are not prescribed by EU WFD, specific for some partner countries because of some particular reasons (type of industry, agriculture legislative different than in EU,...).

# Hazardous substances measured in sediments – priority substances prescribed by the EU WFD and specific substances – review

- the problem with the missing information is not incomplete questionnaires missing question in the Qs about hazardous substances measured in sediments;
- preliminary excel table with a summary of data (HSs recommended in the Directive marked in green);



- question for partners: the HSs in bottom, floodplain and suspended sediment
   is there any difference in the analyses in the different type of sediments;
- contradiction between the statement that most countries are sampling sediments bottom, floodplain, suspended, but NO HSs are listed as analyzed;
- list of hazardous substances measured in SOILS;
- list of substances analyzed in sediments no data,

### except for

 Slovakia: - list of hazardous substances concentration levels in sediments and overview of legislation limiting the management of sediments on the basis of the limit values for selected elements in sediments (sediment leachates).



**HU-BME** (Budapest University of Technology and Economics), Barbara Keri

- sediment sampling methods related to DTP DanubeSediment project on sediment quantity;

Presentation: Sampling in large rivers

MD-IGS-ASM (Institute of Ecology and geography of the Academy of Sciences of Moldova)

- review if there are some specific sampling procedures related to physiographic and climatic conditions in partner countries across the DRB; This is more appropriate for evaluation purposes, but still, maybe there are some specific conditions for sampling.

RS-JCI (Institute for Development of Water Resources "Jaroslav Černi")

- bottom sediment sampling procedures; The review includes methodology for bottom sediment sampling. That means position in the stream (for example riverbed, inner/outer side of meander,...), sample volume/mass, tools and procedure.



### **HR-HGI-CGS** (Croatian Geological Survey)

sampling strategy, (including spatial and temporal sediment sampling design). The review includes methodologies for selection of sediment sampling locations and setting sediment sampling frequency. It also includes information on number of replicate samples and fraction to be analyzed.

### The legal basis for the monitoring of PSs in sediment in EU

+

the state of the art in particular country and knowledge of a topic of the partners (WP4 Activity 4.1. Review)

+

knowledge and experience acquired in the projects **FOREGS, GEMAS, DanubeSediment** 



### Sampling WG CIS guidance/WFD framework

Directive 2008/105/EC (Environmental Quality Standards Directive) and Water Framework Directive 2000/60/EC (WFD)

Common Implementation Strategy for the Water Framework Directive (2000/60/EC)

#### **Guidance Document No. 25**

Guidance on Chemical Monitoring of Sediment and Biota under the Water Framework Directive

#### **Guidance Document No. 19**

Guidance on Surface Water Chemical Monitoring under the Water Framework Directive

#### **Guidance Document No. 27**

Technical Guidance for Deriving Environmental Quality Standards

#### Guidance document No. 7

Monitoring under the Water Framework Directive

#### Guidance document No. 9

Implementing the Geographical Information System Elements (GIS) of the Water Framework Directive (unified coordinate system: the ETRS89 coordinate reference system prescribed)



### Monitoring of chemical substances in sediment

(Guidance Document No. 25)

- 1. Sampling strategy for chemical monitoring in sediment
- 2. Technical aspects of sediment sampling
- 3. Analytical methods

### 1. Sampling strategy for chemical monitoring in sediment

### 1.1. Selection of sediment sampling stations

- sediments are temporally variable; heterogeneous;
- anthropogenic source of pollution;
- tributaries often different sediment;
- sites with the sediment fraction <63 μm;</li>
- alternatively suspended solid matter (SPM) river channelization;
- sites should be accessible for years;
- ....



### 1.2. Number of replicate samples per station

- multiple samples in pilot phase (3-5);
- later composite samples;
- field duplicates for quality control;
- ...

### 1.3. Sediment sampling frequency

- once a year for directive 2008/105/EC:
- once every three years for temporal trend analyzes;
- rule higher the sediment changes higher the frequency it could be several times per year;
- suspended solids for trend analyses 4 times per year or better monthly;
- ...



### 1.4. Sediment sampling depth

- thick of the top layer (usually 5 10 cm);
- recommended 1 5 cm depending of the deposition rate;
- different intervals for sediment core profiles;
- ...

### 1.5. Sediment fraction to be analyzed

- recommended <63 μm (clay-silt) fraction:</li>
  - widespread in monitoring,
  - reduce influence of grain size distribution;
  - it is SPM or freshly deposited sediment.



### 2. Technical aspects of sediment sampling

Of the ISO 5667 series of standards important for sediment sampling:

- Design of sampling programs [ISO, 2006];
- Preservation and handling of samples [ISO, 2003];
- Sampling of rivers and streams [ISO, 2005];
- Sampling from lakes [ISO, 1987];
- Sampling of bottom sediments [ISO, 1995];
- Guidance on preservation and handling of sludge and sediment samples [ISO, 1999];
- Sampling of marine sediments [ISO, 2004].

Sample volume, Sediment sampler, Grab samplers, Corers, Collecting of SPM and freshly deposited sediments, Transport and sieving, Preservation and Storage.



# Sampling WG future tasks

- 1. Complete WORK PLAN for WP4 Activity 4.1. (February 2019 March 2019)
  - review missing topics;
  - check/update all reviews with the updated questionnaires.

2. WP4 Activity 2 - Development - April 2019 - August 2019



### Sampling WG - future tasks

### WP4 Activity 2

# Development of transnationally harmonized sediment sampling protocols for HSs of bottom, suspended and floodplain sediment

#### Includes:

- proposal for sampling design and monitoring;
- method/s for sampling technique and procedure;
- protocols.



