

QUESTIONNAIRE FOR EXISTING SAMPLING, LABORATORY AND EVALUATION METHODS

0.0. State your institution and country.

0.1. State institution(s) from which you got data to fill this questionnaire.

I. LEGISLATIVE FRAMEWORK

I.1 Enumeration of national or European 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, drinking water, river sediments, marine sediments, sewage, therapeutic sludge, air and biota.

[PLEASE, SUPPORT YOUR ANSWERS WITH REFERENCES (NATIONAL LEGISLATIVE DOCUMENTS AND/OR WEB LINKS)]

No	Title (in national language)	Title (in English)	Link	Country
1				
2				
3				

I.2 List of dangerous (hazardous) substances (metals, non-metals, PAHs, PCBs, other parameters) concentration levels, their significance (*definition of terms used for thresholds*) in waters, solids or biota, in accordance with the national legislative framework.

Alert threshold = concentrations of pollutants in air, water, soil or in emissions/discharges, which, when reached, warn the competent authorities on a potential impact on environment and trigger an additional monitoring and/or reduction of pollutant concentrations in emissions/discharges.

Intervention threshold = concentrations of pollutants in air, water, soil or in emissions/discharges, which, when reached, determine the competent authorities to order risk assessment studies and reduction of pollutant emissions from emissions/discharges.

Each country, please deliver the definition of specific terms in the respective law.

Table 1 Metal trace elements in soils

Trace Element	Levels in soils (mg/kg)					
	A) normal values*		B) alert threshold		C) intervention threshold	
Values based on use category	A1	A2	Sensitive B1	Less sensitive B2	Sensitive C1	Less sensitive C2
Mercury (Hg)	0,1		1	4	2	10
As						
Cd						
Cr						
Cu						
Ni						
Pb						
Zn						

*Referring to Normal values, for example, in Romania, there is a single set of **normal** values for all types of soils (probably an average value). Taking into account that some other countries could have more sets of normal values (depending on soil type, region etc.), more columns can be added in the table by the respective country.

Table 2 Metal trace elements in river water

Trace Element	Levels in river water (µg/l)					
	A) normal values		B) alert threshold		C) intervention threshold	
Values based on use category	A1	A2	Sensitive B1	Less sensitive B2	Sensitive C1	Less sensitive C2
Mercur (Hg)						
As						
Cd						
Cr						
Cu						
Ni						
Pb						
Zn						

Table 3 Metal trace elements in drinking water

Trace Element	Levels in drinking water ($\mu\text{g/l}$)					
	A)normal values		B)alert threshold		C)intervention threshold	
Values based on use category	A1	A2	Sensitive B1	Less sensitive B2	Sensitive C1	Less sensitive C2
Mercur (Hg)						
As						
Cd						
Cr						
Cu						
Ni						
Pb						
Zn						

Table 4 Non-metal trace elements in soils

Trace Element	Levels in soils (mg/kg)					
	A)normal values		B)alert threshold		C)intervention threshold	
Values based on use category	A1	A2	Sensitive B1	Less sensitive B2	Sensitive C1	Less sensitive C2
F						
Cl						
S						
Br						
I						

Table 5 Non-metal trace elements in river water

Trace Element	Levels in river water (µg/l)					
	A)normal values		B)alert threshold		C)intervention threshold	
Values based on use category	A1	A2	Sensitive B1	Less sensitive B2	Sensitive C1	Less sensitive C2
F						
Cl						
S						
Br						
I						

Table 6 Non-metal trace elements in drinking water

Trace Element	Levels in drinking water (µg/l)					
	A)normal values		B)alert threshold		C)intervention threshold	
Values based on use category	A1	A2	Sensitive B1	Less sensitive B2	Sensitive C1	Less sensitive C2
F						
Cl						
S						
Br						
I						

Please complete the list of HSs according to national documents with:

- Table of Polycyclic Aromatic Hydrocarbons –PAHs,
- Table of Polychlorinated Biphenyls-PCBs,
- Table of microbiological parameters, as well as other parameters that are provided in national legislations

I.3 Quality objectives for hazardous substances (please complete the tables of HSs according to national documents)

Dangerous substance (HS)	Water quality objective (µg/l)	Quality target for sediment (mg/kg)	Quality objective for biocenosis (mg/kg)
Cd	5	10	-mollusks (as far as possible Mytilus edulis) and fish.
Hg	0.1	-	0.3 mollusks and fish

I.4 Listing of analytical standards (national analytics and international e.g. USEPA, ASTM, etc.) recommended in documents for chemical, physical, microbiological analyzes of samples

Element	National analytical standards					International analytical standards					“in-house” developed methods”					
Mercury in drinking water						USEPA-Method 245.1.										
Mercury (Hg) in solids samples (sediments)						-EPA Method 7473 -U.S. EPA Method 245.5(CVAAS) -ASTM D6722 - thermal decomposition * -ASTM D6414-99 (wet digestion)										
Etc.																

