

**SEDIMENT QUALITY  
EVALUATION PROTOCOL  
FOR HAZARDOUS SUBSTANCES  
IN SURFACE WATERS  
PROPOSAL**

**PART OF THE SEDIMENT-QUALITY INFORMATION,  
MONITORING AND ASSESSMENT SYSTEM (SIMONA)**

**THE MAIN AIM IS TO SUPPORT TRANSNATIONAL  
COOPERATION FOR JOINT DANUBE BASIN WATER  
MANAGEMENT**

**30/04/2021**

Project co-funded by the European Union (ERDF, IPA and ENI)



**Authors:** Katalin Mária Dudás and Gyozo Jordan (HU-MATE)

Co-authors:

Ajka Šorša (HR-HGI-CGS)	Dragica Vulić (RS-JCI)
Danijel Ivanišević (HR-HGI-CGS)	Tatjana Mitrović (RS-JCI)
Lidija Galović (HR-HGI-CGS)	Igor Striček (SK-SGIDS)
Ana Čaić Janković (HR-HGI-CGS)	Jozef Kordík (SK-SGIDS)
Ivan Mišur (HR-HGI-CGS)	Zsófia Kovács (HU-OVF)
Jasmina Antolić (HR-CW-HV)	Zsolt Szakacs (RO-TUCN)
Đorđa Medić (HR-CW-HV)	Kristina Šarić (RS-UB-FMG)
Ines Đurđević (HR-CW-HV)	Volodymyr Klos (UA-UGC)
Neven Bujas (HR-CW-HV)	Neda Dević (ME-GSM)
Aleksandra Kovačević (BA-JUVS)	Slobodan Radusinovic (ME-GSM)
Jelena Vićanović (BA-JUVS)	Mileva Milić (ME-GSM)
Jasminka Alijagić (SI-GEOZS)	Milica Mrdak (ME-GSM)
Robert Šajn (SI-GEOZS)	Mária Mörtl (HU-MATE)
Sebastian Pfeleiderer (AT-GBA)	András Székács (HU-MATE)
Atanas Hikov (BG-GI-BAS)	Eszter Takács (HU-MATE)
Zlatka Milakovska (GI-BAS)	Ivana Živadinović (RS-UB-FMG)
Milena Vetseva (BG-GI-BAS)	Ismir Hajdarević (BA-FZG)
Petyo Filipov (BG-GI-BAS)	Albert Baltres (RO-IGR)
Irena Peytcheva (BG-GI-BAS)	Anca-Marina Vijdea (RO-IGR)
Prvoslav Marjanović (RS-JCI)	Veronica Alexe (RO-IGR)
Marko Marjanović (RS-JCI)	Barbara Keri (HU-BME)

Responsible(s) for the output:

Katalin Mária Dudás and Gyozo Jordan (HU-MATE)

Editing and preparation for printing: Katalin Mária Dudás (HU-MATE)

Please cite this protocol as: Katalin Mária DUDÁS and Gyozo JORDAN, The SIMONA Project Team. 2021. Sediment quality evaluation protocol for HSs. EU Interreg Danube Transnational Programme. 57p.

## **Table of Contents**

<b>1. PURPOSE.....</b>	<b>3</b>
<b>2. SCOPE.....</b>	<b>3</b>
<b>3. BASIC TERMS.....</b>	<b>4</b>
<b>4. SOURCES AND PRESENTATION.....</b>	<b>6</b>
<b>5. UNDERSTANDING THE FLUVIAL SEDIMENT SYSTEM.....</b>	<b>7</b>
<b>6. UNDERSTANDING SEDIMENT QUALITY EVALUATION.....</b>	<b>14</b>
<b>7. EVALUATION OF OVERBANK (FLOODPLAIN) SEDIMENT QUALITY.....</b>	<b>16</b>
7.1 PRINCIPAL CONSIDERATIONS.....	16
7.2 PRACTICAL EVALUATION.....	18
7.3 RECOMMENDATION FOR TRANSNATIONAL MONITORING.....	19
<b>8. EVALUATION OF SUSPENDED SEDIMENT QUALITY.....</b>	<b>20</b>
8.1 PRINCIPAL CONSIDERATIONS.....	20
8.2 PRACTICAL EVALUATION.....	25
8.3 RECOMMENDATION FOR TRANSNATIONAL MONITORING.....	29
<b>9. EVALUATION OF BOTTOM SEDIMENT QUALITY.....</b>	<b>30</b>
9.1 PRINCIPAL CONSIDERATIONS.....	30
9.2 PRACTICAL EVALUATION.....	34
9.3 RECOMMENDATION FOR TRANSNATIONAL MONITORING.....	38
<b>10. SELECTION OF HAZARDOUS SUBSTANCES FOR SEDIMENT QUALITY EVALUATION.....</b>	<b>39</b>
10.1 PRINCIPAL CONSIDERATIONS.....	39
10.2 PRACTICAL EVALUATION.....	40

<b>11. TREND ASSESSMENT FOR SEDIMENT QUALITY .....</b>	<b>41</b>
11.1 PRINCIPAL CONSIDERATIONS.....	41
11.2 PRACTICAL EVALUATION.....	50
<b>References .....</b>	<b>52</b>

### **Appendix 1**

Organic carbon – water partition coefficient ( $K_{OC}$ ), sediment – water partition coefficient ( $K_{sed-water}$ ) and octanol-water partition coefficient ( $K_{OW}$ ) for the HSS listed in the EU EQS Directive.