# Sampling WG

### Monitoring of the stream sediment at Rivers: Drava and Mura (Croatia)

<u>Duration:</u> 4 years, 2004-2007

Frequency: 2 times per year, every six months,

1x in spring and 1x in autumn

Locations: Rivers Mura (3 location) and

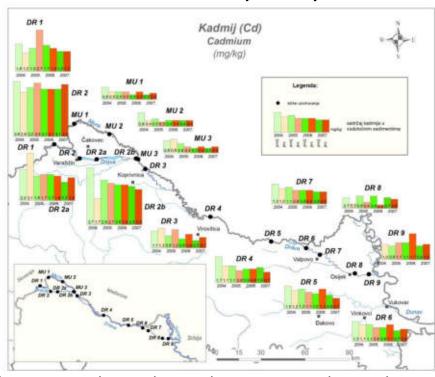
Drava (11 locations)

<u>Samples:</u> composite

Laboratory: fraction < 0.04 mm,

aqua regia, ICP MS

<u>Accuracy:</u> standards: LKSD-2 and DS-7 <u>Precision:</u> duplicate samples (every 10<sup>th</sup>)



<u>Results:</u> Concentration of the elements Pb, Zn and Cd were several times less in the River Mura then in the River Drava. The concentration in the Drava River decreases downstream.

Source of the elevated values of Pb, Zn and Cd: geogenic and anthropogenic (Pb-Zn (Cu, As, Cd)) ore deposits and occurrences, mining, erosion of old slugs (Bleiberg, Austria; Mežica, Slovenia)



# Sampling WG members

sharing

	WG	1 SAMPLIN	G	
Name	Organisation	Org. Code	Email	Role
Ajka Sorsa	Croatian Geological Survey	HR-HGI-CGS	asorsa@hgi-cgs.hr; ajkasorsa@gmail.com	WG LEADER
Gyozo Jordan	Szent Istvan University	HU-SZIE	gyozojodan@gmail.com	SCI. COORDINATOR
Ajka Sorsa	Croatian Geological Survey	HR-HGI-CGS	asorsa@hgi-cgs.hr	WP 4 LEADER
	Austrian Institute of Technology GmbH	AT-AIT		Member
	Geological Survey of Federation of Bosnia and Herzegovina	BA-FZG		Member
	Geological Institute, Bulgarian Academy of Sciences	BG-GI-BAS		Member
	Institute of Geology and Seismology	MD-IGS-ASM		Member
	Geological Survey of Montenegro	ME-GSM		Member
	Geological Institute of Romania	RO-IGR		Member
	Geological Survey of Slovenia	SI-GEOZS		Member
Jozef Kordik	State Geological Institute of Dionyz Stur	SK-SGIDS	jozef.kordik@geology.sk	Member
Volodymyr Klos	State Enterprise "Ukrainian Geological Company"	UA-UGC	v.klos@ukrgeol.com	Member
	Budapest University of Technology and Economics	HU-BME		Member
	Institute for Development of Water Resources "Jaroslav Černi"	RS-JCI		Member
Danijel Ivanišević	Croatian Geological Survey	HR-HGI-CGS	divanisevic@hgi-cgs.hr	Member
Ivan Mišur	Croatian Geological Survey	HR-HGI-CGS	imisur@hgi-cgs.hr	Member
Aleksandra Kovačević	Public institution Waters of Srpska	BA-JUVS	akovacevic@voders.org	ASP
Kristina Šarić	Faculty of Mining and Geology - University of Belgrde	RS-UB	kristina.saric@rgf.bg.ac.rs	Member
Suzana Erić	Faculty of Mining and Geology - University of Belgrde	RS-UB	suzana.eric@rgf.bg.ac.rs	Member

Update.



### Thank you for your contribution to the Review!





# SIMONA - SAMPLING

# **IUGS – FOREGS - GEMAS**

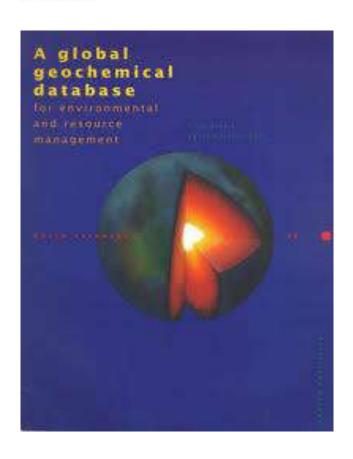
**Sediment sampling protocols** 

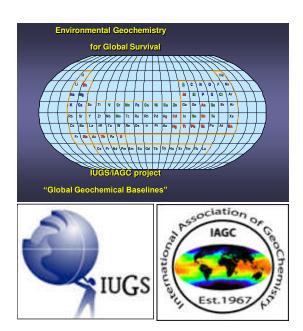
**Gyozo Jordan**, Szent Istvan University



Project co-funded by the European Union







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# **IUGS - Global Geochemical Mapping**

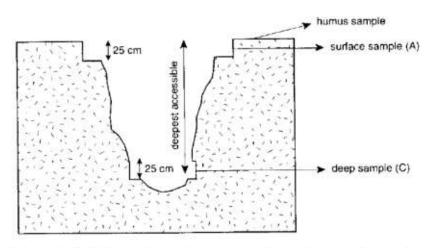


Figure 4-4 Schematic outline of sampling pattern and sampling pit for Geochemical Reference Network.

