

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	Handlungsa nweisung für den Umgang mit Baggergut aus Bundeswas serstraßen im Binnenland (HABAB- WSV 2017)		https://izw.baw.de/publikationen/umwelt-handbuch/0/20180403_HABAB_WSV%202017.pdf	DE
2	Oberflächen gewässerve rordnung vom 20.06.2016	German Directive for the protection of surface waters as of 20.06.2016	https://www.gesetze-im-internet.de/ogewv_2016/OGewV.pdf	DE
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
Mercur (Hg)						
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 (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 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)	AA-EQS for inland waters µg/L	AA-EQS for SPM or sediments (mg/kg dry weight)	Quality objective for biota (mg/kg fresh weight)
As		40	
Cr		640	
Cu		160	
PCB-28	0,0005*	0,02	
PCB-52	0,0005*	0,02	
PCB-101	0,0005*	0,02	
PCB-138	0,0005*	0,02	
PCB-153	0,0005*	0,02	
PCB-180	0,0005*	0,02	
Triphenyltin-cation	0,0005*	0,02	
Zn		800	

AA-EQS for water for PCB and triphenyltin-cation will only be used when the analysis of sediment/SPM is not possible.

For other HSs the AA-EQS for water and the biota-EQS are listed in the German Directive for the protection of surface waters as of 20.06.2016, annexes 6 and 8.

AA-EQS for SPM/sediments refer to

- the total sample when using a centrifuge for sampling
- the fraction <63 µm for metals
- the fraction <2 mm for organic parameters (can only be adopted if the fraction <63 µm is >50%)

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”

Etc.													

No methods specified in the German Directive for the protection of surface waters as of 20.06.2016, but the methods used must fulfil the requirement of Directive 2009/90/EU

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			
2	Transport, storage			
	Sample preparation			

No specific standards mentioned in the documents.

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 = **Surveillance Monitoring Sites according to WFD**

No.	Site	Country
1	Böfinger Halde	DE
2	Schäfstall Pegel	DE
3	Dillingen	DE
4	Bittenbrunn	DE
5	Kelheim	DE
6	Bad Abbach	DE
7	Niederalteich	DE
8	Deggendorf	DE
9	Jochenstein	DE

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**?

Suspended particulate matter (SPM)

III.2.2. Sampling design strategy. How do you choose sampling locations?

Surveillance monitoring sites according to WFD

How do you decide about temporal frequency of collecting samples?

4 samples/year = minimum requirement of WFD

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)?

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

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

- *Sedimentation boxes*

- *High-performance centrifuge (Company: Padberg, Lahr)*

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

Sedimentation boxes are exposed for at least 4 weeks (if possible 1m beneath the surface), wet sieving

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

Shipment of material in brown glass bottles overnight

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

Rests of samples are stored at -20°C

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: *wet sieving, freeze-drying and grinding for metal analysis, chemical drying with sodium sulphate (water-free) and grinding for organic substances*

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.

Freeze-dryer, mills, accelerated solvent extraction (ASE, Thermo Fisher)

Description of internal procedures

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

Sediment: TOC

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.

ICP-MS

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

Al	Aluminium	mg/kg	50
Sb	Antimon	mg/kg	0,05
As	Arsen	mg/kg	0,1
Ba	Barium	mg/kg	10
Bi	Bismut	mg/kg	0,01
Pb	Blei	mg/kg	1
Cd	Cadmium	mg/kg	0,02
Ce	Cer	mg/kg	0,1
Cr-ges	Chrom gesamt	mg/kg	3
Co	Cobalt	mg/kg	0,02
Fe	Eisen	mg/kg	20
Cu	Kupfer	mg/kg	1
La	Lanthan	mg/kg	0,02
Mn	Mangan	mg/kg	0,25
Mo	Molybdän	mg/kg	0,05
Ni	Nickel	mg/kg	1
Nb	Niob	mg/kg	0,05
Rb	Rubidium	mg/kg	0,05
Se	Selen	mg/kg	0,1
Ag	Silber	mg/kg	0,1
Sr	Strontium	mg/kg	0,5
Tl	Thallium	mg/kg	0,02
Ti	Titan	mg/kg	10
U	Uran	mg/kg	0,01
V	Vanadium	mg/kg	0,2
W	Wolfram	mg/kg	0,2
Zn	Zink	mg/kg	5
Sn	Zinn	mg/kg	0,5

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.).

According to standards

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?

Sediments: GC-MS

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

Sediments: PAH, tinorganic compounds, PCB, dioxins, PBDE, DEHP, nonylphenol, octylphenol, triclosan, triclosan-methyl, AHTN, HHCB

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

We use LOQ

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

Accuracy: control samples, precision: repeated analysis of real samples and statistical evaluation

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.

you are kidding: how could I get all these data from all the labs in Germany???

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).

There is a national guidance "Länderarbeitsgemeinschaft Wasser, RaKon Arbeitspapier IV.4" where a procedure for calculating water concentrations from SPM-concentrations is described for highly accumulative substances

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

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

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.).

EQS are derived according to EU rules (WFD implementation)

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.

According to WFD: operative monitoring, program of measures every 6 years

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?

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

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

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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.

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