

D.5.1.1. Report

Review of the sediment evaluation methods' current status and problems in the DTP Countries

Photo: Bird's-eye view of Danube-Ipoly National Park
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A DUNA-IPOLY NEMZETI PARK MADÁRTÁVLABÓL

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For further information on the project, partnership and the Danube Transnational Programme:
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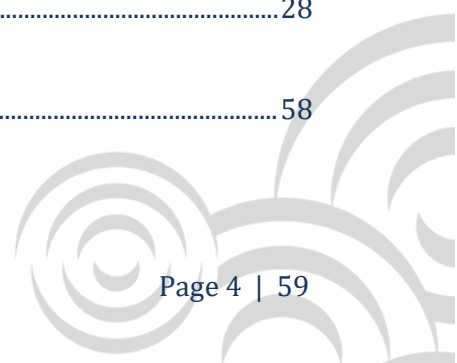
This document is for thought-provoking purposes. SIMONA Evaluation WG would like to start discussions to find the best solution for sediment-quality monitoring evaluation process. Therefore, the authors encourage everyone to send their comments and additions to the authors by using the following contact:

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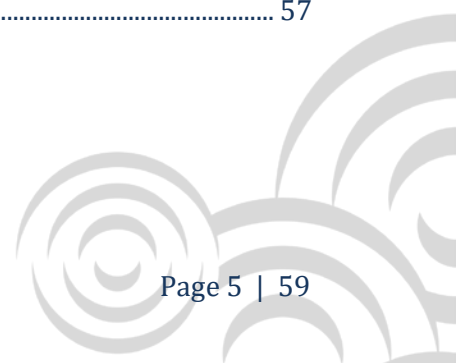
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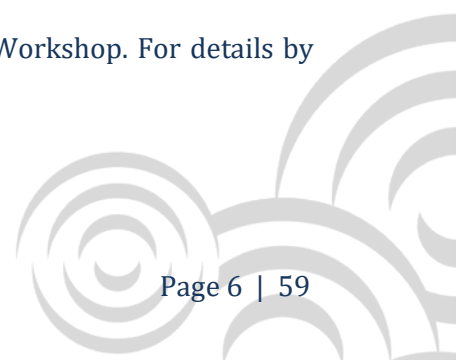
FOREWORD

Nowadays, Europe is paying increasing attention to the quality of surface waters' bottom sediments. Large numbers of chemicals are emitted into the environment from anthropogenic sources. Many of them are deposited/accumulated in the sediments. The significant role that sediments play in aquatic ecosystems is well known. They serve as both a sink and a source of organic and inorganic materials. Sediment contamination can have many detrimental effects on an ecosystem, some of which are evident and others more invisible or unknown. For example, benthic invertebrate communities can be totally lost or converted from sensitive to pollution-tolerant species. For most determinands, biodegradation is the dominant transformation pathway to remove their environmental concentration significantly. However, some degradation products may have significantly higher toxic effects than basic contaminants. Many factors such as contaminant properties, temperature, pH, microbial population density etc. can influence the rate and extent of toxicity. This is especially important for the flowing water systems (rivers, streams, creeks). [Liška, 2008].

On one hand, hazardous substances' trend monitoring in sediment is an independent indicator for the mid- and long-term changes of water status, it is independent from the other water quality measurements. On the other hand, sediment monitoring supplements the conventional water monitoring to characterize the chemical status of surface waters. Some cases sediment quality monitoring helps to understand the behavior of the hazardous substances in the environment. The Inventory Report says that sediment-quality monitoring was not really exploited in any of the Danube Basin Countries. Only a few experiments were done, especially for metals. See the conclusions of the Inventory Report in Chapter 3 section 3 Highlights from Inventory Report.

This report "Review of the sediment evaluation methods' current status and problems in the DTP Countries" is dedicated to describe the main steams/causes of the methodological problems of the Danube Basin Countries and point out main questions, that should be answered related to sediment contamination. Based on this report, the WP5 of SIMONA project is going to develop the ready-to-deploy evaluation protocol, which will be a standardized guidance for the sediment measurement data (1) evaluation and (2) evaluation results integration into the WFD overall chemical status assessment of surface water bodies. The protocol, as a tool, ensures harmonized QA/QC procedures for mid- and long-term transboundary and transnational sediment quality assessment in surface waters across the Danube River Basin.

This report is based on the results of the WP3 Inventory and the Inventory Workshop. For details by Countries, please check the SIMONA Inventory Report.



Structure of the report:

For common understanding the first chapter gives brief review of the WFD documents related to sediment contamination. Subchapters are the following: List of the reviewed WFD documents, Main purpose defined by WFD, Legislative framework of the EQS directive and The proposals of sediment-quality monitoring based on CIS guidance documents. For the purposes of WFD Directive the common definitions shall apply, these are collected in Annex I Definitions. Annex II is listing the Priority Substances and the Priority Hazardous Substances of WFD.

The second chapter is focusing on the identified problems and main tasks of the near future. This chapter also contains briefly the First proposal for the focus of the Evaluation Protocol, and tries to answer what should be the aims of the harmonized sediment monitoring program.

The third chapter is focusing on good practices and available methods for sediment-quality monitoring evaluation, including Quality Standards for bottom sediment. The end of this chapter highlights some of the most useful practices from other DTP Countries, that are detailed in Inventory Report. Annex III is listing Environmental quality standards for priority substances and certain other pollutants. Annex IV is listing Quality Standards to protect benthic community (sediment dwelling species) in freshwaters. Annex V contains useful examples from Elbe river-basin sediment management plan. Annex VI List of PNEC/EQS_{sed, eco} from 'JRC, Second Review of the Priority Substances List under the Water Framework Directive: Monitoring- based exercise, 2016' report.

Based on Heavy Metals specific properties, they need specific evaluation methodology. Annex VII is collecting the current status and problems of heavy metals risk evaluation methods.



1. BRIEF REVIEW OF THE WFD DOCUMENTS FOR COMMON UNDERSTANDING

1.1. The main relevant EU directives/guidelines in the field of water policy related to the measurement of the hazardous substances from the surface water sediment

Water Framework Directive (WFD):

DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy (OJ L 327, 22.12.2000, p. 1).

Its latest consolidated version ([20/11/2014](#)) can be found at:

<https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02000L0060-20141120>.

EQS Directive:

DIRECTIVE 2008/105/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (OJ L 348, 24.12.2008, p. 84). Latest consolidated version ([13/09/2013](#)) can be found at:

<https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1577871061397&uri=CELEX:32008L0105>.

Technical specifications for chemical analysis and monitoring of water status:

COMMISSION DIRECTIVE 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status. Can be found at:

<https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1577871352311&uri=CELEX:32009L0090>.

Monitoring guidance document:

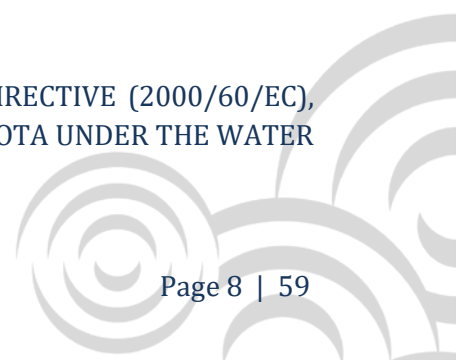
COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC), *Guidance Document No 7*, Monitoring under the Water Framework Directive, Produced by Working Group 2.7. Monitoring, European Communities, 2003

Chemical monitoring guidance document:

COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC), *Guidance Document No. 19*, GUIDANCE ON SURFACE WATER CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE, European Communities, 2009

Sediment and biota monitoring guidance document:

COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC), *Guidance document No. 25* ON CHEMICAL MONITORING OF SEDIMENT AND BIOTA UNDER THE WATER FRAMEWORK DIRECTIVE, European Union, 2010



TDG-EQS:

Common Implementation Strategy for the Water Framework Directive (2000/60/EC), Guidance Document No. 27, Technical Guidance For Deriving Environmental Quality Standards, European Communities, 2016

TDG-metal:

Common Implementation Strategy for the Water Framework Directive (2000/60/EC), Technical Guidance for implementing Environmental Quality Standards (EQS) for metals, Consideration of metal bioavailability and natural background concentrations in assessing compliance, Draft version 1 / 15 November 2019

1.2. Main purpose

From WFD Article 1: The purpose of this Directive is to establish a framework for the **protection of inland surface waters, transitional waters, coastal waters and groundwater** which

(c) aims at enhanced **protection and improvement of the aquatic environment**, inter alia, through specific measures for the progressive **reduction** of discharges, emissions and losses of **priority substances** and the cessation or **phasing-out** of discharges, emissions and losses of the **priority hazardous substances**;

and (e): contributes to mitigating the effects of floods and droughts and thereby contributes to:

- the **provision of the sufficient supply** of good quality surface water and groundwater as needed for sustainable, balanced and equitable water use,
- a significant **reduction in pollution of groundwater**,
- the **protection of territorial and marine waters**, and
- achieving the objectives of relevant international agreements, including those which aim to prevent and eliminate pollution of the marine environment, by Community action under Article 16(3) to cease or phase out discharges, emissions and losses of priority hazardous substances, with the ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and **close to zero for man-made synthetic substances**.

For the purposes of WFD Directive the common definitions shall apply, these are collected in Annex I Definitions.



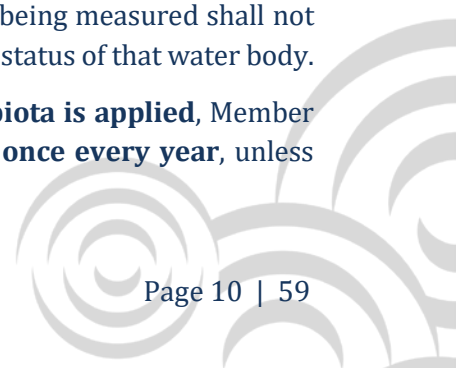
1.3. Legislative framework of the EQS directive

The 2013/39/EU Directive lays down environmental quality standards (EQS) for priority substances and certain other pollutants as provided in Article 16 of Directive 2000/60/EC, with the aim of achieving good surface water chemical status and in accordance with the provisions and objectives of Article 4 of that Directive.

ANNEX II contains the list of the priority substances which are listed in EQS directive, and in WFD Annex X. The Substances' identification numbers are also listed in Annex II.

From Article 3, related to Environmental quality standards:

- Paragraph 2:
 - For the substances numbered **5, 15, 16, 17, 21, 28, 34, 35, 37, 43 and 44** in Part A of Annex I, Member States **shall apply the biota EQS** laid down in Part A of Annex I.
 - **For other substances** (listed in Par. 1), Member States **shall apply the water EQS** laid down in Part A of Annex I.
- Paragraph 3: Member States may opt, in relation to one or more categories of surface water, to apply an EQS for a matrix other than that specified in paragraph 2, or, where relevant, for a biota taxon other than those specified in Part A of Annex I.
 - Member States that use the option referred to in the first subparagraph shall apply the relevant EQS laid down in Part A of Annex I or, if none is included for the matrix or biota taxon, **establish an EQS that offers at least the same level of protection as the EQS laid down in Part A of Annex I.**
 - Member States may use the option referred to in the first subparagraph **only where the method of analysis used for the chosen matrix or biota taxon fulfils the minimum performance criteria laid down in Article 4 of Directive 2009/90/EC.** Where those criteria are not met for any matrix, Member States shall ensure that monitoring is carried out using best available techniques not entailing excessive costs and that the method of analysis performs at least as well as that available for the matrix specified in paragraph 2 of this Article for the relevant substance.
 - 3a. Where a potential risk to, or via, the aquatic environment from **acute exposure** has been identified as a result of measured or estimated environmental concentrations or emissions and where a biota or sediment EQS is being applied, Member States shall ensure that monitoring in surface water is also carried out and shall apply the MAC-EQS laid down in Part A of Annex I to this Directive where such EQS have been established.
 - 3b. Where, pursuant to Article 5 of Directive 2009/90/EC, the calculated mean value of a measurement, when **carried out using the best available technique** not entailing excessive costs, is referred to as 'less than limit of quantification', and the limit of quantification of that technique is above the EQS, the result for the substance being measured shall not be considered for the purposes of assessing the overall chemical status of that water body.
- Paragraph 4: For substances for which an **EQS for sediment and/or biota is applied**, Member States **shall monitor the substance in the relevant matrix at least once every year**, unless technical knowledge and expert judgment justify another interval.



- Paragraph 6: Member States shall arrange for the **long-term trend analysis of concentrations** of those **priority substances listed** in Part A of Annex I that **tend to accumulate in sediment and/or biota**, giving particular consideration to the substances **numbered 2, 5, 6, 7, 12, 15, 16, 17, 18, 20, 21, 26, 28, 30, 34, 35, 36, 37, 43 and 44** listed in Part A of Annex I, on the basis of the monitoring of surface water status carried out in accordance with Article 8 of Directive 2000/60/EC. Member States shall take measures aimed at ensuring, subject to Article 4 of Directive 2000/60/EC, that such concentrations do not significantly increase in sediment and/or relevant biota.

Member States shall determine the frequency of monitoring in sediment and/or biota so as to provide sufficient data for a reliable long-term trend analysis. As a guideline, **monitoring should take place every three years**, unless technical knowledge and expert judgment justify another interval.

1.4. The proposals of sediment-quality monitoring

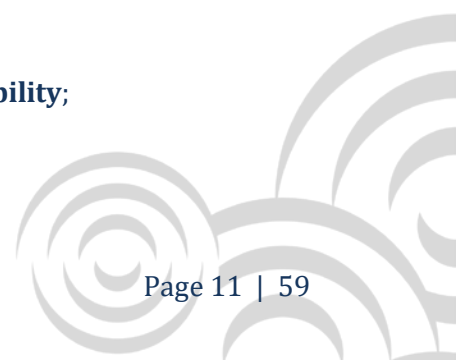
Look out to SIMONA Sampling and Laboratory Protocols for detailed proposals. This section briefly listed the main points of the Guidance Documents.

Why needed to monitor 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:
 - (a) **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,
 - (b) **assess long-term changes** in natural conditions and those resulting from widespread anthropogenic activity,
 - (c) **monitor the progressive reduction** in the concentrations of PS and the phasing out of PHS.
- Other reasons to measure contaminants in sediment
Use of sediment in monitoring priority (hazardous) substances is important in other issues of WFD implementations, viz.:
 - (a) identify **fate and behaviour of pollutants**,
 - (b) **describe the general contaminant status** and supply reference values for regional and local monitoring programmes,
 - (c) **accumulating matrixes 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

Locations for sediment trend monitoring

- Samples should be
 - collected from areas characterised by **relatively low natural variability**;
 - **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.

Monitoring frequencies

- Typical sampling frequency will vary from
 - once every 1 to 3 years for large rivers or estuaries that are characterised 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).

The selection of the Sampling Fraction

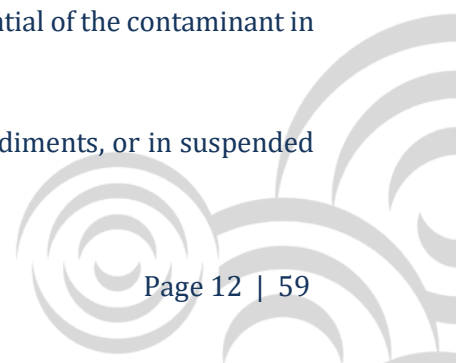
- < 2 mm fraction of the sediment should be analysed for organic contaminants
- < 63 μm fraction should be analysed for metals.