*ASTM=American Society for Testing and Materials

I.5. List of chronic or acute toxicity tests and determination of bioaccumulation or persistence in biota according to the specificity of the dangerous substance in the trophic chain (Ex: Microtox test - The potential ecological impacts of anaerobic degradation of vegetable oil on freshwater sediments; Hyalella Azteca etc).

I.6 List of national, and international guides of techniques on the design of sampling, transport, storage, samples preparation (sieving, fraction extraction, separation, etc.) recommended in documents

Nr		sediment	soil	water
1	sampling	SR ISO 5667-12/2001 https://www.iso.org/standard/32423.html		
2	Transport, storage	No	ISO 10381-2/2001 https://www.iso.org/standard/32424.html	

I.7 Specify the recommended remedy measures associated with the contents of the hazardous substances (alert threshold, intervention threshold)

II PRACTICES, EXPERIENCES

II.1. Significant national, European, finalized or ongoing projects related to geochemistry of waters, soils, sediments in the Danube basin

No.	Project title (national language, if available)	Project Title (EN)	Year	Country	Project coordinators, Partners

II.2. Significant scientific papers, books, related to geochemistry of waters, soils, sediments in the Danube basin

No.	Paper title (national language, if available)	Title (EN)	Year	Country	Authors

II.3 Existent waterbodies and sampling sites (Ramsar, Natura2000 etc.) and current quality monitoring stations of the Danube River

Danube River Quality Monitoring Stations

No.	Site	Country
1		
2		
3		
4		
5		
6		

No.	Site coordinates (North, East) in WGS84 system (at least seven decimals points)	Project title (national language)	Project title (EN)	Year	Country	Obs.(type of analysis, purpose of monitoring, sampling rate)
1						
2						
3						

II.4. Data and metadata availability (including information on ambient or natural concentrations of HSs for establishing intervention measures)

The list of past or current economic polluters referring to the direct effect on the quality of sediment in the Danube (the HSs whose possible concentrations are likely to be exceeded), information on the HSs biological effects, evidence of impact of anthropogenic activities.

II.5. Problems of current monitoring procedures in DRB

III. INVENTORY OF SAMPLING METHODOLOGIES

III.1. Water

III.1.1. Sampling design strategy. How do you choose sampling locations, number of sites, sampling position within the national Danube sector, distance from confluence points, distance from point industry/agriculture polluters, distance from big cities, sampling depth, distance from the water course/bodies banks? How do you decide about temporal frequency of collecting samples?

III.1.2. Which parameters of water **quality/quantity** are measured *in situ*?

III.1.3. Which **instruments** are used for *in situ* measurements (include manufacturer and type)?

III.1.4. Please, describe **methodology** for *in situ* measurements.

III.1.5. Which **tools** are used for collecting samples for **laboratory** measurements (include manufacturer and type)?

III.1.6 Sample preservation (samples chemical preservation according to their type and used analysis method).

III.1.7 Please, describe a **methodology** for collecting samples

III.2 Sediment

III.2.1. Which type(s) of sediment do you sample/measure **bottom, suspended, floodplain**?

III.2.2. Sampling design strategy. How do you choose sampling locations? How do you decide about temporal frequency of collecting samples?

III.2.3. Which parameters of sediment **quality/quantity** are measured *in situ*?

III.2.4. Which appropriate sampling devices (e.g. GRAIFER, CAROTIER etc.) and instruments are used for *in situ* measurements (include manufacturer and type)?

III.2.5. Please, describe **methodology** for *in situ* measurements.

III.2.6. Which **tools** are used for collecting samples for **laboratory** measurements (include manufacturer and type)?

III.2.7. Please, describe a **methodology** for collecting samples for **laboratory** measurements.