The site distribution in A is greatly preferable to B.

The sample pit applies to all residual soil locations.

Collection of the lower sample is optional in overbank and floodplain situations.

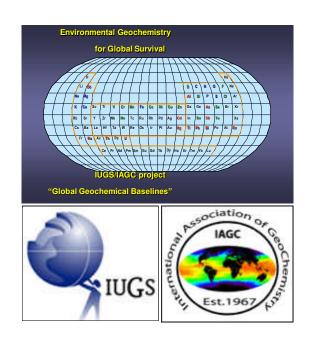
#### 4.5.2.1 Stream sediment

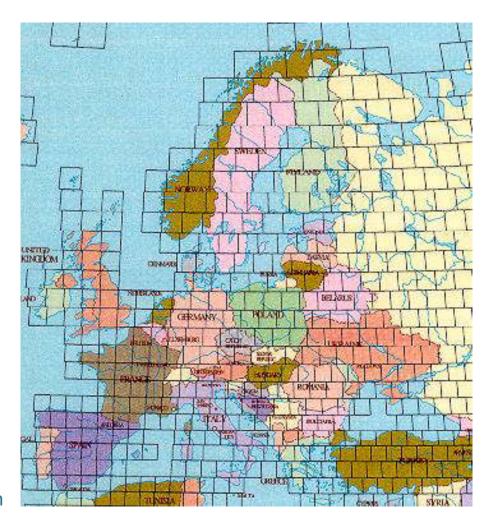
Samples should be collected at the outflow of basins, preferably not exceeding 100 km<sup>2</sup> in area. Basin size is the prime consideration in site selection for drainage samples and all types of sample should be collected in the same vicinity. The basins to be sampled will be from within the 20 (or 40) km sub-cells selected as indicated in Section 4.4 above. It is acceptable to sample basins which extend into adjoining subcells.

Samples should be collected from the inorganic fine-grained silt and clay fraction of the stream bed load. *In situ* precipitates should be avoided. Active sediment is the preferred material. A minimum of 10 grab samples should be collected in each stream from different parts of the stream bed over a minimum distance of 500 m. Collectively these constitute one site.



# FOREGS – European Geochemical Mapping



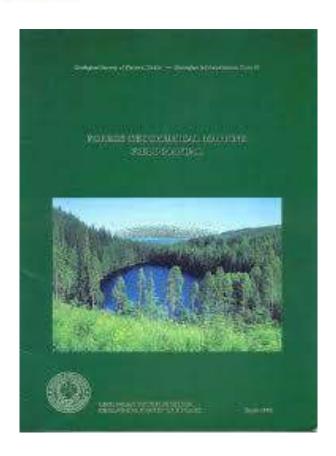


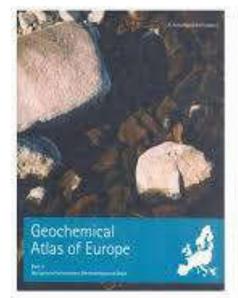
Project co-funded by the European Union

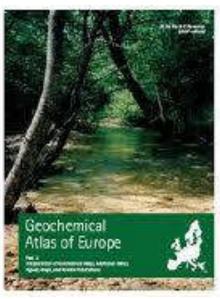
http://www.interreg-danube.eu/approved-projects/simona