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 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 normalised results to assess the degree of contamination. Therefore, particle size analyses, measurements of organic carbon content or measurement of other common normalisation 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 JAMP Guideline for Monitoring Contaminants in Sediments.

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_{ow}), which is a good predictor of the partitioning potential of the contaminant in the organic fraction of the sediment (K_{oc}).
- As a rule of thumb,
 - compounds with a $\log K_{ow} > 5$ should preferably be measured in sediments, or in suspended particulate matter (SPM), while



- compounds with a $\log K_{ow} < 3$ should preferably be measured in water.
- For compounds with a $\log K_{ow}$ 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).

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.)



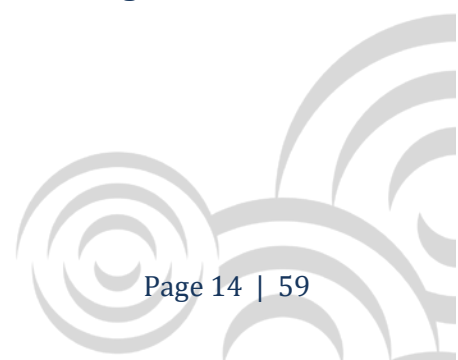
2. IDENTIFIED PROBLEMS AND MAIN TASKS IN THE WP5

2.1. Possible added values of the Sediment-quality monitoring programs

The first and maybe the most important question is 'Why measure contaminated bottom sediment?'. Necessary to describe the reason why we need a harmonized Sediment-quality monitoring, so what will be on the focus of the Evaluation Protocol.

Based on reviewed studies, Inventory report and WFD guidelines we can separate the following aims. We tried to collect them to under the scope of investigation, operational and surveillance monitoring programs. During the WP5, and **in the Evaluation workshop we need to improve and discuss the following aims**, that should be focused on:

- **Investigation** monitoring programs and their evaluation process to
 - (I) identify **fate and behaviour of pollutants** at local or regional scale;
 - (II) **find the pollution sources**;
 - (III) **supply reference values** for regional and local monitoring programs (e.g. for ecotoxicity test, metal background concentrations);
 - (IV) **monitor** local sediment **contamination changes** (e.g. for reuse possibilities, control of treatments (in situ and ex situ));
 - (V) help to **optimize the monitoring programs** (where should be measured next time).
- **Operational** monitoring programs and their evaluation process to
 - (VI) identify **fate and behaviour of pollutants** in general;
 - (VII) **supply reference values** for larger river basins' monitoring programs;
 - (VIII) conduct effective trend monitoring for **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;
 - (IX) conduct effective trend monitoring for **assess long-term changes in natural conditions** and those resulting from **widespread anthropogenic activity**;
 - (X) conduct effective trend monitoring for **monitor the progressive reduction** in the concentrations of PS and the phasing out of PHS.
- **Surveillance** monitoring programs and their evaluation process to
 - (XI) describe the general **contaminant status of sediments to protect benthic community**;
 - (XII) **accumulating matrixes 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 (**supplement the conventional water monitoring in cost-effective way**);
 - (XIII) **locate the most risky / polluted areas**.



2.2. Major limitations of sediment monitoring in the Danube Countries

Major problems of the Danube Countries (based on Inventory Report):

- lack of environmental standards for sediment quality;
- sediment can be very inhomogeneous, therefore representativity is important;
- water monitoring is already expensive, so it would be preferred to help the optimized monitoring and save the cost for sediment analysis, instead of additional costs;
- uncertainty analysis methodology is missing, or not used for sediment monitoring;
- Most of the Countries have limited information if their rivers' bottom sediments are contaminated or not.

2.3. Preliminary proposal for the focus of the Evaluation Protocol

SIMONA Evaluation Protocol is dedicated to build a harmonized sediment-quality evaluation methodology for the Danube River Basin and Sub-basins. Therefore, the site-specific questions are not our priority. The WP3 case studies of 3 test areas should be a good practice, and help to solve the site-specific problems No. (I)-(IV).

First of all, the need for harmonized sediment-quality monitoring program should be defined. Which monitoring aims have the highest added value for the Danube Countries. At this stage, we propose the following focuses for harmonized sediment-quality monitoring program:

		No. of the direct aims from the section 2.1. list
Focus on help to optimize monitoring programs by integrating sediment-quality monitoring to chemical status assessment, therefore, aiming to		
	supply reference values and sites for larger river basins' monitoring programs;	(VII)
develop methodology for effective trend monitoring for		
	assess compliance with the no-deterioration objective (concentration of substances are below detection limits, declining or stable and there is no obvious risk of increase) of the WFD;	(VIII)
	assess long-term changes in natural conditions and those resulting from widespread anthropogenic activity ;	(IX)
	monitor the progressive reduction in the concentrations of PS and the phasing out of PHS.	(X)
Focus on help to find the most risky/polluted areas by sediment-quality monitoring, therefore, aiming to		
	give quality standards for describing the contaminant status of sediments to protect benthic community ;	(VI); (XI)
	give methodology for scanning the basins, sub-basins to locate the most risky / polluted areas .	(V); (XII); (XIII)



As a preliminary proposal for sediment monitoring program, the following structure is proposed for further development:

Goal	Monitoring sites	Evaluation type	Type of the monitoring program	Percentage of the monitoring sites
assess long-term changes in natural conditions	pristine waters, their status is certainly good (=reference sites)	trend assessment	operational	15%
monitor the progressive reduction in the concentrations of PS and the phasing out of PHS*	contaminated sites, their status is bad. They should be before or / after treatment	trend & regular assessment	operational	20%
locate contaminated areas				
systematically scan contaminations in large rivers near their estuary*	status is unknown	regular assessment	surveillance	20%
systematically scan contaminations in medium and smaller rivers, which are inside contaminated large rivers* to locate pollution source	status is unknown	regular assessment	surveillance	20%
randomly scan contaminations in medium and smaller rivers, which are outside contaminated rivers* to be control bodies	status is unknown	regular assessment	surveillance	15%
other strategically important points				
other strategically important points (eg. protected areas)*	fixed strategically important points, status is unknown, high monitoring frequency is required	trend & regular assessment	surveillance	10%

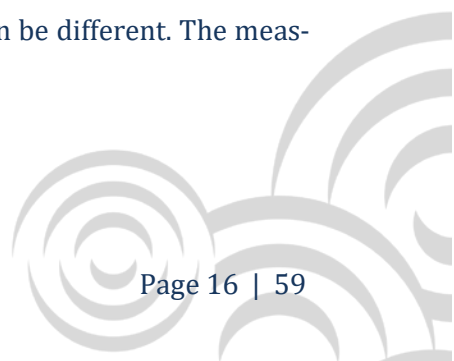
GOOD
BAD
GOOD

* also protect benthic community, with regular assessment in surveillance monitoring program: 65 %

Important notes:

- One monitoring site can be used to support many goals.
- It is not necessary to measure all the parameters from all sites. SIMONA proposes **3 separate Sediment-quality monitoring programs:**
 1. focus on **pollution from diffuse sources** (such as agricultural pollution);
 2. focus on **pollution from point sources at wastewater treatment facilities** (pollution from households, built-in areas and industrial sites);
 3. focus on **metals and metalloids.**

The monitoring sites of these 3 Sediment-quality monitoring programs can be different. The measured parameters should be focused on the pollution types.



The presented monitoring program needs the following tools for evaluation:

- trend assessment needs
 - evaluation methodology for the long-term changes in natural conditions;
 - reference values from the reference sites;
 - evaluation methodology for the results of monitor the progressive reduction in the concentrations of PS and the phasing out of PHS;
- regular assessment to protect benthic community, and to locate contaminated areas:
 - QS sediment, and evaluation methodology (such as LOQ value assessment, uncertainty analysis);
 - warning indicator parameters and threshold values to indicate the potentially risky sites;
 - methodology to plan the next monitoring program based on the preliminary results;
- monitoring site selection
 - land-use data (such as Corine);
 - locations and volume of the wastewater sites;
 - catchments of waterbodies and flow data.



3. GOOD PRACTICES / AVAILABLE METHODS FOR SEDIMENT-QUALITY EVALUATION

3.1. Quality Standards

By the protection level we should differentiate two types of quality standard for sediment:

- **QS sediment** to protect benthic community (sediment dwelling species) of river basin;
- **overall EQS** for measurements in sediment matrix to protect the all ecosystem of waters (sediment monitoring instead of conventional water monitoring for relevant substances);

QS sediment is based on ecotoxicological data, that measured in contaminated sediment. For Hazardous substances the QS values are collected in the following tables:

- Annex IV QS benthic community (freshwater) from EQS dossiers 2006 and 2011
- Annex V Examples for standards of Elbe river

In the 'JRC, Second Review of the Priority Substances List under the Water Framework Directive: Monitoring- based exercise, 2016' report [Carvalho et al., 2016] Section 2.3.3. is briefly collected the most relevant information on PNECs for Sediment:

2.3.3. PNECs for Sediment

The derivation of $EQS_{sed, eco}$ for the protection of freshwater benthic organisms is explained in the EQS guidance document [TGD-EQS, 2011; page 93]. Sediment PNECs are available for some substances in EQS substance datasheets / dossiers (from the year 2005 or 2011) or from ECHA substance dossiers. In some cases, the marine water sediment PNECs are different from the freshwater PNECs.

If no reliable sediment toxicity data are available, Equilibrium Partitioning (EqP) can be used to estimate the $PNEC_{sed, eco}$, based on the REACH Guidance [ECHA, 2008; TGD-EQS, 2011; page 96-99]. The INERIS prioritisation report [James et al., 2009] gives in Annex VII.2 PNECs for protection of sediment dwelling organisms ($PNEC_{sediment}$), which have been derived from $PNEC_{water}$ via the EqP approach using the K_{oc} values of the substances. This EqP approach appears to be a reasonable and convenient compromise for assessing ecotoxicity for sediments [see pages 38-40 of the INERIS report; James et al., 2009], but the assumptions and uncertainties inherent in the equilibrium partitioning approach have to be acknowledged [TGD-EQS, 2011].

The K_{oc} values were retrieved by INERIS from the PCKOC of EPISUITE v1.66 software [EPISUITE].

First, $K_{\text{sediment-water}}$, the partition coefficient between sediment and water is calculated according to TGD-EQS (2011), using the following formula. Input parameter is the K_{oc} , the partition coefficient between organic carbon and water.

$$K_{\text{sed-water}} = F_{\text{air}_{\text{sed}}} \times K_{\text{air-water}} + F_{\text{water}_{\text{sed}}} + F_{\text{solid}_{\text{sed}}} \times \frac{K_{p_{\text{sed}}}}{1000} \times RHO_{\text{solid}}$$

with

$$K_{p_{\text{sed}}} = F_{oc_{\text{sed}}} \times K_{oc}$$

and

$$K_{\text{sed-water}} = \frac{C_{\text{total}_{\text{sed}}}}{C_{\text{porew}_{\text{sed}}}}$$

Default value

K_{sed}	Partition coefficient between sediment and	
$F_{\text{air-}}$	Fraction air in sediment	0
$K_{\text{air-}}$	Air-water partition coefficient	
F_{wat}	Fraction water in sediment	0.8
F_{sol}	Fraction solids in sediment	0.2
K_{p-}	Partition coefficient solid-water in sediment	
F_{oc-}	Weight fraction of organic carbon in sediment	0.05
RH	Density of the solid phase	2500
K_{oc}	Partition coefficient between organic carbon	
C_{to-}	Total concentration in sediment	
C_{por}	Total concentration in pore water of sediment	

Then, $PNEC_{\text{sediment}}$ (= QS ; wet or dry weight) is calculated according to TGD-EQS (2011), using the following formula.

$$QS_{\text{sediment, EqP, ww}} = \frac{K_{\text{sed-water}}}{RHO_{\text{sed}}} \times QS_{\text{fw, eco}} \times 1000$$

$$CONV_{\text{sed}} = \frac{RHO_{\text{sed}}}{F_{\text{solid}_{\text{sed}}} \times RHO_{\text{solid}}}$$

$$QS_{\text{sediment, EqP, dw}} = CONV_{\text{sed}} \times QS_{\text{sediment, EqP, ww}}$$

		Default value
$QS_{\text{sediment,EqP,w}}$	Wet weight quality standard for sediment based on equilibrium partitioning ($PNEC_{\text{sed}}$)	
$K_{\text{sed-water}}$	Partition coefficient between sediment and water	
RHO_{sed}	Bulk density of wet sediment	1300
$QS_{\text{fw,eco}}$	Quality standard for direct ecotoxicity on freshwater aquatic organisms ($PNEC_{\text{water}}$)	
$CONV_{\text{sed}}$	Conversion factor for sediment concentration wet-dry	
$F_{\text{solid-sed}}$	Fraction solids in sediment	0.2
RHO_{solid}	Density of the solid phase	2500
$QS_{\text{sediment,EqP,dw}}$	Dry weight quality standard for sediment based on equilibrium partitioning ($PNEC_{\text{sed,dw}}$)	

When the QS_{sediment} has been calculated using EqP and $\log K_{OW}$ is > 5 for the compound of interest, QS_{sediment} is divided by 10. This correction factor is applied because EqP only considers uptake via the water phase. Extra uncertainty due to uptake by ingestion of food should be covered by the applied assessment factor of 10.

The calculated PNEC values from the INERIS report [James et al., 2009] were compared with our calculations applying the formulas given above [taken from the TGD-EQS, 2011]. The results of the calculations were not identical, but very similar. The conversion factor of the wet weight to dry weight ratio was 4.6 for suspended matter and 2.6 for wet sediment (personal communication by Els Smit). The difference of the calculations is shown in Table 13.

Table 13. Comparison between available PNEC values for sediment

Substance	PNEC _{sed dw} (INERIS) ($\mu\text{g}/\text{kg}$)	PNEC _{sed dw} (JRC) ($\mu\text{g}/\text{kg}$) Calculated with $CONV_{\text{sed}}$
DDD - o,p'	0.99	0.50
Benzo(a)anthracene	27.7	13.9
Phenanthrene	2708	1356
Tetrabutyltin	0.202	0.101
Indeno(1,2,3-c,d)pyrene	72.1	36.1
Triphenyltin	2.9	14.4
Monobutyltin	1.17	0.57
Dicofol	1.05	0.53

For dibutyltin, the ECHA dossier gives a $PNEC_{sed}$ of 7.0 $\mu\text{g}/\text{kg}$ (for dibutyltin dichloride). INERIS gives a $PNEC_{sed}$ of 3.09 $\mu\text{g}/\text{kg}$. Our calculated PNEC is 15.46 $\mu\text{g}/\text{kg}$ (using the same $PNEC_{water}$ and K_{oc}) (Table 14).