III.2.8. Please, describe a **transport** methodology for samples intended for laboratory measurements.

III.2.9. Do you **archive** samples? If yes, please describe how.

III.3 . Biota

III.3.1. Which type(s) of **biota** do you sample/measure: **flora, fauna** (name species)?

III.3.2. Sampling design strategy. How do you choose sampling locations? How do you decide about temporal frequency of collecting samples?

III.3.3. Which parameters of biota **quality/quantity** are measured *in situ*?

III.3.4. Which **instruments** are used for *in situ* measurements (include manufacturer and type)?

III.3.5. Please, describe **methodology** for *in situ* measurements.

III.3.6. Which **tools** are used for collecting samples for **laboratory** measurements (include manufacturer and type)?

III.3.7. Please, describe a **methodology** for collecting samples for **laboratory** measurements.

III.3.8. Please, describe a **transport** methodology for samples intended for laboratory measurements.

III.3.9. Do you **archive** samples? If yes, please describe how.

[PLEASE, SUPPORT YOUR ANSWERS WITH REFERENCES (NATIONAL LEGISLATIVE DOCUMENTS AND/OR WEB LINKS)]

IV. INVENTORY OF LABORATORY METHODOLOGIES

IV.1. How do you **mechanically prepare samples** for measurement (drying, sieving, grinding, homogenization, etc.)?

- a) water
- b) sediment
- c) biota?

IV.2 Chemicals.

Granulometric analysis (information on the correlation of particle sizes and the absorption of toxic metals or metal compounds in sediments).

Analytical methods (including sample preparation: e.g. acid digestion, etc.) for the hazardous substance analyzed in agreement with the matrix in which it is being analyzed (water, sediment, sludge).

Type of analytical equipments.

Description of internal procedures

IV.2.1. Organic matter. What is the **procedure** for **organic matter** content determination in water and sediment?

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

IV.2.2.1. Which system of analysis do you use (ICP-MS, ICP-AES, etc.)? Please, include manufacturer and type.

IV.2.2.2. Which **elements (HSs)** do you measure by this system? Please, state **detection limits** for measured elements (HSs).

IV.2.2.3. Please, describe **sample preparation and procedure** for these measurements (microwave acid digestion, another disintegration procedure, gas velocity, temperature of atomization, mirrors position, nebulizer type, excitation power, wavelengths etc.).

IV.2.2.4. How do you calculate **accuracy and precision** (references)?

IV.2.3. AAS systems

IV.2.3.1. Please, state manufacturer and type of AAS (F-AAS, GF-AAS) instrument you use.

IV.2.3.2. Which **elements (HSs)** do you measure by AAS? Please, state **detection limits** for measured elements (HSs).

IV.2.3.3. Please, describe **sample preparation and procedure** for AAS measurements (dissolution, radiation source, source temperature, wavelengths, etc.).

IV.2.3.4. How do you calculate **accuracy and precision** (references)?

IV.2.4. XRF

IV.2.4.1. Please, state manufacturer and type of XRF(EDXRF,WDXRF) instrument you use.

IV.2.4.2. Which **elements and/or compounds** (HSs) do you measure by **XRF**? Please, state **detection limits** for measured elements and/or compounds (HSs).

IV.2.4.3. Please, describe **preparation of the sample and procedure** for XRF measurements.

IV.2.4.4. How do you calculate **accuracy and precision** (references)?

IV.2.5 DC-arc –AES

IV.2.5.1. Please, state manufacturer and type of instrument you use (type of detectors etc.).

IV.2.5.2. Which **elements and/or compounds** (HSs) do you measure by **DC-arc-AES**? Please, state **detection limits** for measured elements and/or compounds (HSs).

IV.2.5.3. Please, describe **preparation of the sample and procedure** for DC-arc-AES measurements.

IV.2.5.4. How do you calculate **accuracy and precision** (references)?

IV.2.6. Radionuclides

IV.2.6.1. **Which instrumental method(s)** you use to detect radionuclides in water, sediment and/or biota? Please, state manufacturer and type of radionuclide detection instrument you use.

IV.2.6.2. **Which radionuclides** do you measure? Please, state **detection limits** for measured radionuclides.

IV.2.6.3. How do you calculate **accuracy and precision** (references)?