# FOREGS – European Geochemical Mapping

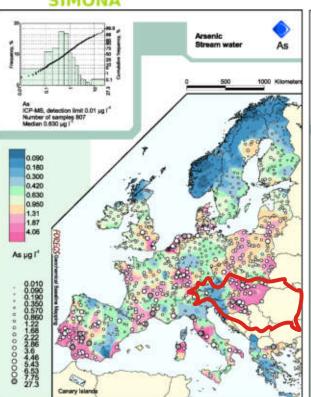


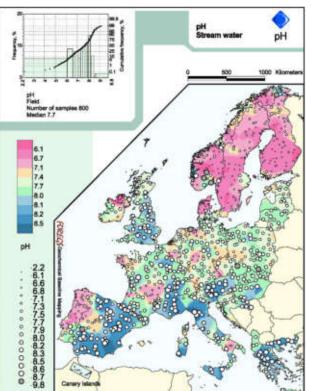


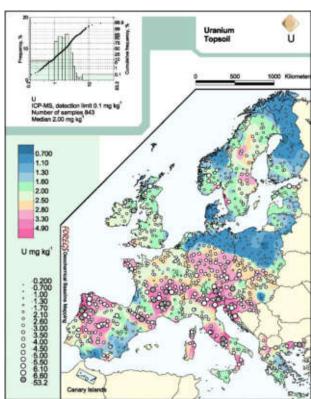




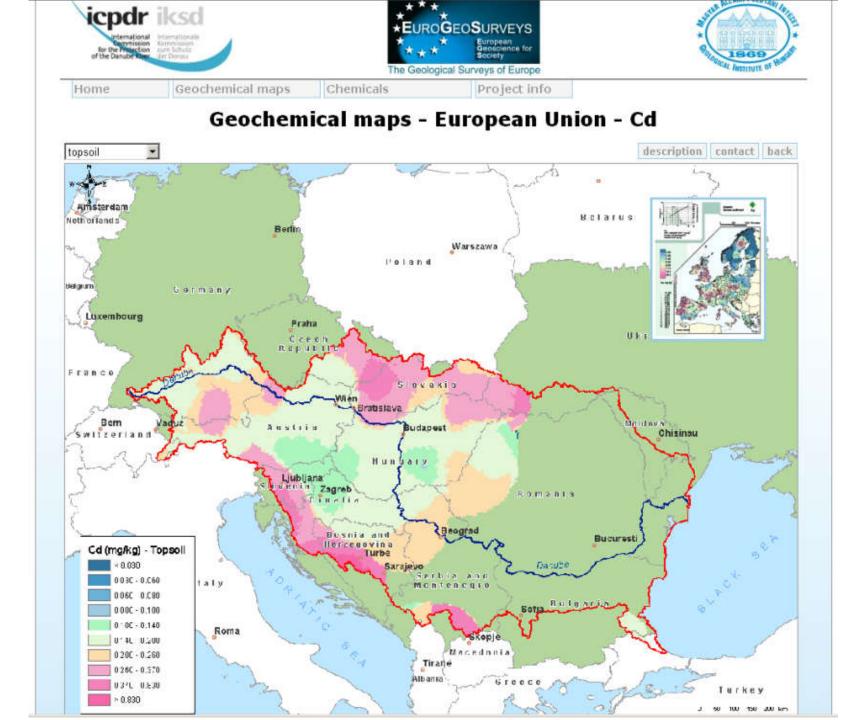
# FOREGS – European Geochemical Mapping





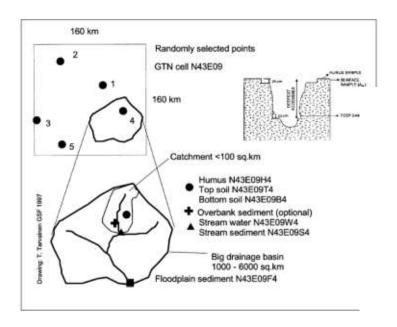


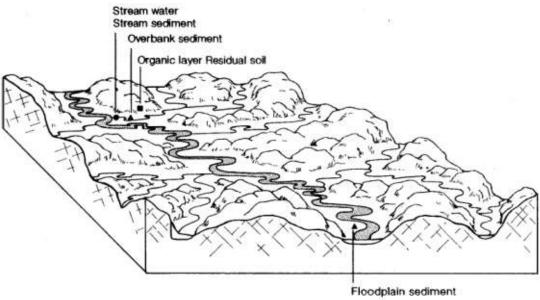
- Multi-media stream water, stream and floodplain sediment, soil (A and C horizons)
- Multi-element
- Composite (elements, parameters: pH, OM, etc.)
- Catchment-based
- Continental



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APPENDIX 1: Field observation sheets: Stream water/stream sediment, humus, soil, floodp sediment, overbank sediment	lain





fiagram showing possible sampling sites of GTN sampling media (modified after Strahler 1969).

Old terrace
Old floodplain sediment

Bedrock

Residual overburden

Gravel bed

Present floodplain sediments

Fig. 5. Block diagram showing residual overburden (soil), colluvium, old and present day floodplain sediments (modified after Strahler 1969).

- 3. Place the bottles in a cool unit, e.g. refrigerator.
- Send water samples to the laboratory soon after sampling.

#### 3.2 Stream sediment

Active stream sediment represents the fine- to medium-grained bed load material (silty-clayey-sandy), which is transported by running water. The active stream sediment is collected from the small, second order, drainage basin (< 100 km²) at a suitable site above its confluence point with the third order, channel of the large drainage basin

Studies into the distribution of trace eleme relation to the size fraction of stream sediments erally show that several elements including Mozn, Mn and Fe are concentrated in the finest tions of the sediment. The majority of stream ment surveys have, therefore, been based on the lection of <0.200 mm material. The IGCP 25 FOREGS standard sieve mesh is <0.150 mm a is fine enough to only include the very fine silt, clay and colloidal fractions, but is coarse ento yield sufficient fine material in the major

# 3.2.1 Stream sediment samples to be collected

Each stream sediment sample comprises material taken from 5-10 points over a stream stretch of 250 - 500 m. Prior to stream water and stream sediment collection, it is important to identify the 250 - 500 m stream stretch where obvious signs of contamination can be avoided and suitable sediment can be collected from 5-10 different locations. Sites should be located at least 100 m upstream of roads and settlements. Stream sediment sampling should start from the wa-

situations.

Studies in the UK have shown the recovery of stream sediments by dry sieving methods is not quantitative owing to the agglomeration of fine material to form larger particles which are then screened out in varying amounts. A system of wet sieving stream sediments wherever possible is therefore recommended for IGCP 259/360 and FOREGS.

It is important to avoid metal contamination at every stage of sampling as follows;

No hand jewellery or medical dressings should be worn during sampling. If medical dressings are worn, heavy duty rubber gloves must be worn at all times to avoid contamination of the samples.

Metal free polyethylene or unpainted wooden spades/ scoops should be used.

Metal free nylon sieve-mesh housed in inert wooden or metal free plastic frames should be used.

Metal free funnels and sample collection containers should be used.

If it is not possible to use non-metal equipment (e.g. spades and sieve frames), unpainted steel equipment should be used. Aluminium and brass equipment should be avoided.