Table 14. PNEC sediment for dibutyltin (dichloride)

	PNECsed dw (ECHA) ($\mu\text{g}/\text{kg}$)	PNECsed dw (INERIS) ($\mu\text{g}/\text{kg}$)	PNECsed dw (JRC) ($\mu\text{g}/\text{kg}$)
Dibutyltin (dichloride)	7.0	3.09	15.46

In case of 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183), the calculated PNEC (266 $\mu\text{g}/\text{kg}$) was preferred over the non-specific PNEC of 49000 $\mu\text{g}/\text{kg}$ given in the EQS data sheet from 2005. Also for the priority BDEs 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154), 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) and hexachlorobenzene (HCB) there is a large difference between the PNEC given in the EQS data sheet from 2005 and the calculated PNECs (Table 15).

Table 15. PNEC sediment for BDEs and HCB

Substance	PNECsed dw (EQS data sheet 2005) ($\mu\text{g}/\text{kg}$)	PNECsed dw (JRC) ($\mu\text{g}/\text{kg}$)
2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	310	1.34
2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154)	310	52.5
2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	310	0.0979
2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183)	49000	266
Hexachlorobenzene (HCB)	16.9	0.392



3.2. Other types of quality standards

Ecotoxicity tests

We should focus on microcosm ex-situ ecotoxicity tests. These tests can provide indicator parameters for risk assessment. For example, in Joint Danube Survey 2 the method of the ecotoxicity test of bottom sediments was the following:

12.2 Methods

Pore water was recovered from 62 deep frozen raw sediment samples. After the sediment unfreezing, the visible animals were removed and a centrifugation of 15 minutes by 6000 rpm was used to obtain up to 400 ml of pore water. Pore water samples were adjusted to the test temperature and then immediately used for the toxicity tests.

A battery of three tests was used for this study - two tests of producent organisms (7-day growth inhibition test with *Lemna minor* and a 72-hour algal growth inhibition test with *Desmodesmus subspicatus*) and one test of destruent organism (15 and 30 minute inhibition of the light emission of *Vibrio fischeri*). Between two to three replicates were used in each test. Determination of the limit toxic effect of pore water to *Lemna minor* via growth inhibition was based on EN ISO 20 079. Frond number and frond area were measured. Data were evaluated and the percentage of inhibition was calculated. The algal growth limit inhibition test followed EN ISO 8692 with *Desmodesmus subspicatus*. The percentage of inhibition of growth rate was calculated. Both tests (with *Lemna minor* and *Desmodesmus subspicatus*) fulfilled the validity criteria of the tests (e.g. specific growth rate). The inhibition of luminescence of *Vibrio fischeri* was evaluated within the test procedure following the International Standard ISO 11348-2 using liquid-dried bacteria. The percentage of inhibition of the light emission by cultures of *Vibrio fischeri* was calculated for a contact time of 15 and 30 minutes. EC50 was calculated for selected samples of pore water.

Other tests with *Vibrio fischeri* were performed using dry sediment fraction 63 µm in RECETOX Ecotoxicology Laboratories. A whole sediment (solid phase / suspension) toxicity test with FLASH *Vibrio fisheri* bioluminescence test was done. The test was performed with modifications according to Lappalainen [1999].

The method can be good for indicating if the sediment has high, medium or low risk. In addition, it would be beneficial if some reference site would be measured (without anthropogenic activity) in the project to compare the ecotoxicity results.



Passive sampling tests

Passive sampling tests can yield indicator parameters for risk assessment.

Section 7.1. of CIS Guidance Doc. No. 25.

Passive samplers are the tried and tested technology for the determination of dissolved phase concentrations of bioaccumulative organics in the aquatic environment. This sampling technique is based on the deployment *in situ* or use in the laboratory of devices capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs by diffusion, typically over periods of days to weeks. Contaminants accumulated in the sampler are eluted and their concentration levels measured, allowing the quantification of time-weighted average concentrations in water or equilibrium pore water concentrations in sediment. It enables time- integrated sampling or sampling of truly dissolved concentrations of contaminants in water or aquatic sediments. Even for those chemicals that are present at extremely low concentrations in the dissolved phase and are primarily accumulated in biota via dietary uptake, passive samplers generally extract sufficient amounts of residues for analysis. Passive sampling can also be employed in batch sediment extractions under laboratory conditions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable concentrations of contaminants in sediment [Harmsen, 2007, ISO 2008].

We should collect and consider the pros and cons of passive sampling. For example:

	passive sampling in aquatic phase	bottom sediment
to protect benthic community	results cannot be used directly to protect benthic community	results can be used directly to protect benthic community
to protect freshwater community	not directly	not directly
timely accumulated information	short period of time (1-3 weeks)	long period of time (1-3 years)
spatial homogeneity	spatially more homogeneous	spatial inhomogeneity: need to collect composite sample
representativity in time	always representative for the last period	the representativity in time is uncertain



Suspended particular matter

Suspended particular matter can be an alternative parameter for risk assessment.

Section 5.1.1 of CIS Guidance Doc. No. 25.

Alternatively, especially in the cases of rivers without sediments or with perturbed sediments, SPM and freshly deposited sediment can be used to collect the desired fine fraction. Knowing that deposition of suspended particles from the water column is favoured in areas with relatively low energy in the water (waves, currents), the following general criteria can be provided for the selection of the sampling sites:

- in rivers and transitional waters (estuaries), the currents are highest in the central channel or river bed, in which means that a relatively low amount of fines deposited on the bottom. Higher concentrations of fine-grained deposits are found in areas where the water flow is lower, such as near the side of the river (in concave stretches of the river) and in accumulation areas within estuaries;
- in natural estuaries with complex suspended solids dynamics (i.e. estuaries with settling and erosion zones, tidal flats, etc.), representative sampling is possible only upstream of the tidal limit. In such cases, the sampling site should be located in the non-tidal zone of unidirectional flow (e.g. upstream of a weir);
- in lakes and reservoirs the highest energy dissipation occurs near the inlet of rivers, and on the shores (wave action). The highest concentration of fines may therefore be found away from these sites;
- in coastal waters, areas with high tidal currents must be avoided. Sedimentation areas, such as embayments or areas of relatively deep water, are preferred.



3.3. Highlights from Inventory Report (except metals)

Conclusions of SIMONA Inventory Report

Conclusions of SIMONA Inventory Report, 2019 (related to Evaluation Methodology) is the following:

National legislation includes concern for monitoring the environmental quality of groundwater, surface water, air, soils and sediments, for drinking water, waste water (used in industry or by population). Also, European water legislation is implemented in all these countries, annually monitoring the water bodies, in line with EU-WDF (Water Framework Directive).

As concerns the monitoring of toxic substances content, there is an impressive number of national or European laws that act to reduce or even prohibit polluting technologies, reduce the discharge of wastewater (from industry) in the Danube and improve the purification technologies of sewage or waste water. In this respect, the maximum and normal limits of hazardous substances in air, water, sediment, biota may be lower in the future, the chronic pollution being remedied over the years, depending on the results of their remedial measures. The activity in this field is carried out in all partner countries, by applying the information provided by international guides and a rich experience gained over years in this field.

Noteworthy is the fact that the international guidelines can be applied with restrictions, because the geological particularities, biota specificity, demographic peculiarities, pollution sources and pollutant categories for waters in partner countries could not be found in the general common legislation.

Regarding the legal norms on sediment pollution, monitoring and establishing quality classes, there is national legislation only in the Republics of Slovakia and Serbia. Some countries (Romania, Slovenia) have some provisions related to sediments in the laws regarding water. For example, in Romania, within the legislation on water quality, there are also mentioned the admissible levels of harmful substances in sediments.

In conclusion, the elaboration of SIMONA guide, based on the data in the Danube River Basin, and on the informations in the general guides, is necessary.

The quality standard values are fixed set 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 (clayey, sandy, silty), the geological specificities 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) and besides "Total Metal Analysis", analyzes of metal compounds are also made (speciation of metals).

The legislation reflects the phenomenon of selective bioaccumulation and traceability of metals to a small extent (the accumulation of mercury in large fish or PAH in certain biota). Establishing a bioconcentration factor and association with a certain type of biota is not reflected in the general legislation.

Generally there is no difference in the national legislations between pollution and contamination.

In every country generally it is known that specific HSs are generated by specific industries.

The results of monitoring are generally open to public in all countries.

The legislation does not specify exact methods for remedying pollution because laws have a general character, but when developing an ecosystem guide, these details must be reflected. There are differences regarding the establishment of the ecological quality classes, although the classification criteria are the same.

Chemical status assessment method in HUNGARY

Environmental Quality Standards (EQSs) are delivered for the surface waters and biota according to EU-WFD. AA-EQS for annual average concentrations and MAC-EQS for maximum acceptable concentrations. HU has three status classes for metals: 1) below natural background, 2) good status, 3) bad status; and two classes for other priority (hazardous) substances: 1) good status, 2) bad status. In some cases, HU uses EQS_{added} based on added risk approach, when the ABC (ambient background concentration) is known.

Surface water status assessment: Art. 16 of the WFD sets out the strategy to prevent chemical pollution of Surface Waterbodies (SW). The chemical status assessment is used alongside the ecological status assessment to determine the overall quality of a waterbody. Environmental Quality Standards (EQSs) are tools used for assessing the chemical status of waterbodies. The EQS Directive (2008/105/EK and 2013/39/EU) established

- the maximum acceptable concentration (MAC-EQS) and/or
- annual average concentration (AA-EQS)

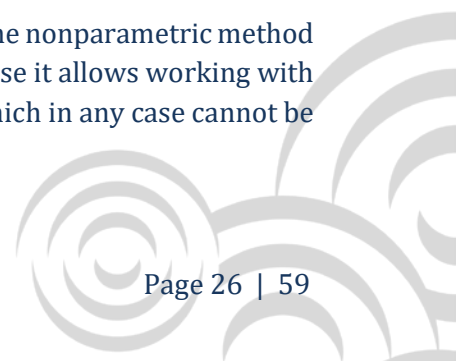
for 45 priority substances and 8 other pollutants which, if met, allows the chemical status of the waterbody to be described as 'good'.

Criteria of high confidence:

- The classification has high confidence if analysed
 - 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 1 year;
- and all LOQs $\leq 0.3 \cdot$ EQSs.

Space-time risk assessment method of BULGARIA

When obtaining at least 4 consecutive results as a trend assessment approach, the nonparametric method of Mann Kendall (Hirsch and Slack, 1984) is used. The method is suitable because it allows working with less than 6 results. There is no claim for a normal distribution of the results, which in any case cannot be assessed with such scarce data.



The nonparametric method of Mann Kendall is applicable when the pollutant values (x_i) are considered to follow the model:

$$x_i = f(t_i) + \varepsilon_i$$

where:

$f(t_i)$ - a continuous decreasing or increasing function of time and the residues

ε_i - are assumed to belong to the same distribution with an average value of zero.

Other scientific assessment methods are also applied.

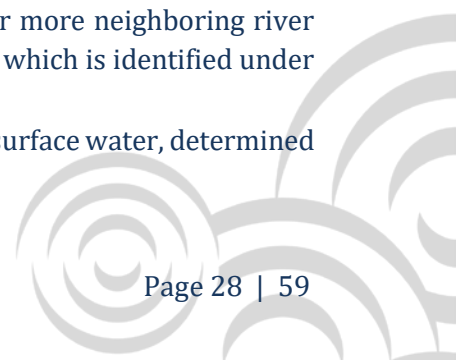


ANNEXES

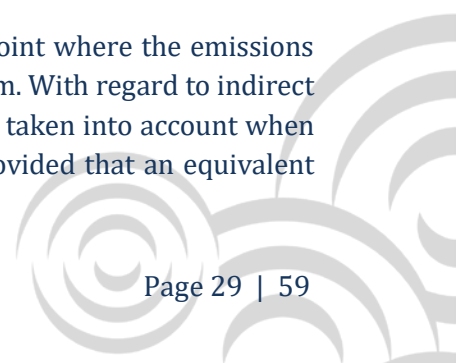
ANNEX I DEFINITIONS

For the purposes of WFD Directive the following definitions shall be applied (collection from WFD):

- 'Surface water' means inland waters, except groundwater; transitional waters and coastal waters, except in respect of chemical status for which it shall also include territorial waters.
- 'Groundwater' means all water which is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil.
- 'Inland water' means all standing or flowing water on the surface of the land, and all groundwater on the landward side of the baseline from which the breadth of territorial waters is measured.
- 'River' means a body of inland water flowing for the most part on the surface of the land but which may flow underground for part of its course.
- 'Lake' means a body of standing inland surface water.
- 'Transitional waters' are bodies of surface water in the vicinity of river mouths which are partly saline in character as a result of their proximity to coastal waters but which are substantially influenced by freshwater flows.
- 'Coastal water' means surface water on the landward side of a line, every point of which is at a distance of one nautical mile on the seaward side from the nearest point of the baseline from which the breadth of territorial waters is measured, extending where appropriate up to the outer limit of transitional waters.
- 'Artificial water body' means a body of surface water created by human activity.
- 'Heavily modified water body' means a body of surface water which as a result of physical alterations by human activity is substantially changed in character, as designated by the Member State in accordance with the provisions of Annex II.
- 'Body of surface water' means a discrete and significant element of surface water such as a lake, a reservoir, a stream, river or canal, part of a stream, river or canal, a transitional water or a stretch of coastal water.
- 'River basin' means the area of land from which all surface run-off flows through a sequence of streams, rivers and, possibly, lakes into the sea at a single river mouth, estuary or delta.
- 'Sub-basin' means the area of land from which all surface run-off flows through a series of streams, rivers and, possibly, lakes to a particular point in a water course (normally a lake or a river confluence).
- 'River basin district' means the area of land and sea, made up of one or more neighboring river basins together with their associated groundwaters and coastal waters, which is identified under Article 3(1) as the main unit for management of river basins.
- 'Surface water status' is the general expression of the status of a body of surface water, determined by the poorer of its ecological status and its chemical status.



- 'Good surface water status' means the status achieved by a surface water body when both its ecological status and its chemical status are at least 'good'.
- 'Good surface water chemical status' means the chemical status required to meet the environmental objectives for surface waters established in Article 4(1)(a), that is the chemical status achieved by a body of surface water in which concentrations of pollutants do not exceed the environmental quality standards established in Annex IX and under Article 16(7), and under other relevant Community legislation setting environmental quality standards at Community level.
- 'Hazardous substances' means substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern.
- 'Priority substances' means substances identified in accordance with Article 16(2) and listed in Annex X. Among these substances there are 'priority hazardous substances' which means substances identified in accordance with Article 16(3) and (6) for which measures have to be taken in accordance with Article 16(1) and (8).
- 'Pollutant' means any substance liable to cause pollution, in particular those listed in Annex VIII.
- 'Pollution' means the direct or indirect introduction, as a result of human activity, of substances or heat into the air, water or land which may be harmful to human health or the quality of aquatic ecosystems or terrestrial ecosystems directly depending on aquatic ecosystems, which result in damage to material property, or which impair or interfere with amenities and other legitimate uses of the environment.
- 'Environmental objectives' means the objectives set out in Article 4.
- 'Environmental quality standard' means the concentration of a particular pollutant or group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment.
- 'Combined approach' means the control of discharges and emissions into surface waters according to the approach set out in Article 10.
- 'Water intended for human consumption' has the same meaning as under Directive 80/778/EEC, as amended by Directive 98/83/EC.
- 'Water services' means all services which provide, for households, public institutions or any economic activity:
 - abstraction, impoundment, storage, treatment and distribution of surface water or groundwater,
 - waste-water collection and treatment facilities which subsequently discharge into surface water.
- 'Water use' means water services together with any other activity identified under Article 5 and Annex II having a significant impact on the status of water.
This concept applies for the purposes of Article 1 and of the economic analysis carried out according to Article 5 and Annex III, point (b).
- 'Emission limit values' means the mass, expressed in terms of certain specific parameters, concentration and/or level of an emission, which may not be exceeded during any one or more periods of time. Emission limit values may also be laid down for certain groups, families or categories of substances, in particular for those identified under Article 16.
The emission limit values for substances shall normally apply at the point where the emissions leave the installation, dilution being disregarded when determining them. With regard to indirect releases into water, the effect of a waste-water treatment plant may be taken into account when determining the emission limit values of the installations involved, provided that an equivalent



level is guaranteed for protection of the environment as a whole and provided that this does not lead to higher levels of pollution in the environment.