IV.2.7. Organic compounds (HSs)

IV.2.7.1. **Which instrumental method(s)** you use to detect organic compounds (HSs) in water, sediment and/or biota?

IV.2.7.2. **Which organic compounds (HSs)** do you measure?

Please, state **detection limits** for measured organic compounds (HSs).

IV.2.7.3. How do you calculate **accuracy and precision** (references)?

IV.2.8. XRD

IV.2.8.1. Please, state manufacturer and type of XRD instrument you use.

IV.2.8.2. Do you use **XRD for sediment analysis**?

IV.2.8.3. Please, describe **preparation of the sample and procedure** for XRD measurements

IV.3 Inventory of national laboratories where dangerous substances are analyzed, specifying whether they have accreditations on the quality of analyzes (certificate issued by the national body attesting the quality of the analyzes), price and time of analyses.

IV.4 Description of "good practices" in laboratory and "in situ" analysis. For example, ways to convert analytical data obtained from sediment analysis to water quality assessments (taking into account the high cost of water analysis compared to the sediment).

IV.5 Description of protocols for intercomparison and intercalibration between laboratories. List of national and international projects which had developed the Protocols.

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V .INVENTORY OF EVALUATION METHODS

V.1. How **threshold values** for HSs are set in each type of media (sediment, water, biota)? (e.g. average of the last measured values, average with the treatment of outliers, average of the values measured in areas without anthropogenic influence, enrichment factor, conservative **elements** for normalization, etc.).

V.2. Are **threshold values fixed or variable** and do they depend on the sample form, drainage basin lithology, time of the year, etc.?

V.3. Do you use **corrections for threshold values**? (amount of **quartz, organic matter** etc.).

V.4 The environmental quality objectives are based on measuring the total metal concentration and / or some dangerous compounds of that metal in different valence states?

V.5 How the legislation reflects the phenomenon of “bioaccumulation”? Is the type of biota correlated with the ecosystem?

V.6. Does your national legislative find **categories of environment quality** based on deviations from threshold values?

V.7. Can these categories be **defined by quality of more than one medium**?

V.8. Please, describe **algorithm** for **defining** these **categories**? (e.g. weight coefficients).

V.9. How does your legislative framework define **difference** between **contamination** and **pollution**?

V.10. Do you **relate specific HSs** with **sources of contamination and pollution** and how?

V.11. Please, describe **actions** in case of contamination and pollution.

V.12. How do you **present results** in your **reports**, e.g. do you use complex representation for scientific community or simple representation for target groups? Does the report include methodology, full results, QA/QC, models? Are these results public or can be obtained by request?

V.13. Do you have a method for **space-time risk assessment** after determination of contamination and/or pollution?

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VI. SELECTED REFERENCES:

Stuart L Simpson, Graeme E Batley, Anthony A Chariton, Jenny L Stauber, Catherine K King, John C Chapman, Ross V Hyne, Sharyn A Gale, Anthony C Roach, William A Maher ***Handbook for Sediment Quality Assessment***, CSIRO, 2005

Williamn, R.B., Mills, G.N. (2009) sediment Quality Guidelines for the Regional Discharges Project. Prepared by Diffuse Sources Ltd. For Auckland Regional Council. Auckland Regional Council Technical Report 2009/050

Watch Your Danube Joint Danube Survey Fact Sheet 1 ICPDR IKSD. JDS3 Scientific Scope

Method Implementation Document for EN 14385. BS EN 14385:2004. Stationary source emissions – Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V. Measurement of metals including an option to measure mercury. Environment Agency, Version 4, December 2013.

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G. Allen Burton, Jr. Sediment quality criteria in use around the world. Received: December 26, 2000 / Accepted: December 28, 2001

Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Protocol for the Derivation of Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Canadian Council of Ministers of the Environment 1995. CCME EPC-98E.

Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Summary Tables. Canadian Council of Ministers of the Environment. Updated 1999, Winnipeg.

Environment Canada and Ministère du Développement durable, de l'Environnement et des Parcs du Québec. 2007. Criteria for the Assessment of Sediment Quality in Quebec and Application Frameworks: Prevention, Dredging and Remediation. 39 pages.

Review of Sediment Quality Data for the Similkameen River Department of Ecology. Publications Distributions Office. Address: PO Box 47600, Olympia WA 98504-7600 E-mail: ecypub@ecy.wa.gov

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