Sampling sites should be selected sufficiently upstream of confluences with higher order streams to avoid sampling sediment that may result from a mixing of material from the two channels during flood



#### 3.2.2 Equipment

# 3.2.2.1 Equipment to be provided by regional laboratories:

- -Kraft paper bags
- -Polyethylene bags

# 3.2.2.2 Equipment to be purchased by each participant:

- -Heavy duty elbow length rubber gloves
- -Metal free polyethylene funnel
- -Sieve set with 2 preferably wooden or plastic frames containing nylon 2.0 mm mesh and nylon 0.150 mm mesh screens
- -Metal free gold pan or plastic bucket
- -Metal free plastic crates
- -Metal free plastic buckets or containers with lids
- -Trenching tool metal free, polyethylene (PE) or polypropylene (PP)
- -Permanent drawing ink marker (preferably black or blue)
- -Permanent ink pen
- -Maps (topographical maps, preferred scale 1:50 000)
- -Chisel-end geological hammer for dry areas (e.g. Mediterranean countries)
- -Bristle brush (dry sediment samples)

Field observation sheets are included in this

## 3.2.3 Sampling procedure

Mark the sample identifier on the Kraft paper bag using permanent ink marker. Mark the exact site location of the first and last subsamples on the field map by means of a small lines perpendicular to the stream flow. Complete the details of the field observation sheet.

Wet sieving is recommended whenever it is possible. Instructions for sampling with wet sieving method are presented in section 3.2.3.1. If it is not possible to wet sieve the stream sediment sample in the field, the collected stream sediment material should be dry sieved. Instructions for sampling and dry sieving are given in section 3.2.3.2.

## 3.2.3.1 Sampling and wet sieving

Once the site for sampling has been selected, mark the exact location of the first and last sampling points on the field map by means of a small line perpendicular to the stream flow using the ink pen. Mark the sample identifier number on map next to the sampling location. Complete the details on the field observation sheet. Write the sample identifier on the collection bucket and lid using the permanent drawing ink marker.

Rubber gloves are recommended for protection

-Enough coarse grained material should be collected to yield a minimum of 0.5 kg <0.150 mm material (dry weight).

The amount of coarse material required will vary substantially depending on the underlying geology and terrain. Geochemists should use their knowledge and judgement to assess how much coarse material will be required.

- -Mix the buckets of the coarse sediment thoroughly with the plastic stirring rod and carry them to the sieving location
- -Load sediment into the top sieve with the spade. If more than one bucket of coarse sediment has been collected, equal amounts of sediment should be loaded into the sieve from each bucket in turn.
- -Rub the material through the top sieve wearing rubber gloves for protection.
- -Take care to remove large stones from the sediment by hand.
- -Once the bottom sieve contains a reasonable quantity of <2 mm sediment, remove the top sieve and discard the >2 mm material.
- -The <2 mm sediment in the bottom sieve is washed and rubbed through the sieve with the aid of water and shaken down.
- -It is very important at this stage that coarse material which would bias the sample does not enter the collection bucket. This may be avoided by carefully washing the outside of the bottom sieve prior to shaking.

-In order to enhance the trace element signature, it is

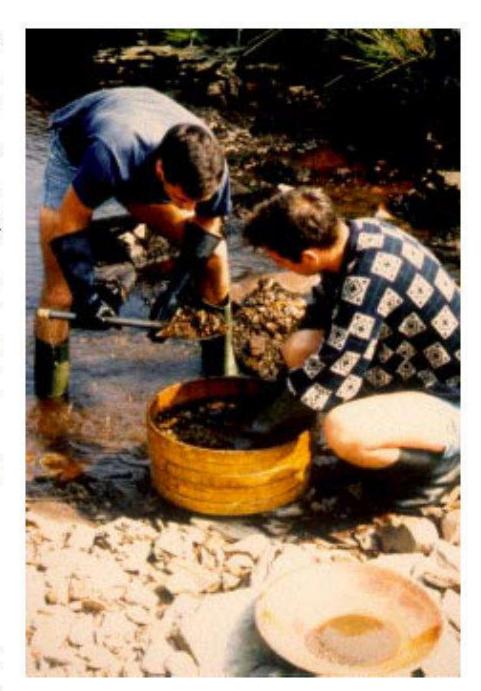
recorded on the field sheet and on a sample check-list sheet.

- -Once the sample has been homogenized, carefully transfer the sample into the Kraft bags using a clean plastic funnel.
- -The Kraft bags should be hung out to air dry at the field base for as long as possible.
- -When moving the samples, place each Kraft bag in a 15 x 40 cm polythene bag and secure the top of the bag with a knot to prevent loss or cross contamination of samples during transport.
- -The samples should be secured upright in a plastic crate or box and transported carefully to the next location or to the Survey base for further drying.
- -At the Survey base or laboratory, the samples should be completely dried at < 40°C. Freeze drying is a recommended as this helps to disaggregate the samples. Dried samples should be sent to LAB I.

All sampling equipment must be thoroughly cleaned between each site to avoid cross contamination.

### 3.2.3.2 Sampling and dry sieving

The procedure for the selection of sample sites, recording their location on the field map, completion of field observation sheets, wearing of rubber



be a field composite sample from 3 - 5 subsamples in the field. Minimum distance between any two subsamples should be 5 m. Avoid sampling adjacent to roads (minimum distance 10 m) or ditches (minimum distance 5 m), but you are free to use your discretion depending on the traffic density and prevailing local conditions.

Living surface vegetation, fresh litter, big roots and rock fragments (stones) are removed.

In case the whole soil profile does not reach a depth of 75 cm, the lower sample should be taken from a depth, that can be undoubtely identified as the BCor C-horizon (do not forget to note this down under remarks on the field observation sheet!). If this is not possible another sample site should be selected.

The subsoil sample is taken first, and then the topsoil sample. This procedure avoids cleaning the surface of the subsoil from fallen top soil, if the latter is taken first.