- 'Emission controls' are controls requiring a specific emission limitation, for instance an emission limit value, or otherwise specifying limits or conditions on the effects, nature or other characteristics of an emission or operating conditions which affect emissions. Use of the term 'emission control' in this Directive in respect of the provisions of any other Directive shall not be held as reinterpreting those provisions in any respect.

For the purposes of WFD Directive the following definitions shall be applied (collection from 2013/39/EU):

- 'matrix' means a compartment of the aquatic environment, namely water, sediment or biota;
- 'biota taxon' means a particular aquatic taxon within the taxonomic rank 'sub-phylum', 'class' or their equivalent.

Specific Terms and Definitions from the Guidance of Chemical Monitoring:

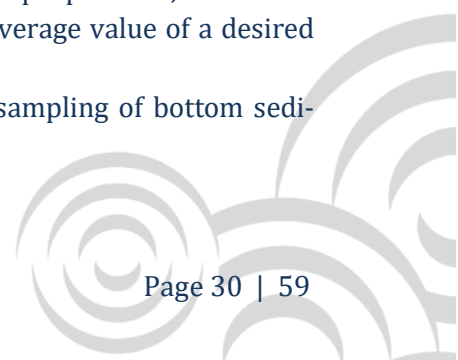
- "Whole water" is synonym for the original water sample and shall mean the water sample when solid matter and the liquid phase have not been separated.
- "Liquid (dissolved) fraction" shall mean an operationally defined fraction of whole water from which suspended particulate matter has been removed by an appropriate methodology.
- "Suspended particulate matter (SPM)" shall mean the particulate matter fraction of the whole water sample after separation with an appropriate methodology.
- "Total concentration of the analyte" shall mean the total concentration of the analyte in the whole water sample, reflecting both dissolved and particle bound concentrations of the analyte.
- "Dissolved concentration of the analyte" shall mean the concentration of the analyte in the liquid (dissolved) fraction of a whole water sample.
- "Particle bound concentration of the analyte" shall mean the concentration of the analyte bound to SPM.
- "Discharged": A substance is considered being discharged into a river basin when it is being introduced via point or diffuse sources or accidental releases.

Specific Terms and Definitions from the Guidance of Sediment and biota monitoring:

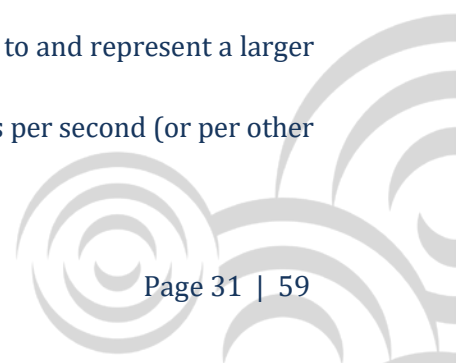
- Composite sample: two or more samples or subsamples mixed together in appropriate proportions, from which the average result of a designed characteristic may be derived from the same stratum or at the same sediment thickness. The sample components are taken and pretreated with the same equipment and under the same conditions.

Two or more increments or sub-samples mixed together in appropriate proportions, either discretely or continuously (blended composite sample), from which the average value of a desired characteristic may be obtained.

[ISO 5667-12:1995 Water quality – Sampling - Part 12: Guidance on sampling of bottom sediments ISO 11074 2:1998].



- Environmental specimen banking: ESB may be defined as the storage, under appropriate conditions, of material from which information about the state of the environment may be obtained afterwards.
- Grab sample: samples taken of a homogeneous material, usually water, in a single vessel. Filling a clean bottle with river water is a very common example. Grab samples provide a good snap-shot view of the quality of the sampled environment at the point of sampling and at the time of sampling. Without additional monitoring, the results cannot be extrapolated to other times or to other parts of the river, lake or ground-water.
- Lentic: refers to standing or still water. It is derived from the Latin *lentus*, which means sluggish. Lentic ecosystems can be compared with lotic ecosystems, which involve flowing terrestrial waters such as rivers and streams. Together, these two fields form the more general study area of freshwater or aquatic ecology.
- Lotic: refers to flowing water, from the Latin *lotus*, past participle of *lavere*, to wash. Lotic ecosystems can be contrasted with lentic ecosystems, which involve relatively still terrestrial waters such as lakes and ponds. Together, these two fields form the more general study area of freshwater or aquatic ecology.
- Limit of detection: (LOD) means the output signal or concentration value above which it can be affirmed, with a stated level of confidence that a sample is different from a blank sample containing no determinand of interest. [Commission Directive 2009/90/EC]
- Limit of quantification: (LOQ) means a stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank. [Commission Directive 2009/90/EC]
- Octanol-water partition coefficient: (k_{ow}) indicates hydrophobicity of a chemical substance.
- Quality: all the features and characteristics of a measurement result that bear on its ability to satisfy given requirements of quality. [EN 14996:2006]
- Quality assurance: all those planned and systematic actions necessary to provide adequate confidence that a product will satisfy given requirements of quality.
NOTE This include AQC, audit, training, documentation of methods, calibration schedule, etc. [EN 14996:2006]
- Quality control: operational techniques and activities that are used to fulfil requirements for quality. [EN 14996:2006]
- Random sampling: form of sampling whereby the chances of obtaining different concentration values of a determinand are precisely those defined by the probability distribution of the determinand in question. [ISO 5667- 6:2005 Water quality-Sampling- Part 6 Guidance on sampling of rivers and streams]
- Reference material: (RM) material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process. [ISO Guide 35:2006]
- Sample: a limited quantity of something which is intended to be similar to and represent a larger amount of that thing(s).
- Sampling frequency: Sampling frequency defines the number of samples per second (or per other unit) taken from a continuous signal to make a discrete signal.



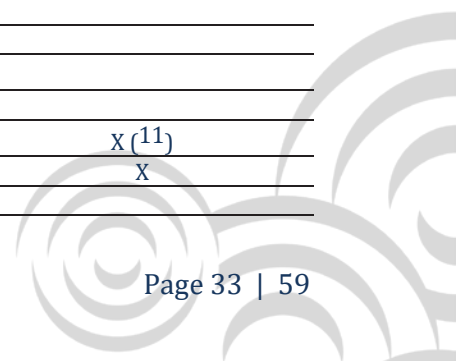
- Sampling point: precise position within a sampling site from which samples are taken. [ISO 5667-6:2005 Water quality-Sampling- Part 6 Guidance on sampling of rivers and streams. Modified definition]
- Sampling station: a well delimited area, where sampling operations take place. [IUPAC 2005 Pure and Applied Chemistry 77, 827–841]
- Sampling strategy: The result of the selection of the sampling points within a sampling site. [IUPAC 2005 Pure and Applied Chemistry 77, 827–841]
- Soil adsorption coefficient: (koc) Soil adsorption coefficient normalised by soil organic carbon content. Usually measured for environmental chemicals according to OECD Test guideline 106.
- Statistical sampling: sampling whereby the samples are taken at predetermined intervals (in space or time). [ISO 5667- 6:2005 Water quality-Sampling- Part 6 Guidance on sampling of rivers and streams. Modified definition]
- Test portion: The amount or volume of the test sample taken for analysis, usually of known weight or volume.
- Uncertainty of measurement: a non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used. [Directive 90/2009/EC]
- Uncertainty arising from sampling: The part of the total measurement uncertainty attributable to sampling. [EURACHEM/CITAC:2007 Measurement uncertainty arising from sampling: A guide to methods and approaches]



ANNEX II LIST OF PRIORITY SUBSTANCES

WFD ANNEX X - LIST OF PRIORITY SUBSTANCES IN THE FIELD OF WATER POLICY

Number	CAS number (1)	EU number (2)	Name of priority substance (3)	Identified as priority hazardous substance
(1)	15972-60-8	240-110-8	Alachlor	
(2)	120-12-7	204-371-1	Anthracene	X
(3)	1912-24-9	217-617-8	Atrazine	
(4)	71-43-2	200-753-7	Benzene	
(5)	not applicable	not applicable	Brominated diphenylethers	X (4)
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(7)	85535-84-8	287-476-5	Chloroalkanes, C10-13	X
(8)	470-90-6	207-432-0	Chlorfenvinphos	
(9)	2921-88-2	220-864-4	Chlorpyrifos (Chlorpyrifos-ethyl)	
(10)	107-06-2	203-458-1	1,2-dichloroethane	
(11)	75-09-2	200-838-9	Dichloromethane	
(12)	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	X
(13)	330-54-1	206-354-4	Diuron	
(14)	115-29-7	204-079-4	Endosulfan	X
(15)	206-44-0	205-912-4	Fluoranthene	
(16)	118-74-1	204-273-9	Hexachlorobenzene	X
(17)	87-68-3	201-765-5	Hexachlorobutadiene	X
(18)	608-73-1	210-168-9	Hexachlorocyclohexane	X
(19)	34123-59-6	251-835-4	Isoproturon	
(20)	7439-92-1	231-100-4	Lead and its compounds	
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(22)	91-20-3	202-049-5	Naphthalene	
(23)	7440-02-0	231-111-4	Nickel and its compounds	
(24)	not applicable	not applicable	Nonylphenols	X (5)
(25)	not applicable	not applicable	Octylphenols (6)	
(26)	608-93-5	210-172-0	Pentachlorobenzene	X
(27)	87-86-5	201-778-6	Pentachlorophenol	
(28)	not applicable	not applicable	Polyaromatic hydrocarbons (PAH) (7)	X
(29)	122-34-9	204-535-2	Simazine	
(30)	not applicable	not applicable	Tributyltin compounds	X (8)
(31)	12002-48-1	234-413-4	Trichlorobenzenes	
(32)	67-66-3	200-663-8	Trichloromethane (chloroform)	
(33)	1582-09-8	216-428-8	Trifluralin	X
(34)	115-32-2	204-082-0	Dicofol	X
(35)	1763-23-1	217-179-8	Perfluorooctane sulfonic acid and its derivatives (PFOS)	X
(36)	124495-18-7	not applicable	Quinoxifen	X
(37)	not applicable	not applicable	Dioxins and dioxin-like compounds	X (9)
(38)	74070-46-5	277-704-1	Aclonifen	
(39)	42576-02-3	255-894-7	Bifenox	
(40)	28159-98-0	248-872-3	Cybutryne	
(41)	52315-07-8	257-842-9	Cypermethrin (10)	
(42)	62-73-7	200-547-7	Dichlorvos	
(43)	not applicable	not applicable	Hexabromocyclododecanes (HBCDD)	X (11)
(44)	76-44-8/1024-57-3	200-962-3/213-831-0	Heptachlor and heptachlor epoxide	X
(45)	886-50-0	212-950-5	Terbutryn	



- (1) CAS: Chemical Abstracts Service.
- (2) EU-number: European Inventory of Existing Commercial Substances (EINECS) or European List of Notified Chemical Substances (ELINCS).
- (3) Where groups of substances have been selected, unless explicitly noted, typical individual representatives are defined in the context of the setting of environmental quality standards.
- (4) Only Tetra, Penta, Hexa and Heptabromodiphenylether (CAS -numbers 40088-47-9, 32534-81-9, 36483-60-0, 68928-80-3, respectively).
- (5) Nonylphenol (CAS 25154-52-3, EU 246-672-0) including isomers 4-nonylphenol (CAS 104-40-5, EU 203-199-4) and 4- nonylphenol (branched) (CAS 84852-15-3, EU 284-325-5).
- (6) Octylphenol (CAS 1806-26-4, EU 217-302-5) including isomer 4-(1,1',3,3'-tetramethylbutyl)-phenol (CAS 140-66-9, EU 205-426- 2).
- (7) Including benzo(a)pyrene (CAS 50-32-8, EU 200-028-5), benzo(b)fluoranthene (CAS 205-99-2, EU 205-911-9), benzo(g,h,i)perylene (CAS 191-24-2, EU 205-883-8), benzo(k)fluoranthene (CAS 207-08-9, EU 205-916-6), indeno(1,2,3- cd)pyrene (CAS 193-39-5, EU 205-893-2) and excluding anthracene, fluoranthene and naphthalene, which are listed separately.
- (8) Including tributyltin-cation (CAS 36643-28-4).
- (9) This refers to the following compounds:
 - 7 polychlorinated dibenzo-p-dioxins (PCDDs): 2,3,7,8-T4CDD (CAS 1746-01-6), 1,2,3,7,8-P5CDD (CAS 40321-76-4), 1,2,3,4,7,8- H6CDD (CAS 39227-28-6), 1,2,3,6,7,8-H6CDD (CAS 57653-85-7), 1,2,3,7,8,9-H6CDD (CAS 19408-74-3), 1,2,3,4,6,7,8-H7CDD (CAS 35822-46-9), 1,2,3,4,6,7,8,9-O8CDD (CAS 3268-87-9)
 - 10 polychlorinated dibenzofurans (PCDFs): 2,3,7,8-T4CDF (CAS 51207-31-9), 1,2,3,7,8-P5CDF (CAS 57117-41-6), 2,3,4,7,8- P5CDF (CAS 57117-31-4), 1,2,3,4,7,8-H6CDF (CAS 70648-26-9), 1,2,3,6,7,8-H6CDF (CAS 57117-44-9), 1,2,3,7,8,9-H6CDF (CAS 72918-21-9), 2,3,4,6,7,8-H6CDF (CAS 60851-34-5), 1,2,3,4,6,7,8-H7CDF (CAS 67562-39-4), 1,2,3,4,7,8,9-H7CDF (CAS 55673-89-7), 1,2,3,4,6,7,8,9-O8CDF (CAS 39001-02-0)
 - 12 dioxin-like polychlorinated biphenyls (PCB-DL): 3,3',4,4'-T4CB (PCB 77, CAS 32598-13-3), 3,3',4',5'-T4CB (PCB 81, CAS 70362-50-4), 2,3,3',4,4'-P5CB (PCB 105, CAS 32598-14-4), 2,3,4,4',5'-P5CB (PCB 114, CAS 74472-37-0), 2,3',4,4',5'-P5CB (PCB 118, CAS 31508-00-6), 2,3',4,4',5'-P5CB (PCB 123, CAS 65510-44-3), 3,3',4,4',5'-P5CB (PCB 126, CAS 57465-28-8), 2,3,3',4,4',5'-H6CB (PCB 156, CAS 38380-08-4), 2,3,3',4,4',5'-H6CB (PCB 157, CAS 69782-90-7), 2,3',4,4',5',5'-H6CB (PCB 167, CAS 52663-72-6), 3,3',4,4',5,5'-H6CB (PCB 169, CAS 32774-16-6), 2,3,3',4,4',5,5'-H7CB (PCB 189, CAS 39635-31-9).
- (10) CAS 52315-07-8 refers to an isomer mixture of cypermethrin, alpha-cypermethrin (CAS 67375-30-8), beta-cypermethrin (CAS 65731-84-2), theta-cypermethrin (CAS 71697-59-1) and zeta-cypermethrin (52315-07-8).
- (11) This refers to 1,3,5,7,9,11-Hexabromocyclododecane (CAS 25637-99-4), 1,2,5,6,9,10- Hexabromocyclododecane (CAS 3194-55-6), α -Hexabromocyclododecane (CAS 134237-50-6), β -Hexabromocyclododecane (CAS 134237-51-7) and γ -Hexabromocyclododecane (CAS 134237-52-8).



ANNEX III ENVIRONMENTAL QUALITY STANDARDS FOR PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS

EQS directive Part A of Annex I: ENVIRONMENTAL QUALITY STANDARDS FOR PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS

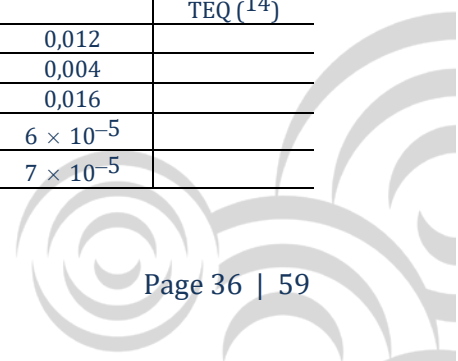
AA: annual average.

MAC: maximum allowable concentration.

Unit: [$\mu\text{g}/\text{l}$] for columns (4) to (7); [$\mu\text{g}/\text{kg}$ wet weight] for column (8)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number (1)	AA-EQS (2) Inland surface waters (3)	AA-EQS (2) Other surface waters	MAC-EQS (4) Inland surface waters (3)	MAC-EQS (4) Other surface waters	EQS Biota (12)
(1)	Alachlor	15972-60-8	0,3	0,3	0,7	0,7	
(2)	Anthracene	120-12-7	0,1	0,1	0,1	0,1	
(3)	Atrazine	1912-24-9	0,6	0,6	2,0	2,0	
(4)	Benzene	71-43-2	10	8	50	50	
(5)	Brominated diphenylethers (5)	32534-81-9			0,14	0,014	0,0085
(6)	Cadmium and its compounds (depending on water hardness classes) (6)	7440-43-9	$\leq 0,08$ (Class 1) 0,08 (Class 2) 0,09 (Class 3) 0,15 (Class 4) 0,25 (Class 5)	0,2	$\leq 0,45$ (Class 1) 0,45 (Class 2) 0,6 (Class 3) 0,9 (Class 4) 1,5 (Class 5)	$\leq 0,45$ (Class 1) 0,45 (Class 2) 0,6 (Class 3) 0,9 (Class 4) 1,5 (Class 5)	
(6a)	Carbontetrachloride (7)	56-23-5	12	12	not applicable	not applicable	
(7)	C10-13Chloroalkanes (8)	85535-84-8	0,4	0,4	1,4	1,4	
(8)	Chlorfenvinphos	470-90-6	0,1	0,1	0,3	0,3	
(9)	Chlorpyrifos (Chlorpyrifosethyl)	2921-88-2	0,03	0,03	0,1	0,1	
(9a)	Cyclodiene pesticides: Aldrin (7) Dieldrin (7) Endrin (7) Isodrin (7)	309-00-2 60-57-1 72-20-8 465-73-6	$\Sigma = 0,01$	$\Sigma = 0,005$	not applicable	not applicable	
(9b)	DDTtotal (7), (9) para-para- DDT (7)	not applicable 50-29-3	0,025 0,01	0,025 0,01	not applicable not applicable	not applicable not applicable	
(10)	1,2-Dichloroethane	107-06-2	10	10	not applicable	not applicable	
(11)	Dichloromethane	75-09-2	20	20	not applicable	not applicable	
(12)	Di(2-ethylhexyl)phthalate (DEHP)	117-81-7	1,3	1,3	not applicable	not applicable	
(13)	Diuron	330-54-1	0,2	0,2	1,8	1,8	

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number (1)	AA-EQS (2) Inland surface waters (3)	AA-EQS (2) Other surface waters	MAC-EQS (4) Inland surface waters (3)	MAC-EQS (4) Other surface waters	EQS Biota (12)
(14)	Endosulfan	115-29-7	0,005	0,0005	0,01	0,004	
(15)	Fluoranthene	206-44-0	0,0063	0,0063	0,12	0,12	30
(16)	Hexachlorobenzene	118-74-1			0,05	0,05	10
(17)	Hexachlorobutadiene	87-68-3			0,6	0,6	55
(18)	Hexachlorocyclohexane	608-73-1	0,02	0,002	0,04	0,02	
(19)	Isoproturon	34123-59-6	0,3	0,3	1,0	1,0	
(20)	Lead and its compounds	7439-92-1	1,2 (13)	1,3	14	14	
(21)	Mercury and its compounds	7439-97-6			0,07	0,07	20
(22)	Naphthalene	91-20-3	2	2	130	130	
(23)	Nickel and its compounds	7440-02-0	4 (13)	8,6	34	34	
(24)	Nonylphenols(4-Nonylphenol)	84852-15-3	0,3	0,3	2,0	2,0	
(25)	Octylphenols ((4-(1,1',3,3'-tetramethylbutyl)phenol))	140-66-9	0,1	0,01	not applicable	not applicable	
(26)	Pentachlorobenzene	608-93-5	0,007	0,0007	not applicable	not applicable	
(27)	Pentachlorophenol	87-86-5	0,4	0,4	1	1	
(28)	Polyaromatic hydrocarbons (PAH) (11)	not applicable	not applicable	not applicable	not applicable	not applicable	
	Benzo(a)pyrene	50-32-8	$1,7 \times 10^{-4}$	$1,7 \times 10^{-4}$	0,27	0,027	5
	Benzo(b)fluor-anthene	205-99-2	see footnote 11	see footnote 11	0,017	0,017	see footnote 11
	Benzo(k)fluor-anthene	207-08-9	see footnote 11	see footnote 11	0,017	0,017	see footnote 11
	Benzo(g,h,i)-perylene	191-24-2	see footnote 11	see footnote 11	$8,2 \times 10^{-3}$	$8,2 \times 10^{-4}$	see footnote 11
	Indeno(1,2,3-cd)-pyrene	193-39-5	see footnote 11	see footnote 11	not applicable	not applicable	see footnote 11
(29)	Simazine	122-34-9	1	1	4	4	
(29a)	Tetrachloroethylene (7)	127-18-4	10	10	not applicable	not applicable	
(29b)	Trichloroethylene (7)	79-01-6	10	10	not applicable	not applicable	
(30)	Tributyltin compounds (Tributyltincation)	36643-28-4	0,0002	0,0002	0,0015	0,0015	
(31)	Trichlorobenzenes	12002-48-1	0,4	0,4	not applicable	not applicable	
(32)	Trichloromethane	67-66-3	2,5	2,5	not applicable	not applicable	
(33)	Trifluralin	1582-09-8	0,03	0,03	not applicable	not applicable	
(34)	Dicofol	115-32-2	$1,3 \times 10^{-3}$	$3,2 \times 10^{-5}$	not applicable (10)	not applicable (10)	33
(35)	Perfluorooctane sulfonic acid and its derivatives (PFOS)	1763-23-1	$6,5 \times 10^{-4}$	$1,3 \times 10^{-4}$	36	7,2	9,1
(36)	Quinoxifen	124495-18-7	0,15	0,015	2,7	0,54	
(37)	Dioxins and dioxin-like compounds	See footnote 10 in Annex X to Directive 2000/60/EC			not applicable	not applicable	Sum of PCDD+PCDF +PCB-DL 0,0065 $\mu\text{g}\cdot\text{kg}^{-1}$ TEQ (14)
(38)	Aclonifen	74070-46-5	0,12	0,012	0,12	0,012	
(39)	Bifenox	42576-02-3	0,012	0,0012	0,04	0,004	
(40)	Cybutryne	28159-98-0	0,0025	0,0025	0,016	0,016	
(41)	Cypermethrin	52315-07-8	8×10^{-5}	8×10^{-6}	6×10^{-4}	6×10^{-5}	
(42)	Dichlorvos	62-73-7	6×10^{-4}	6×10^{-5}	7×10^{-4}	7×10^{-5}	



(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number (1)	AA-EQS (2) Inland surface waters (3)	AA-EQS (2) Other surface waters	MAC-EQS (4) Inland surface waters (3)	MAC-EQS (4) Other surface waters	EQS Biota (12)
(43)	Hexabromocyclododecane (HBCDD)	See footnote 12 in Annex X to Directive 2000/60/EC	0,0016	0,0008	0,5	0,05	167
(44)	Heptachlor and heptachlor epoxide	76-44-8/1024-57-3	2×10^{-7}	1×10^{-8}	3×10^{-4}	3×10^{-5}	$6,7 \times 10^{-3}$
(45)	Terbutryn	886-50-0	0,065	0,0065	0,34	0,034	

(1) CAS: Chemical Abstracts Service.

(2) This parameter is the EQS expressed as an annual average value (AA-EQS). Unless otherwise specified, it applies to the total concentration of all isomers.

(3) Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies.

(4) This parameter is the EQS expressed as a maximum allowable concentration (MAC-EQS). Where the MAC-EQS are marked as 'not applicable', the AA-EQS values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity.

(5) For the group of priority substances covered by brominated diphenylethers (No 5), the EQS refers to the sum of the concentrations of congener numbers 28, 47, 99, 100, 153 and 154.

(6) For Cadmium and its compounds (No 6) the EQS values vary depending on the hardness of the water as specified in five class categories (Class 1: < 40 mg CaCO₃/l, Class 2: 40 to < 50 mg CaCO₃/l, Class 3: 50 to < 100 mg CaCO₃/l, Class 4: 100 to < 200 mg CaCO₃/l and Class 5: ≥ 200 mg CaCO₃/l).

(7) This substance is not a priority substance but one of the other pollutants for which the EQS are identical to those laid down in the legislation that applied prior to 13 January 2009.

(8) No indicative parameter is provided for this group of substances. The indicative parameter(s) must be defined through the analytical method.

(9) DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2 (o-chlorophenyl)-2-(p-chlorophenyl) ethane (CAS number 789-02-6; EU Number 212-332-5); 1,1-dichloro-2,2 bis (p-chlorophenyl) ethylene (CAS number 72-55-9; EU Number 200-784-6); and 1,1-dichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 72-54-8; EU Number 200-783-0).

(10) There is insufficient information available to set a MAC-EQS for these substances.

(11) For the group of priority substances of polyaromatic hydrocarbons (PAH) (No 28), the biota EQS and corresponding AA-EQS in water refer to the concentration of benzo(a)pyrene, on the toxicity of which they are based. Benzo(a)pyrene can be considered as a marker for the other PAHs, hence only benzo(a)pyrene needs to be monitored for comparison with the biota EQS or the corresponding AA-EQS in water.

(12) Unless otherwise indicated, the biota EQS relate to fish. An alternative biota taxon, or another matrix, may be monitored instead, as long as the EQS applied provides an equivalent level of protection. For substances numbered 15 (Fluoranthene) and 28 (PAHs), the biota EQS refers to crustaceans and molluscs. For the purpose of assessing chemical status, monitoring of Fluoranthene and PAHs in fish is not appropriate. For substance number 37 (Dioxins and dioxin-like compounds), the biota EQS relates to fish, crustaceans and molluscs, in line with section 5.3 of the Annex to Commission Regulation (EU) No 1259/2011 of 2 December 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs (OJ L 320, 3.12.2011, p. 18).

(13) These EQS refer to bioavailable concentrations of the substances.

(14) PCDD: polychlorinated dibenzo-p-dioxins; PCDF: polychlorinated dibenzofurans; PCB-DL: dioxin-like polychlorinated biphenyls; TEQ: toxic equivalents according to the World Health Organisation 2005 Toxic Equivalence Factors.



ANNEX IV QS BENTHIC COMMUNITY (FRESHWATER) FROM EQS DOSSIERS 2006 AND 2011

Parameter	CAS	QS Benthic community (freshwater) from EQS dossiers 2006			QS Benthic community (freshwater) from EQS dossiers 2011		
		QS sediment	Unit	Notes	QS sediment	Unit	Notes
Alachlor	15972-60-8	Derivation not required.		A new chironomus study confirms that QS for freshwater can be applied for benthic organisms.			
Aclonifen	74070-46-5				760	µg/kg dw	
Anthracene	120-12-7	67.4	µg/kg ww	(≈ 310 µg/kg dw TGD standard sediment)	24	µg/kg dw	
Atrazine	1912-24-9	1.12	µg/kg ww	tentative standard (EP method) based on MAC-QS			
		5.2	µg/kg dw				
BDE penta	32534-81-9	310	µg/kg dw	(≈ 1550 µg/kg dw TGD standard sediment)	1 550	µg/kg dw	
BDE octa	32536-52-0	Derivation of effect based QS not possible					
BDE deca	1163-19-5	Derivation of effect based QS not possible					
Benzene	71-43-2	Not required		log Kow = 2.13, sediment quality standards is not required.			
Bifenox	42576-02-3				0.33	µg/kg dw	
Cadmium	7440-43-9	MPA: 2.3	mg/kg dw	QS = Cbackground + MPA corresponding concentration in water: 0.018 µg/l			
Cybutryne	28159-98-0				0.18	µg/kg dw	
Cypermethrin	52315-07-8				0.033	µg/kg dw	
Chlorfenvinphos	470-90-6	Derivation of QS not required		sorption to sediment presumably low, trigger value for QS derivation not met			
Chlorpyrifos	2921-88-2	No specific standard necessary		Protection of sediment covered by the QS referring to the pelagic community			
C10-13-Chloralkanes	85535-84-8	217	µg/kg ww	tentative (EP method)			
		998	µg/kg dw				
Dichlorvos	62-73-7				0.0021	µg/kg	

Parameter	CAS	QS Benthic community (freshwater) from EQS dossiers 2006			QS Benthic community (freshwater) from EQS dossiers 2011		
		QS sediment	Unit	Notes	QS sediment	Unit	Notes
						dw	
Diclofenac	15307-86-5				No QS de-rived		
Dicofol	115-32-2				No QS derived		
Dichloromethane	75-09-2	Derivation of QS not required		The log Kpsusp is <3 and therefore the trigger criterion to derive a QSsediment is not met.			
Diethylhexylphthalate (DEHP)	117-81-7	100	mg/kg dw				
Dioxins and dioxin-like compounds	(1)				Derivation not possible due to insufficient level of information on data		Freshwater sediment value – Upper Effect Threshold (UET) = 8,8 ng TE.kg-1 dw (lowest reliable value among AET tests, on 1% total organic carbon basis and based on Hyalella Azteca exposed to 2,3,7,8-T4CDD)
17β-estradiol (E2)	50-28-2				0.33	µg/kg dw	0,128 [µg/kg ww]
Diuron	330-54-1	Derivation of QS not required		The log Kpsusp of diuron is 1.54 and therefore the trigger criterion to calculate a sediment quality standard is not met.			
Endosulfan (α-Endosulfan & β-Endosulfan & Endosulfan sulphate)	115-29-7 (959-98-8)	0.09	µg/l				
Fluoranthene	206-44-0	0.09	µg/l	corresponding conc. in: freshwater SPM 1069 µg/kg dw	2000	µg/kg dw	
Hexabromocyclododecane	(2)				860	µg/kg dw	
Heptachlor	76-44-8				0,015	µg/kg dw	
Hexachlorobenzene	118-74-1	3.7	µg/kg ww	tentative standard based on EP-method			
		16.9	µg/kg dw				
Hexachlorobutadiene	87-68-3	107	µg/kg ww	tentative standard based on EP-method			
		493	µg/kg dw				
Hexachlorocyclohexanes incl. Lindane	608-73-1 (HCHs) 58-89-9 (Lindane)	2.4	µg/kg ww	(≈ 10.3 µg/kg dw) tentative standard based on EP-method			
Isoproturon	34123-59-6	not required		Since the log Kow is only 2.5 the calculation of sediment quality standards is not required (trigger value not met).			