After collection of each sample clean thoroughly the sampling equipment.

#### OPTIONAL:

From one sampling site of a duplicate cell 2 kg of bottom floodplain sediment + 2 kg of bottom floodplain sediment (duplicate sample) and from all other sampling sites 2 kg of bottom floodplain sediment.

from the same site, the close-up photo can show both the character of organic layer and mineral soil horizons (see below). In this case, separate photographs for the soil sample site will not be needed.

At each soil sample site two photographs should be taken; the first to show the general view about the sampling site (Fig. 9), and the second a close-up of one of the soil sample pits (Fig. 10). Before taking

#### 3.4 Floodplain sediments

A floodplain sediment, representing the alluvium of the whole drainage basin will be collected from the alluvial plain at the lowermost point (near to the mouth) of the large catchment basin (1000 - 6000 km<sup>2</sup>).

Both floodplain and overbank sediments are finegrained (silty-clay, clayey-silt) alluvial soils of large and small floodplains respectively, according to the size distinction made by Darnley et al. (1995). Floodplain and overbank sediments are deposited during flood events in low energy environments (Ottesen et al., 1989); they should, therefore, be devoid of pebbles, which indicate medium energy environments. The surficial floodplain and overbank sediments are normally affected by recent anthropogenic activities, and may be contaminated. Deeper samples, which are optional sample media, normally show the natural background variation.

# 3.4.1Floodplain sediment samples to be taken

From the first sampling site of a duplicate cell (one in each country) collect:

- 2 kg of top floodplain sediment + 2 kg of top floodplain sediment (duplicate sample)

From all other sampling sites collect:

- 2 kg of top floodplain sediment

Enough material must be taken to yield minimum 0.5 kg of <2 mm grain size sediment. Larger sample quantities can be taken and stored separately in each country.

Floodplain sediments



Fig. 11. Floodplain sampling in southwestern Finland (Photo: Reijo Salminen, GSF).

#### 3.5 Overbank sediments

An overbank sediment, representing the alluvium of the small drainage basin will be collected from its alluvial plain near to the confluence point of the small, second order, stream (< 100 km<sup>2</sup>) with the main, third order, river.

#### 3.5.1 Overbank sediments to be taken

All overbank sediment samples are optional. FOREGS laboratories will not provide analyses of



Fig. 12. Floodplain sediment sequence with soil development in Greece. Meter: coloured sections 20 cm. Fine-grained clay and silt down to a depth of 75 cm (low energy floodplain sediment - good for sampling, soil has developed down to a depth of 25-29 cm). Coarse-grained sandy and bebbly unit between 75-100 cm (high energy environment). Sandyclay unit between 100-134 cm (low-energy environment). Gravel bed below a depth of 134 cm. Photo: A. Demetriades, IGME.

### **Sample preparation**

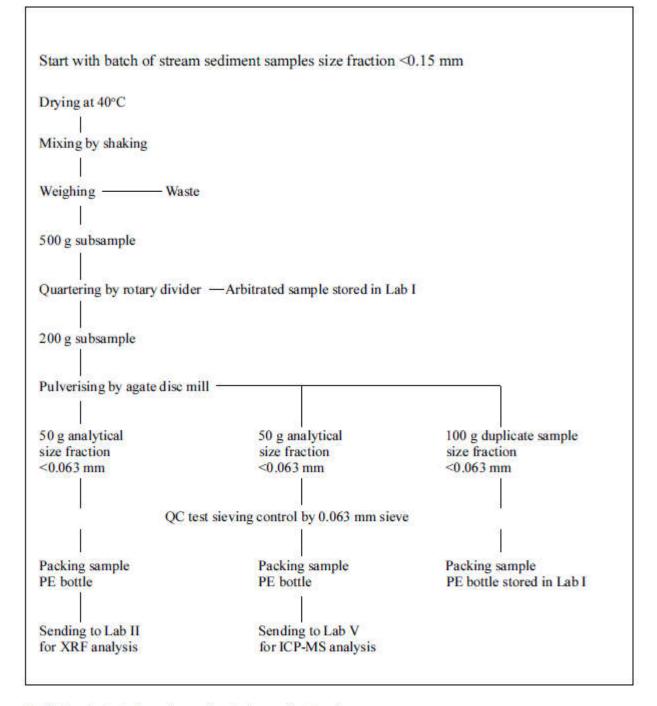


Fig. 13. Screening standard operating procedure for stream sediment samples.