Parameter	CAS	QS Benthic community (freshwater) from EQS dossiers 2006			QS Benthic community (freshwater) from EQS dossiers 2011			
		QS sediment	Unit	Notes	QS sediment	Unit	Notes	
Lead and its compounds	7439-92-1	53.4	mg/kg dw	MPA sediment QS = Cbackground + MPA	131	mg/kg dw	(based on total Pb) or 41 (accounting for bioavailability with AVS/SEM correction)	
Mercury and its Compounds	7439-97-6	470	µg/kg dw	MPA (by EP-method, with Kp 100,000 l/kg as example). QS based on toxicity test: 9.3 mg/kg dw. Tentative values derived by EP method or by the only toxicity test available; no reliable MPA/QS could be derived				
Naphthalene	91-20-3	Derivation not required		As the log Kpsusp is <3, it is not necessary to calculate a quality standard for sediment (trigger value not met)	138	µg/kg dw		
Nickel and its compounds	7440-02-0	2.9	mg/kg ww	tentative values derived by EP method in the risk assessment; ⇒ no reliable MPA/QS could be derived	Under development			
4-Nonylphenol (branched) and Nonylphenol	84852-15-3 25154-52-3	39	µg/kg ww	tentative values derived by EP method				
		180	µg/kg dw					
Octylphenols (para-tert-octylphenol)	1806-26-4 140-66-9	7.4	µg/kg ww	tentative values derived by EP method				
		34	µg/kg dw					
5-6 rings polycyclic aromatic hydrocarbons (PAHs)	Benzo[a]pyrene	50-32-8	2497	µg/kg dw	tentative values derived by EP method	91.50	µg/kg dw	
	Benzo[b]fluoranthene	205-99-2				70.7	µg/kg dw	
	Benzo[k]fluoranthene	207-08-9	1743	µg/kg dw	tentative values derived by EP method	67.5	µg/kg dw	
	Benzo[g,h,i]perylene	191-24-2				42	µg/kg dw	
	Indeno[1,2,3-cd]pyrene	193-39-5				No derivation possible		
Pentachlorobenzene	608-93-5	87	µg/kg ww	tentative values derived by EP method				
		400	µg/kg dw					
Pentachlorophenol	87-86-5	25.9	µg/kg ww	tentative values derived by EP method				
		119	µg/kg dw					
PFOS (Perfluorooctane sulphonates)	(3)				-			
Quinoxifen	124495-18-7				5.5	µg/kg dw		
Terbutryn	886-50-0				ACUTE EFFECTS Algae & aquatic			

Parameter	CAS	QS Benthic community (freshwater) from EQS dossiers 2006			QS Benthic community (freshwater) from EQS dossiers 2011		
		QS sediment	Unit	Notes	QS sediment	Unit	Notes
						plants Sediment: Myriophyllum aquaticum / 14 d EC50: 2.0 mg.kg dw CHRONIC EFFECTS Algae & aquatic plants Sediment: Myriophyllum aquaticum / 14 d NOEC: 0.977 mg.kg dw (corresponding pore water concentration 22 µg.L-1)	
Simazine	122-34-9	3.4	µg/kg ww	tentative values derived by EP method			
		15.5	µg/kg dw				
Tributyltin compounds (TBT-ion)	688-73-3 (36643-28-4)	0.0046	µg/kg ww	tentative values derived by EP method			
		0.02	µg/kg dw				
Trichlorobenzenes	12002-48-1	Derivation of QS not required		A PNECsediment of 90 µg 1,2,4-TCB per kg sediment (ww) has been calculated in the risk assessment with the equilibrium partitioning method. As the log Kpsusp is <3, the calculation of a quality standard for sediment is normally not required.			
Trichloromethane	67-66-3	12	µg/kg ww	corresponding concentration in water: 2.5 µg/l			
Trifluralin	1582-09-8	3.14	µg/kg dw	corresponding concentration in water: 3.7 µg/l			
		0.683	µg/kg ww				

(1) PCDDs

- 2,3,7,8-T4CDD 1746-01-6
- 1,2,3,7,8-P5CDD 40321-76-4
- 1,2,3,4,7,8-H6CDD 39227-28-6
- 1,2,3,6,7,8-H6CDD 57653-85-7

PCDFs

- 2,3,7,8-T4CDF 51207-31-9
- 1,2,3,7,8-P5CDF 57117-41-6
- 2,3,4,7,8-P5CDF 57117-31-4
- 1,2,3,4,7,8-H6CDF 70648-26-9
- 1,2,3,6,7,8-H6CDF 57117-44-9
- 1,2,3,7,8,9-H6CDF 72918-21-9
- 2,3,4,6,7,8-H6CDF 60851-34-5
- 1,2,3,4,6,7,8-H7CDF 67562-39-4
- 1,2,3,4,7,8,9-H7CDF 55673-89-7
- 1,2,3,4,6,7,8,9-O8CDF 39001-02-0

DL-PCBs

- 3,3',4,4'-T4CB [77] 32598-13-3
- 3,3',4',5-T4CB [81] 70362-50-4



2,3,3',4,4'-P5CB [105] 32598-14-4
2,3,4,4',5-P5CB [114] 74472-37-0
2,3',4,4',5-P5CB [118] 31508-00-6
2,3',4,4',5'-P5CB [123] 65510-44-3
3,3',4,4',5-P5CB [126] 57465-28-8
2,3,3',4,4',5-H6CB [156] 38380-08-4
2,3,3',4,4',5'-H6CB [157] 69782-90-7
2,3',4,4',5,5'-H6CB [167] 52663-72-6
3,3',4,4',5,5'-H6CB [169] 32774-16-6
2,3,3',4,4',5,5'-H7CB [189] 39635-31-9
1,2,3,7,8,9-H6CDD 19408-74-3
1,2,3,4,6,7,8-H7CDD 35822-46-9
1,2,3,4,6,7,8,9-O8CDD 3268-87-9

(2) 25637-99-4 (1,3,5,7,9,11-Hexabromocyclododecane)
3194-55-6 (1,2,5,6,9,10- Hexabromocyclododecane)
134237-50-6 (α -Hexabromocyclododecane)
134237-51-7 (β -Hexabromocyclododecane)
134237-52-8 (γ - Hexabromocyclododecane)

(3) 1763-23-1 (acid)
2795-39-3 (potassium salt)
29081-56-9 (ammonium salt)
29457-72-5 (lithium salt)
70225-39-5 (diethanolamine salt)
56773-42-3 (tetraethyl-ammonium salt)
251099-16-8 (didecyldimethyl-ammonium salt)



ANNEX V EXAMPLES FORM ELBE RIVER-BASIN SEDIMENT MANAGEMENT PLAN

source:

Heininger et.al. (2015) Sediment Management on River-Basinscale: The River Elbe, Heininger and Cullmann (Ed.) (2015) Sediment matters. 247 p. Koblenz, ISBN 978-3-319-14695-9, Page 217-218

and

Flussgebietsgemeinschaft Elbe, Sedimentmanagementkonzept der FGG Elbe

Vorschläge für eine gute Sedimentmanagementpraxis im Elbegebiet zur Erreichung überregionaler Handlungsziele, 25.11.2013

https://www.fgg-elbe.de/tl_files/Downloads/News/Sedimentmanagementkonzept/sedimentmanagementkonzept_fgg_final.pdf

Scheme of the risk analysis—sediment quality aspect

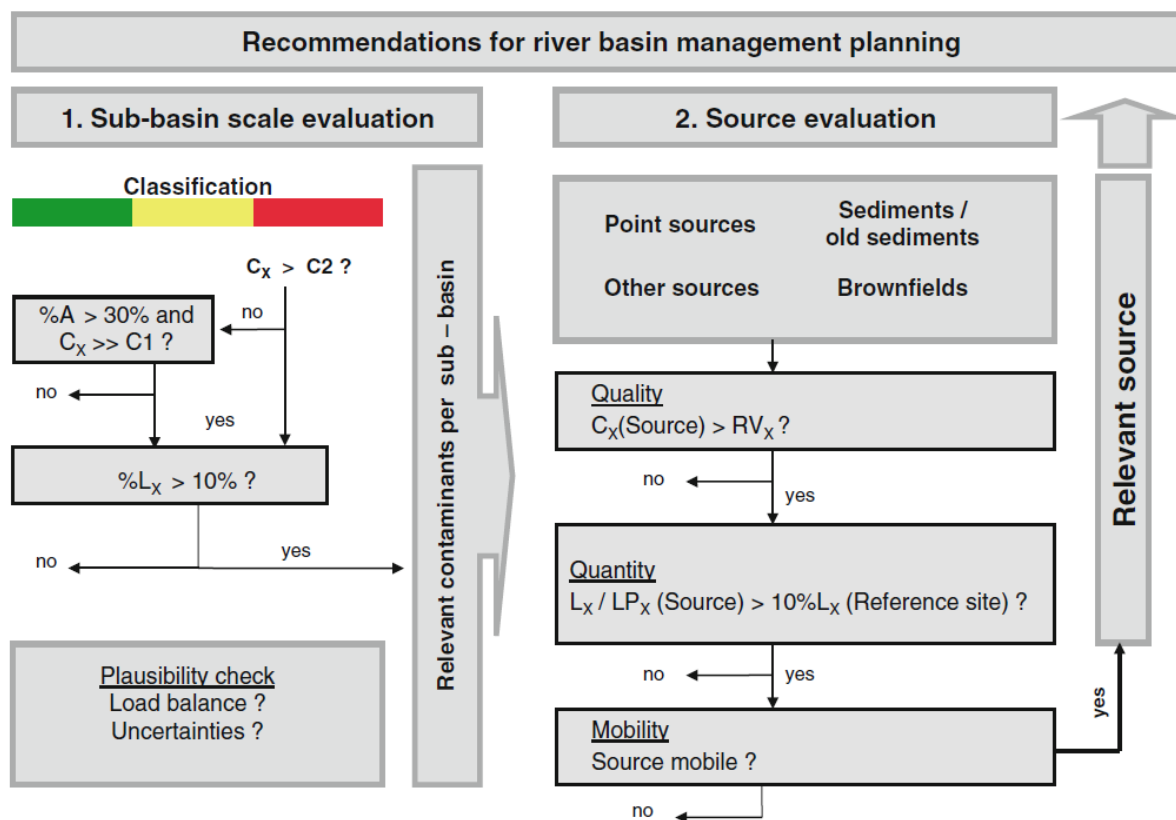


Fig. 8 Scheme of the risk analysis—sediment quality aspect. A area of the catchment, C concentration, $C1/C2$ lower/upper threshold value, L load, LP load potential, RV reference value, X relevant contaminant

Elbe-relevant contaminants in the context of river-basin sediment management

Table 1 Elbe-relevant contaminants in the context of river-basin sediment management

No.	Contaminant	Unit	Lower threshold (C1)	Upper threshold (C2)	Source of C2
1	Hg	mg/kg	0.15	0.47	Sb (2011)
2	Cd	mg/kg	0.22	2.3	Sb (2011)
3	Pb	mg/kg	25	53	Sb (2011)
4	Zn	mg/kg	200	800	OGewV (2011)
5	Cu	mg/kg	14	160	OGewV (2011)
6	Ni ^a	mg/kg	–	3	Sb (2011)
7	As	mg/kg	7.9	40	OGewV (2011)
8	Cr	mg/kg	26	640	OGewV (2011)
9	α-HCH	µg/kg	0.5	1.5	GÜBAK (2009)
10	β-HCH ^a	µg/kg	–	5	RHmV (2009)
11	γ-HCH	µg/kg	0.5	1.5	GÜBAK (2009)
12	p,p'DDT	µg/kg	1	3	GÜBAK (2009)
13	p,p'DDE	µg/kg	0.31	6.8	De Deckere et al. (2011)
14	p,p'DDD	µg/kg	0.06	3.2	De Deckere et al. (2011)
15	PCB-28	µg/kg	0.04	20	OGewV (2011)
16	PCB-52	µg/kg	0.1	20	OGewV (2011)
17	PCB-101	µg/kg	0.54	20	OGewV (2011)
18	PCB-118	µg/kg	0.43	20	OGewV (2011)
19	PCB-138	µg/kg	1	20	OGewV (2011)
20	PCB-153	µg/kg	1.5	20	OGewV (2011)
21	PCB-180	µg/kg	0.44	20	OGewV (2011)
22	Pentachlorobenzene	µg/kg	1	400	Sb (2011)
23	Hexachlorobenzene (HCB)	µg/kg	0.0004	17	Sb (2011)
24	Benzo(a)pyrene (BaP)	mg/kg	0.01	0.6	De Deckere et al. (2011)
25	Anthracene	mg/kg	0.03	0.31	Sb (2011)

(continued)

Table 1 (continued)

No.	Contaminant	Unit	Lower threshold (C1)	Upper threshold (C2)	Source of C2
26	Fluoranthene ^a	mg/kg	–	0.18	Sb (2011)
27	Sum of five PAH (Σ 5PAH) ^b	mg/kg	0.6	2.5	Sb (2011)
28	Tributyltin-Cation ^a (TBT)	μ g/kg	–	0.02	Sb (2011)
29	Sum of dioxins/ furanes (PCDD/F)	ng TEQ/kg	5	20	Evers et al. (1996)

^a Only upper threshold value C2 defined yet due to recent legislation specifics

^b 5 PAH: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3)pyrene

See more details about Elbe river sediment management plan in: Peter Heininger and Johannes Cullmann Editors, *Sediment Matters*, Springer International Publishing Switzerland 2015, ISBN 978-3-319-14695-9 ISBN 978-3-319-14696-6 (eBook), DOI 10.1007/978-3-319-14696-6



ANNEX VI LIST OF PNEC/EQS_{SED}, EQO

Source: 'JRC, Second Review of the Priority Substances List under the Water Framework Directive: Monitoring-based exercise, 2016' report Table III-6.

CAS number	Substance name	PNEC/EQS _{sed} (µg/kg) dw	Country / Institution	Available PNEC/EQS		Reference	µg/kg ww	Selected PNEC/EQS
				Sediment-type				
7440-47-3	Chromium	90000	US, ECHA	fresh water	US-EPA, 2000; EU risk assessment report, 2005	90000		
		640000	DE		DG Environment report, 2012, Johnson, I., et al., WRcRef: UC8981/1			
		205700	ECHA		Chromium ECHA dossier			
53-19-0	DDD, o,p'	0.99			James et al., 2009	0.99		EqP INERIS
56-55-3	Benzo(a)anthracene	27.7			James et al., 2009	27.7		EqP INERIS
		10000	DK		DG Environment report, 2012, Johnson, I., et al., WRcRef: UC8981/1			
		7240	UK; CAN	marine water	Cole et al., 1999			
		12000	IT	coastal water	Maggi et al., 2012			
7440-38-2	Arsenic	17000	US, ECHA	fresh water	US-EPA, 2000	17000		
		25000	FR		Mamindy-Pajany, Y., et al., 2013			
		87000	ECHA		Copper ECHA dossier	87000		
7440-50-8	Copper	160000	DE		DG Environment report, 2012, Johnson, I., et al., WRcRef: UC8981/1			
		197000	US	fresh water	US-EPA, 2000			
7440-66-6	Zinc	117800	ECHA		Zinc ECHA dossier	117800		
		315000	US	fresh water	US-EPA, 2000			
85-01-8	Phenanthrene	2708			James et al., 2009	2708		EqP INERIS
		3000	DK		DG Environment report, 2012, Johnson, I., et al., WRcRef: UC8981/1			
1002-53-5	Dibutyltin (dichloride)	7.0	ECHA	fresh water	Dibutyltin dichloride ECHA dossier	6.526		
		100	DE		DG Environment report, 2012, Johnson, I., et al., WRcRef: UC8981/1			
1163-19-5	Decabromodiphenyl ether (BDE-209)	384000	ECHA	fresh water	BDE-209 ECHA dossier	384000		
1461-25-2	Tetrabutyltin	0.202			James et al., 2009	0.202		EqP INERIS
207122-16-5	2,2',3,4,4',5',6'-Heptabromodiphenyl ether (BDE-183)	266			EqP (calculated by JRC)	266		
		49000			BDE EQS datasheet, 2005			
		25.6			EqP (calculated by JRC)			
668-34-8	Triphenyltin	20	DE		DG Environment report, 2012, Johnson, I., et al., WRcRef: UC8981/1	20		
78763-54-9	Monobutyltin	1.17			James et al., 2009	1.17		EqP INERIS
1336-36-3	Polychlorinated biphenyls (PCB) sum	0.403			James et al., 2009			EqP INERIS; STE score is not reported since PCBs were measured only in 3MS

Note: EqP= Equilibrium Partitioning

ANNEX VII HEAVY METALS EVALUATION METHODS' CURRENT STATUS AND PROBLEMS

Gheorghe Damian, Gheorghe Iepure, Daniel Nasui & Zsolt Szakacs (RO-TUCN)

1. Legislative background

The relevant directives in the field of water policy are:

- I. **DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy (OJ L 327, 22.12.2000, p. 1).** Its latest consolidated version ([20/11/2014](#)) can be found at: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02000L0060-20141120> . This Directive was amended by:

		Official Journal		
		No	page	date
M1	Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001	L 331	1	15.12.2001
M2	Directive 2008/32/EC of the European Parliament and of the Council of 11 March 2008	L 81	60	20.3.2008
M3	Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008	L 348	84	24.12.2008
M4	Directive 2009/31/EC of the European Parliament and of the Council of 23 April 2009	L 140	114	5.6.2009
M5	Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013	L 226	1	24.8.2013
M6	Council Directive 2013/64/EU of 17 December 2013	L 353	8	28.12.2013
M7	Commission Directive 2014/101/EU of 30 October 2014	L 311	32	31.10.2014

ANNEX VIII, INDICATIVE LIST OF THE MAIN POLLUTANTS contains, among others:

3. Organotin compounds
6. Cyanides.
7. Metals and their compounds.
8. Arsenic and its compounds.
11. Substances which contribute to eutrophication (in particular, nitrates and phosphates).

ANNEX X LIST OF PRIORITY SUBSTANCES IN THE FIELD OF WATER POLICY contains

Number	CAS number (1)	EU number (2)	Name of priority substance (3)	Identified as priority hazardous substance
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(20)	7439-92-1	231-100-4	Lead and its compounds	
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(23)	7440-02-0	231-111-4	Nickel and its compounds	

It states in section 1.3.4

- a.) "For the surveillance monitoring period, the frequencies for monitoring parameters indicative of physico-chemical quality elements given below should be applied unless greater intervals would be justified on the basis of technical knowledge and expert judgement
- b.) Frequencies shall be chosen so as to achieve an acceptable level of confidence and precision. Estimates of the confidence and precision attained by the monitoring system used shall be stated in the river basin management plan.
- c.) Monitoring frequencies shall be selected which take account of the variability in parameters resulting from both natural and anthropogenic conditions. The times at which monitoring is undertaken shall be selected so as to minimise the impact of seasonal variation on the results, and thus ensure that the results reflect changes in the water body as a result of changes due to anthropogenic pressure. Additional monitoring during different seasons of the same year shall be carried out, where necessary, to achieve this objective.

Physico-chemical Quality element	Rivers	Lakes	Transitional	Coastal
Other pollutants	3 months	3 months	3 months	3 months
Priority substances	1 month	1 month	1 month	1 month

It also states in section 1.3.5 that the monitoring programmes required above shall be supplemented in order to fulfil the special requirements for:

- a.) Drinking water abstraction points
- b.) Habitat and species protection areas

In section 1.3.6 Standards for monitoring of quality elements it is underlined that "Any relevant CEN/ISO standard" must be applied for physico-chemical parameters

- II. **DIRECTIVE 2008/105/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (OJ L 348, 24.12.2008, p. 84).** This Directive was amended by: Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013, L 226, page 1, date: 24.8.2013. Its latest consolidated version ([13/09/2013](#)) can be found at: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02008L0105->

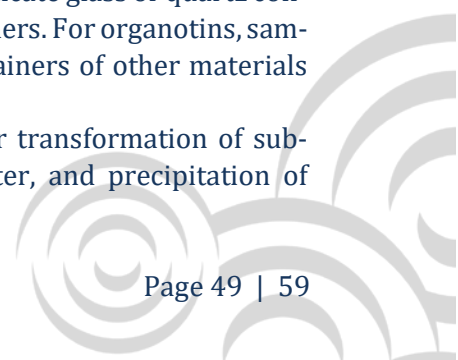
20130913. In ANNEX I ENVIRONMENTAL QUALITY STANDARDS FOR PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS PART A: ENVIRONMENTAL QUALITY STANDARDS (EQS) presents the EQS's of heavy metals for waters and biota, but no specific values are given for sediments. Moreover, sediments are excluded from quantification because by way of derogation, in the case of cadmium, lead, mercury and nickel, the water EQS refer to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0,45 µm filter or any equivalent pre-treatment, or, where specifically indicated, to the bioavailable concentration. Also, it is stated that Member States may, when assessing the monitoring results against the relevant EQS take into account

- (a) natural background concentrations for metals and their compounds where such concentrations prevent compliance with the relevant EQS;
- (b) hardness, pH, dissolved organic carbon or other water quality parameters that affect the bioavailability of metals, the bioavailable concentrations being determined using appropriate bioavailability modelling.

CEN/ISO standard” must be applied for physico-chemical parameters

III. COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC) Guidance Document No. 19 GUIDANCE ON SURFACE WATER CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE states that

- a.) For many substances, screening of the levels in water as well as in biota with limited mobility and in sediment will be the best way to get the optimum information within a given amount of resources. When the problem areas are identified, analysis of a limited number of water samples can be performed.
- b.) Important principles of sampling strategy have been described in the CIS guidance document No.7 (e.g., 2.4., 2.7.2, 5.2.5). Depending on the objective of the monitoring, the physicochemical properties of the substance to be monitored and the properties of the water body under study water, sediment and/or biota samples have to be taken.
- c.) If the monitoring programme requires analysis of the fine sediment fraction, the sample should be split using appropriate sieving techniques.
- d.) Passive samplers (e.g., Semi-Permeable Membrane Devices (SPMD), Polar Organic Chemical Integrative Samplers (POCIS), Diffusion Gradient Thin Films (DGTs), Chemcatcher) are exposed in the aquatic environment for several days or up to weeks to yield time-integrated average concentration of organic contaminants or heavy metals. Passive sampling is less influenced by short-term fluctuations in concentrations than spot sampling. Since one of the primary objectives of the WFD is the assessment of the average concentrations of pollutants in water bodies, the determination of time-integrated concentrations using passive samplers seems to be a promising approach. Some of the passive samplers have been validated and provide high sampling rates (litre/day) for various contaminants (e.g., heavy metals), and thus, allow quantification of extremely low pollution levels in water. This is a first step towards an internationally recognized standard.
- e.) Samples collected for analysis of metals can be stored in closed plastic or glass containers. For mercury, samples must be stored in acid-washed borosilicate glass or quartz containers, as mercury can move through the walls of plastic containers. For organotins, samples are preferably stored in amber glass containers, but containers of other materials such as polycarbonate or aluminium are also suitable.
- f.) Sample preservation is needed in many cases to avoid loss or transformation of substances due to redox processes, degradation of organic matter, and precipitation of



metals as hydroxides. If samples are analysed within 24 h and stored in the dark at 1-5 °C, sample composition, and hence, results of chemical analyses will not change significantly. Storage of samples at temperatures below -20 °C may allow the sample to be stored for longer time periods. However, freezing is not appropriate in some circumstances. Freeze-drying samples at low temperature (e.g., < 10 °C) is the preferred alternative to freezing.

- g.) Bioavailable metal concentrations depend on various parameters including pH, Ca and Mg concentrations, as well as dissolved organic carbon concentration. Hence, measuring these parameters in parallel with the metals can assist in the interpretation of results, where appropriate. In case of cadmium, the measurement of hardness is mandatory because EQS values have been derived for five classes of hardness.
- h.) The less than 63 µm fraction should be analysed for metals. If the specific purpose of the monitoring requires analysis of the fine sediment fraction, the sample should be split using appropriate sieving techniques.
- i.) For sediments, measurements of the two operationally defined parameters Acid Volatile Sulfides (AVS) and Simultaneously Extractable Metals (SEM) can provide information on the bioavailability of metals, although guidance on the interpretation of AVS is still in preparation in the EU EQS Technical Guidance – Metals section.

IV. COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC) Guidance document No. 27 Technical Guidance For Deriving Environmental Quality Standards states in section 2.10.1 that metals are essential nutrients so, when they are not present in sufficient concentrations, can limit growth, survival and reproduction of the organisms. Excess amounts of certain metals, on the other hand, are potentially toxic (essential metals: Cr, Cu, Ni, Zn, non-essential metals: As, Cd, Pb, Hg). When evaluating toxicity data to derive quality standards for metals, total metal concentrations are not usually directly related to ecotoxicological effects because many abiotic and biotic processes can modify the availability of metals, even rendering them unavailable for uptake. This means that the fraction available for uptake and toxicity may be a very small part of the total metal present. It is also stated that “Freshwater and saltwater toxicity data for metals should be separated a priori.” The Derivation of EQSs for metals is done in section 3.5.

V. COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC) Guidance document No. 25 ON CHEMICAL MONITORING OF SEDIMENT AND BIOTA UNDER THE WATER FRAMEWORK DIRECTIVE deals with analytical methods for metal concentration determinations from sediments in section 5.3.

For the determination of metal concentrations in sediment, samples must be digested with concentrated inorganic acids in a traditional open system or, more commonly, in sealed vessels in a microwave oven and analysed by methods such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) or ICP-MS, graphite furnace atomic absorption spectroscopy (GFAAS) or atomic fluorescence spectrometry.

OSPAR recommends the inclusion of HF in the digesting medium [OSPAR, 2003]. By this approach, the total metal content, including that part which is of geochemical origin, is measured and that procedure allows the application of normalisation co-factors based on Al or Li content (see 5.4). This approach requires knowledge of the distribution of background concentrations of trace metals of geochemical origin.

In surface waters, background concentrations are less assessed and are very variable in a water body. HF digestion could lead to an overestimation of the trace metals content. The use of less aggressive acid mixtures (such as for example concentrated nitric acid + hydrochloric acid, Aqua regia), which are moreover safer substitutes, is therefore recommended, depending also on the final detection technique.

SEM-AVS (Simultaneously Extracted Metals – Acid Volatile Sulphides) analysis should be carried according to the United States Environmental Protection Agency (US-EPA) method [U.S. EPA, 1991] integrated by the Dutch National Institute for Public Health and the Environment (RIVM). Extraction with 6M HCl solution should be carried out on a homogenised wet sample. The formed H₂S gas, collected in a NaOH-solution, is spectrophotometrically determined at 660 nm using dimethyl-p-phenylenediamine hydrochloride as colour reagent. Metals are determined on the filtered supernatans.

- VI.) **List of Priority Substances for the Danube River Basin dated 25 April 2003**, which besides Cd, Pb, Ni, Hg and their compounds introduces in list B the following General Parameters and Priority Substances specific for the Danube River Basin to be monitored:

B1: General Parameters

	CAS number	EU number	Name of priority substances or groups of substances
(34)	not applicable	not applicable	Chemical Oxygen Demand (COD)
(35)	not applicable	not applicable	Ammonical Nitrogen (NH ₄ -N)
(36)	not applicable	not applicable	Total Nitrogen (tot N)
(37)	not applicable	not applicable	Total Phosphorus (tot P)

B2: Danube Specific Priority Substances

(38)	7440-38-2	231-148-6	Arsenic and its compounds
(39)	7440-50-8	231-159-6	Copper and its compounds
(40)	7440-66-6	231-175-3	Zinc and its compounds
(41)	7440-47-3	231-157-5	Chromium and its compounds

It can be seen that, this list contains some of the parameters mentioned in DIRECTIVE 2000/60/EC ANNEX VIII, INDICATIVE LIST OF THE MAIN POLLUTANTS such as As and its compounds, P and N, completing it with other three metals (Cu, Zn, Cr) and their compounds.

2. Sediment heavy metal content evaluation standards

Because the relevant Directives, Guidances and Lists described in Cap 1 states that ISO standards should be used in evaluation of metal contents in sediments, naming them in the case of DRB the following ISO standards can be found to be relevant in evaluation of sediment heavy metal contents:

- a.) for Cd, Cr, Cu, Pb, Ni, Zn: **ISO 11047: 1998** Soil quality — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc — Flame and electrothermal atomic absorption spectrometric methods.