#### **Field sheet**

#### FOREGS GEOCHEMICAL BASELINE PROGRAMME

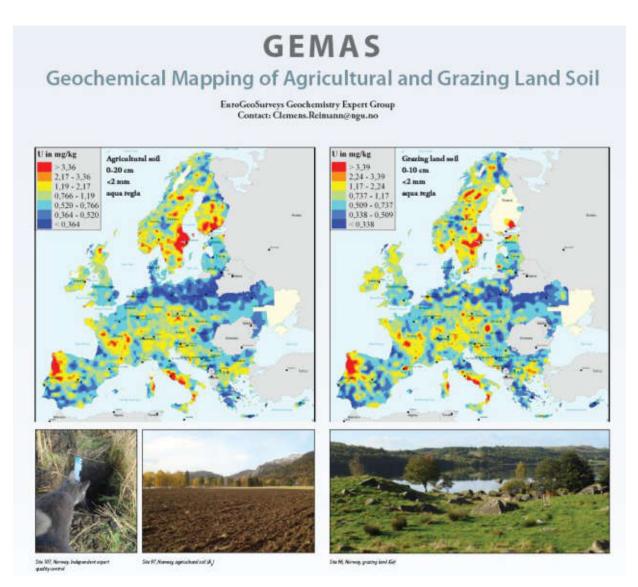
#### FLOODPLAIN SEDIMENT

TOP ID	Date		Sampler	
BOTTOM ID		Country		
(Bottom floodplain sample i	is optional)	Organisation	n	
55 4000 505	200	rent from above		
SAMPLE SITE LOCATION	I BEGIC	ON	Κ.	MAP SHEET
COORDINATES (De				Mr Office)
		s mandatory)	Modhina	
National grid Decimal degrees			Northing Latitude	
	Longitude		Latitude	Datum
Altitude (m) DESCRIPTION OF CATCH	MENT DACIN	_		
			15.2	
Approximate size of				
	apny			
Land use				
□ Agriculture		22.77		
7/=: 18	rassland, fallow	field		
□ Forest:				
□ Wetland				
	ated, moorland	etc.		
□ Other, spe	NG 55	5		
Predominant bedroo				
catchment basin _			<del></del> 0	
SITE DESCRIPTION				
River width	m, de	epth	m	
Grain size range at :				
Abundance of clasts	> 2 mm in %:			
Depth of observed g				
				cm
Possible sources of				
	and photo ID			
Site				
GAMMA-RADIATION	Total	Th	U	к
Instrument	9====			
REMARKS				



# GEMAS – European Soil Chemistry Atlas

#### **Quality Control**





# GEMAS – European Soil Chemistry Atlas

#### **TRAINING!**





# Harmonisation of Analytical methods for Sediment-quality Information, Monitoring and Assessment System

Péter Fodor Szent István University

Fodor.Peter@etk.szie.hu



## **Self introduction:**

Diploma at Technical University of Leningrad.

PhD at Technical University of Budapest (Dept. of General and Analytical Chemistry)

Post doc at Univ. of Massachusetts (Amherst)

From 1988-2008. Head of Dept. Applied Chemistry of Food Science Faculty

From 1992 Doctor of Hung.Sci. Ac.

From 1995 Head of the Accreditation board of Hungary and member of Codex Alimentarius.











## **Our Task: Develop Protocols for:**

- 1. Analytical methods for measuring pesticides
- 2. Analytical methods for measuring organic industrial pollutions
- 3. Analytical methods for measuring inorganic compounds as heavy metals



## Which component to measure?

COMMON IMPLEMENTATION STRATEGY
FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC)
Guidance Document No. 25

As a rule of thumb, compounds with a log Kow>5 (octanol-water) should *preferably* be measured in **sediments,** or in suspended particulate matter (SPM), while compounds with a log Kow<3 should preferably be measured in water.



Anthracene (PAH)

**Brominated diphenyl ethers** 

**C10-13-chloroalkanes**  $C_{10}H_{18}CI_4$  and  $C_{13}H_{21}CI_7$ 

Chlorpyrifos (-ethyl, -methyl)

Di(2-ethylhexyl)phthalate (DEHP) (PVC)

Fluoranthene (PAH)

Hexachlorobenzene

Hexachlorobutadiene

Hexachlorocyclohexane -Lindane

Nonylphenols (detergent)

Pentachlorobenzene (PAH-pesticide)

Polyaromatic Hydrocarbons: Benzo(a)pyrene,

Benzo(b)fluoranthene, Benzo(g,h,i)perylene,

Benzo(k)fluoranthene, Indeno(1,2,3-cd)-pyrene

**Trifluralin** 

**DDT** (including DDE, DDD)

**Aldrin** 

**Endrin** 

Dieldrin



Priority Substances relevant to the European Comission's 2012 proposal under the Water Framework Directive:

Pesticides (herbicides, insecticides): Aclonifen, Bifenox, Cypermethrin, Dicofol, Heptachlor, Heplataclorepoxide, Quinoxyfen, Cybutrine, Dichlorvos, Tetrabutryn Industrial chemicals: Perflourooctane sulfonic acid(PFOS), Hexabromocyclo-dodecane (HBCDD)

Combustion by products: Dioxins and dioxin-like PCB-s
Pharmaceutical substances (steroids-hormons): 17-alphaethinylestradiol, 17-beta-estradiol, Diclofenac



16 Pesticides (herbicides, insecticides): Aclonifen,
Aldrin, Bifenox, Cypermethrin, Chlorpyrifos (-ethyl, -methyl),
DDT (including DDE, DDD), Dicofol, Dieldrin, Endrin,
Heptachlor, Heplataclorepoxide, Quinoxyfen, Cybutrine,
Dichlorvos, Tetrabutryn, Trifluralin
+ Hexachlorobenzene, Hexachlorocyclohexane

**EPA 8270** 

Degradation of DDT to form DDE (by elimination of HCl, left) and DDD (by reductive dechlorination, right)



Polyaromatic Hydrocarbons: Anthracene, Benzo(a) pyrene, Benzo(b) fluoranthene, Benzo(g,h,i) perylene, Benzo(k) fluoranthene, Indeno(1,2,3-cd)-pyrene, Fluoranthene,

EN 16181:2018



# Semivolatile organic compounds:

Brominated diphenyl ethers EPA 1614A

C10-13-chloroalkanes EN ISO 12010

Hexachlorobutadiene EPA 8260C



## **Industrial chemicals:**

Perflourooctane sulfonic acid(PFOS)

**CEN/TS 15968** 

Nonylphenols

EN ISO 18857-2

**Hexabromocyclo-dodecane (HBCDD)** 

No standardized method

Chemosphere 82 (2011) p. 698-707:

"Determination of HBCD isomers by isotopic dilution

LC-MS/MS"



# Pharmaceutical substances: steroids

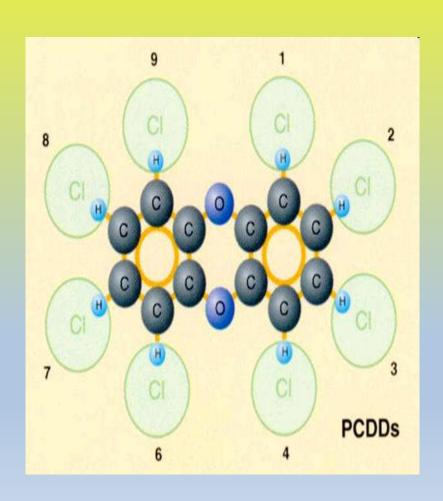
17-alpha-ethinylestradiol, 17-beta-estradiol EPA 1698

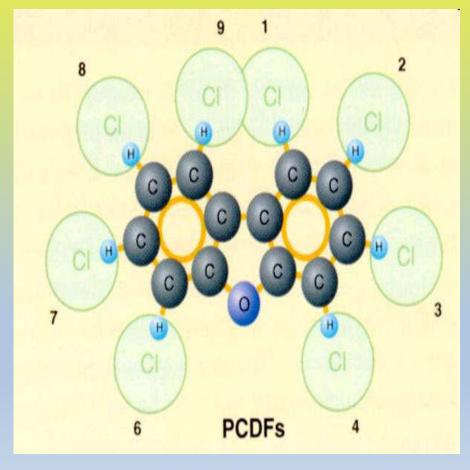
Hormon Diclofenac

**EPA 542** 



# Combustion by products: Dioxins and dioxin-like PCB-s EPA 8280B





Congener	TEF value	Congener	TEF value
Dibenzo-p-dioxins (PCDDs)		Dioxin-like PCBs: Non-ortho PCBs	
2,3,7,8-TCDD	ī	+ Mono-ortho PCBs	
1,2,3,7,8-PeCDD	1	Non-ortho PCBs	
1,2,3,4,7,8-HxCDD	0.1	PCB 77	0,0001
1,2,3,6,7,8-HxCDD	0,1	127 Market 179-1	
1,2,3,7,8,9-HxCDD 0,1		PCB 81	0,0001
1,2,3,4,6,7,8-HpCDD	0,01	PCB 126	0,1
OCDD	0,0001	PCB 169	0,01
Dibenzofurans (PCDFs)		Mono-ortho PCBs	
2,3,7,8-TCDF	0,1	PCB 105	0,0001
1,2,3,7,8-PeCDF	0,05	PCB 114	0.0005
2,3,4,7,8-PeCDF	0,5	Discribe-36 Artist-43	in processors
1,2,3,4,7,8-HxCDF	0,1	PCB 118	0,0001
1,2,3,6,7,8-HxCDF	0,1	PCB 123	0,0001
1,2,3,7,8,9-HxCDF	0,1	PCB 156	0,0005
2,3,4,6,7,8-HxCDF	0,1 0,01	PCB 157	0,0005
1,2,3,4,6,7,8-HpCDF		Sease and Sease	
1,2,3,4,7,8,9-HpCDF	0,01	PCB 167	0,00001
OCDF	0,0001	PCB 189	0,0001







<u>Inorganic components</u>: Elements of the periodical system-mainly not contaminats but geochemical (like soil) characterisation.

Suggested method: EN 21470-50:2006

2 g soil + 5 ml cc.HNO<sub>3</sub> +2 ml H<sub>2</sub>O<sub>2</sub> =>> 50ml

Any detection method can be used, but please report:

- -traceability
- -validation
- -proficiency testing



## What I dont plan:

- 1. Harmonize home made analytical methods-when we have internationally accepted method.
- 2. Analyses samples in a lab., which has not real possibility to get positive data.



## Tasks I.

- 1. Please obtain the recommended methods.
- 2.Read carefully and make decision, are you able to fulfil all requirements, or you have to give the task to an accreditated lab. in the future.
- 3.Please let to know to...... until....., who will do the analysis at home, who will give to accreditated lab.
- 4.Those who will do at home, let to know to....., until......what kind of Proficiency Test the lab past, or do the lab needs to participate in the future.



<u>Tasks II</u>: (As Analytical methods are in the middle beetwen Sampling and Evaluation)

Task for sampling:

On the basis of recomended Analytical method.

II.1. Pls calculate the amount of samples (how many grams from one sampling place)

II.2.Plan the physical condition of sampling and the shipment Task for evaluation:

How many data is needed for evaluation.



Thank you for attention! Questions Please!



Participants	Suggested method for pesticide analysis
AITB-GBA	non
Bulgaria	VIM 1014/2010, EN ISO12918
Croatia	non
Hungary	WBSE-125:2016 GC-MS, WBSE-123:2016 LC-MS
Moldova	EPA 1699, EN ISO12918
Montenegro	non
Republika Srpska	EPA 508.1:1994
Romania	ISO 10382:2002
Slovakia	US EPA 8010 US EPA 8015
BH-Federation	EPA-508.1:1994
Slovenia, Ukraina	non