This International Standard specifies the methods flame, respectively electrothermal atomic absorption spectrometry for the determination, by atomic absorption spectrometry, of one or more of cadmium, chromium, copper, lead, nickel and zinc, in aqua regia extracts of soil obtained in accordance with ISO

11466:1994, Soil quality — Extraction of trace elements soluble in aqua regia. The choice of method for any element depends on the amount of that element expected to be in a sample, and both methods might be needed to cover all the elements in one sample. The methods are applicable when the extractable element content is above or below the amount of 2mg/kg for Cd, 12mg/kg for Cr, 5mg/kg for Cu, 15mg/kg for Pb, 12mg/kg for Ni, 2mg/kg for Zn dry matter. The determination of dry matter should be done using ISO 11465:1993, Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method.

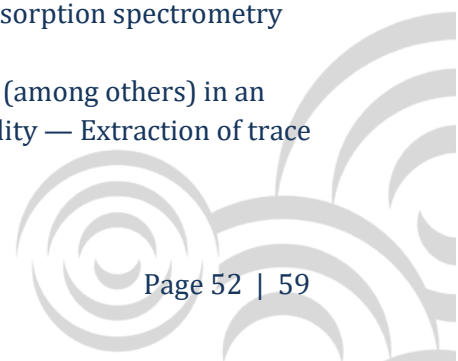
The samples should be prepared according to ISO 11464:2006 Soil quality — Pretreatment of samples for physico-chemical analysis, which are: drying, crushing, sieving, dividing and milling. The samples should also have a content of organic carbon less than about 20 % (m/m), according to ISO 10694:1995 Soil quality — Determination of organic and total carbon after dry combustion (elementary analysis). Materials containing more than about 20 % (m/m) organic carbon will require treatment with additional nitric acid, according to this standard. It also warns that in high solute concentrations in extract solutions, spectral interferences and background enhancement should be expected. Also, it warns that aqua regia will not totally dissolve most soils and similar materials. The efficiency of extraction for particular elements differs from element to element, and for the same element in different matrices, so that a prior analysis using reference materials should be done by the laboratory to quantify the extraction efficiency. Moreover, the elements extractable in *aqua regia* cannot be described as "totals" and they cannot be regarded as the "bio-available" fraction, as the extraction procedure is too vigorous to represent any biological process.

- b.) for Hg: **ISO 16772:2004** Soil quality — Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry along the technical specifications: **ISO/TS 16727:2013** Soil quality — Determination of mercury — Cold vapour atomic fluorescence spectrometry (CVAFS).

Combining these two specifications the limit of determination of at least 0,1 mg/kg can be reduced to 0,003 mg/kg of dry matter. The determinations should be made from an aqua regia soil extract, obtained in accordance with ISO 11464:2006 Soil quality — Pretreatment of samples for physico-chemical analysis and ISO 11466:1995 Soil quality — Extraction of trace elements soluble in aqua regia, using cold-vapour atomic absorption spectrometry or cold-vapour atomic fluorescence spectrometry. Because of this, the observations mentioned at point 1.1.a. remain valid. The 0,003 mg/kg of dry matter limit of determination can be attained when microwave-assisted nitric acid digestion of mercury is done from sludge (Municipal sludge), treated biowaste (Compost) and soil (Sludge-amended soils), where the standard is applicable and is validated. It is also true that this digestion will not necessarily accomplish total decomposition of the sample, and the extracted analyte concentrations may not necessarily reflect the total content in the sample.

- c.) for As: ISO 20280:2007 Soil quality — Determination of arsenic, antimony and selenium in aqua regia soil extracts with electrothermal or hydride-generation atomic absorption spectrometry

This International Standard specifies methods for the determination of arsenic (among others) in an aqua regia extract of soil obtained in accordance with ISO 11466:1995 Soil quality — Extraction of trace



elements soluble in aqua regia, by electrothermal or hydride-generation atomic absorption spectrometry.

This way, one can conclude that, in this case, the relevant ISO Standards are:

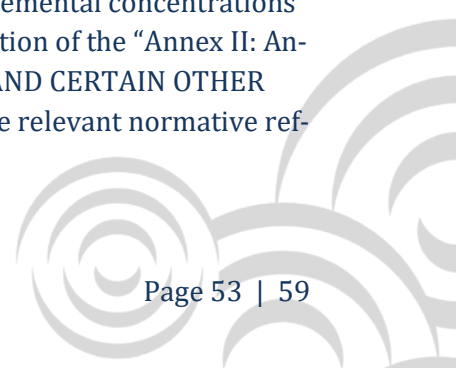
- ISO 11464:2006, Soil quality — Pretreatment of samples for physico-chemical analysis
- ISO 11465:1993, Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method
- ISO 11466:1995, Soil quality — Extraction of trace elements soluble in aqua regia
- ISO 16729, Soil quality — Digestion of nitric acid soluble fractions of elements
- ISO 10694:1995, Soil quality — Determination of organic and total carbon after dry combustion (elementary analysis)
- ISO 11047: 1998 Soil quality — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc — Flame and electrothermal atomic absorption spectrometric methods
- ISO 16772:2004 Soil quality — Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry
- ISO/TS 16727:2013 Soil quality — Determination of mercury — Cold vapour atomic fluorescence spectrometry (CVAFS)
- ISO 20280:2007 Soil quality — Determination of arsenic, antimony and selenium in aqua regia soil extracts with electrothermal or hydride-generation atomic absorption spectrometry

The trueness and precision of the measurement methods should be checked using ISO 5725-1:1994, Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions

One must note that ISO 11047: 1998 Soil quality — Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc — Flame and electrothermal atomic absorption spectrometric methods includes both priority (hazardous) heavy metals named in “Annex I: Annex X: LIST OF PRIORITY SUBSTANCES IN THE FIELD OF WATER POLICY” from DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL regarding priority substances in the field of water policy, and in “List of Priority Substances for the Danube River Basin” from 25 April 2003 as Danube Specific Priority Substances. So that, the same elemental concentration quantification method has to be applied to fulfil the guidance slayed out in both documents.

Moreover, the above presented standards also cover Co, Mn, Sb and Se, elements which are not included in the relevant directives. This allows to extend the analysis at least to cover these elements, in the case of their inclusion into HS list, making the protocol sustainable.

The above-mentioned standard methods are applicable to a broad domain of elemental concentrations so that the protocol would not be needed to be modified in the case of modification of the “Annex II: Annex I: ENVIRONMENTAL QUALITY STANDARDS FOR PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS” in the case of the priority (hazardous) heavy metals stated in the relevant normative references.



3. National differences in legislation and sampling methodology

Regarding the legal norms concerning sediment pollution, monitoring and the establishment of quality classes, there are national level of legislation only in Slovakia and Serbia. Romania and Slovenia have some predictions related to sediments from water laws.

In Deliverable 3.1.1 – COUNTRIES MAPS AND METADATA REPORT, Table 7 – List of legislation related to sediments) national legislation regarding sediments is available only for Slovakia (Smernica MŽP SR č. 4/1999-3, Metodický pokyn MŽP SR č.549/98-2, Vyhláška MZe ČR s MŽP ČR č. 257/2009) and partially for Romania (RO Ord.161/2006 Order no. 161 of 16/02/2006) and SR.

Country	AT	BA	BA-SRP	BG	HR	DE	HU	MD	ME	RO	SK	SI	SR	UA
National legislation related to sediments	-	-	-	-	-	-	-	-	-	Partial	Yes	-	Yes*	-

* Although SR provided details referring to the content of HSs in sediments, the law title was not listed

Maximum content of heavy metals trace elements in river sediments (D3.1.1 - Table 25) is determined in the following DRB countries: HR, MD, RO, RS, SK

Country acronym	Trace elements[$\mu\text{g/g}$]- Maximum content - River sediments							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
AT	-	-	-	-	-	-	-	-
BA	-	-	-	-	-	-	-	-
BA-SRP	-	-	-	-	-	-	-	-
BG	-	-	-	-	-	-	-	-
HR	55	12	380	190	10	210	530	720
DE	-	-	-	-	-	-	-	-
HU	-	-	-	-	-	-	-	-
MD	2	3	-	-	2.1	75	32	300
ME	-	-	-	-	-	-	-	-
RO	29*-	0.8*-	100*	40*	0.3*	35*	85*	150*
RS	29	0.8	100	-	36	35	85	140
SK	55	12	380	190	10	210	530	720
SI	-	-	-	-	-	-	-	-
UA	-	-	-	-	-	-	-	-

*means that for Romania the following valence states: As³⁺, Cd²⁺, Cr³⁺, Cr⁶⁺, Cu²⁺, Pb²⁺, Hg²⁺, Zn²⁺, Ni²⁺ (Order 161/16.02.2006 pg. 119 "Elements and chemical quality standards for sediments with the granulometric fraction 63 μm).

Normal content of trace elements in river sediments (table 26) is available only in: HR, SK

Country acronym	Trace elements[$\mu\text{g/g}$]- Normal Content - River sediments							
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn

HR	29	0.8	100	36	0.3	35	85	140
SK	29	0.8	100	36	0.3	35	85	140

In UA there are methods for complex environmental assessment but those are not approved on an official level. In situ measurements are being determined only in Austria (electrical conductivity, pH, redox potential).

Tools for collecting samples for laboratory measurements are being described in Austria (stainless steel shovels and sieves), Moldavia (Ekman dredge for soft sediments on deeper water sites, simple cylinders for soft and thin sediments (10 – 30 cm), Auger sampler for thicker sediments) and Ukraine (a plastic scoop, or a stainless steel blade is used for 0.2 - 0.3 m thick silt and sandy sediments. For 0.3 - 3.0 m thick mud, the Giller peat drill is used).

In Table 33 - Protocols for sampling, transport and storage used for sediments, soil, water and biota, the following protocols are being used across DRB countries for sediment sampling: ISO 5667-1:2008. Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques for all aspects of sampling of water (including waste waters, sludges, effluents and bottom deposits); ISO 5667-17:2012. Water quality. Sampling. Part 17: Guidance on sampling banks and suspended material; ISO 5667 Part 12: Bottom sediments. Water quality - Sampling - Part 13:2011 Guidance on sampling of sludges. For transport and storage of sediments only one protocol is being used: ISO 5667-15:2013. Water quality - Sampling – Part 15: Guidance on the preservation and handling of sludge and sediment samples.

4. Evaluation of laboratory methodologies for heavy metals

For the standardization of laboratories that will perform the analysis of heavy metals it is recommended to use the ISO / IEC 17025 standard as well as of other protocols:

- ISO11929: 2010 Determination of the characteristic limits (decision threshold, detection limit and confidence interval limits) for measurements of ionizing radiation - Fundamentals and application;
- JCGM 100: 2008 Evaluation of measurement data - Guide to the expression of uncertainty in measurement;
- Measurement uncertainty. IAEA-TECDOC-1585, IAEA, Vienna 2008;
- Guide to expression of Uncertainty in Measurement. (GUM), 1995.ISO;
- The Fitness for Purpose of Analytical Methods; A Laboratory Guide to Method Validation and Related Topics (ISBN 978-91-87461-59-0. Available from www.eurachem.org.)

Detection limits for heavy metals should be less than 0.1mg / Kg for Pb, Hg, Cd, Cu, As, Ni, Cr and 1mg / Kg for Zn. These laboratories must perform a conformity assessment, with the requirement for testing, sampling and calibration.

ICP-MS, ICP-AES systems



The ICM-MS method is a very good analytical method for the determination of heavy metals. In Deliverable 3.1.1. the analytical methods and standards for heavy metals from different types of water including drinking water are described in detail and less for the analytical methods for analyzing heavy metals.

For the analysis of heavy metals in sediments the standard: EN 16171 2016 - Processed sediment and soils should be used. Element determination with (ICPMS), as presented in Deliverable 3.1.1.

AAS systems

This system is indicated for the determination of heavy metals in soils according to ISO 11047/1998 - Soil quality - Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc is performed by flame and electrothermal atomic absorption spectrometric methods. The use of GFAAS (Graphite furnace atomic absorption spectrophotometry) for Pb and CVAAS analyzer for Hg is also very good.

XRF

By this method, heavy metals can be analyzed according to ISO 18227: 2014 (Soil quality - Determination of elemental composition by XRF) specifying the procedure for a quantitative determination of major and trace element concentrations in homogeneous solid waste, soil, and soil-like material by energy dispersive X-ray fluorescence (EDXRF) spectrometry or wavelength dispersive X-ray fluorescence (WDXRF) spectrometry using calibration with matrix-matched standards. By this standard we can analyze: Cr, Ni, Cu, Zn, As, Cd, Hg, Pb. Concentration levels between approximately 0.0001% and 100% can be determined, depending on the element and the instrument used.

XRD

Heavy metals cannot be determined by this method. It is a method of mineralogical analysis. By this method heavy minerals can be determined in which the composition of metals enters. The limit of detection of minerals containing heavy metals by this method is about 1%. At these contents the heavy metals in the soils exceed all the standards of all countries in the Danube Basin.

5 EVALUATION METODS FOR HEAVY METALS

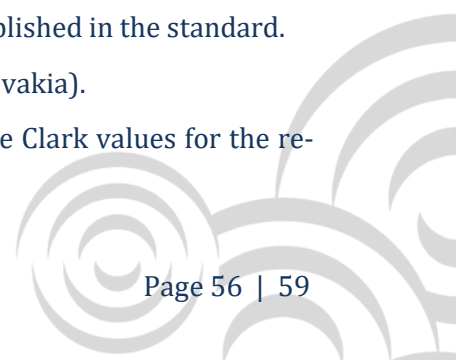
Establishing threshold values for HSs

For heavy metals, threshold limits must be set within the sediments sampled from river water. For many countries in the Danube Basin there are no standards for heavy metals from river sediments (Hungary).

In some countries (Bulgaria) it is calculated as an annual average for each body of water, which means that for each monitoring place representative for a water body, the arithmetic mean value of the concentrations measured at different times of the year does not exceed the value established in the standard.

In other countries the threshold values for soil are used (Moldova, Romania Slovakia).

Another method for assessing the threshold values of heavy metals may be the Clark values for the respective elements (Moldova).



In Slovakia, four sets of values related to heavy metals have been developed for sediments and leachate sediments.

Environmental Quality Standards (EQSs) have been adopted in Hungary, Slovenia, Bosnia and Herzegovina (Srpska Republic), Montenegro and Germany.

Fixed or variable threshold values for HSs

The values of the quality standard are fixed in: Bulgaria, Romania, Bosnia and Herzegovina (Srpska Republic). In some countries the standards are calculated according to the results of the monitoring: Bulgaria. In Slovenia, environmental quality standards are fixed. For some heavy metals, natural background and bioaccumulation are taken into account. In the Republic of Moldavia, the threshold value has been evaluated for different soil types, depending on the granulometric and organic content.

In Croatia, Hungary and Serbia, the threshold values for heavy metals are set according to the WFD (Water Framework Directive), while in Hungary EQS corrections are used.

In Slovakia, the values of the quality standard are established for a specific water management plan taking into account the natural background concentrations of heavy metals and their compounds, water hardness, pH, dissolved organic carbon and other water quality parameters.

The values of the quality standard for heavy metals in the Danube Basin countries are established in national and/or international legislative acts. The legislation reflects the phenomenon of selective bioaccumulation and traceability of metals to a small extent (the accumulation of mercury in large fish or PAH in certain biota). Establishing a bioconcentration factor and association with a certain type of biota is not reflected in the general legislation. That is why common standards should be set for all countries in the Danube Basin.



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