### **Appendix 2**

List of Priority Substances and Danube River Basin Specific Pollutants

### **Appendix 3**

Annex I of the 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

The appendixes are downloadable  
from the SIMONA website:  
<http://www.interreg-danube.eu/simona/>



## **1. PURPOSE**

The purpose of this document to give practical guidance for sediment quality monitoring data evaluation in compliance with the EU Water Framework Directive (EC 2000), with focus on the use for the Danube Basin Countries.

## **2. SCOPE**

This document describes sediment quality monitoring data evaluation for:

- river sediment (sediment associated with the fluvial – flowing surface water – system)
- surveillance monitoring (regular monitoring for long-term changes)
- single monitoring site (sampling station)
- single water body
- hazardous substances listed in the EU WFD Annex X and EQS directive
- single substances (mixtures are not considered)
- monitoring data that is complete and have proper quality for the evaluation
- evaluation is limited to the assessment of sediment quality according to the Water Framework Directive; evaluation of water body status which may require water and biota quality assessment is out of the scope
- Environmental Quality Standard (EQS) contamination limit values are available for surface water HS concentrations.
- development toxicity tests related to EQS values for sediment quality evaluation is outside of the scope.

### 3. BASIC TERMS

The following terms are relevant for the understanding of the scope of this document.

**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 (EC 2000).

**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. ('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.) (EC 2000)

**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. ('Surface water' means inland waters, except groundwater.) (EC 2000)

**Fluvial sediment** is solid material transported (moved and deposited) by river as bottom sediment (river bed and bed load), suspended sediment or overbank (floodplain) sediment.

**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). Sub-basin is also called **catchment**.

**Surveillance monitoring** aims to allow assessment of long-term changes in natural conditions and the assessment of long-term changes resulting from human activity; in addition to the efficient and effective design of future monitoring programmes and the validation of the impact assessment procedure (EC

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

2000). Surveillance Monitoring is different from the other two types of monitoring: Operational Monitoring and Investigative Monitoring.

**Monitoring site** (EC 2000), also called **sampling station** (EC 2010), is a well delimited area, where sampling operations take place [IUPAC 2005 Pure and Applied Chemistry 77, 827–841]

**Hazardous substances** mean 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 (EC 2000). Note that priority substances mean substances identified in accordance with WFD (EC 2000) Article 16(2) and listed in Annex X. Among these substances there are priority hazardous substances which means substances identified in accordance with WFD (EC 2000) 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 WFD (EC 2000) 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.

**Quality Standard** for any measured medium (i.e. water, suspended sediment, bottom sediment, overbank sediment, soil or biota) means the concentration of a particular pollutant or group of pollutants in measured medium which should not be exceeded in order to protect the relevant receptors connected to the measured medium.

### **Monitoring data is complete (no missing data) if**

- all the parameter values necessary for sediment quality evaluation (assessment) are available,
- all the monitoring period is covered that is necessary for sediment quality evaluation (assessment),

and have proper quality if

- analytical method is capable of measuring concentration value at or below the 30% the environmental standard (i.e.  $LOQ \leq 30\% \text{ EQS}$ ),
- it does not require further uncertainty analysis.

## 4. SOURCES AND PRESENTATION

This protocol does not develop or present any new method for sediment quality assessment. It is based exclusively on the existing EU WFD guidance documents, primarily on

EC 2018. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document **No. 27** Technical Guidance for deriving **Environmental Quality Standards**. Luxembourg, Office for Official Publications of the European Communities. (Updated version 2018)

Other primary sources are the following:

EC 2010. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document **No. 25** Guidance on **chemical monitoring of sediment** and biota under the Water Framework Directive. Luxembourg: Office for Official Publications of the European Communities.

EC 2003. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document **No. 7** **Monitoring** under the Water Framework Directive. Luxembourg: Office for Official Publications of the European Communities.

EC 2009. 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 Luxembourg: Office for Official Publications of the European Communities.

The particular feature of this document is the harmonisation of the evaluation with the sampling and laboratory methods which provide the input information into the evaluation procedure. Thus, a practical guidance is provided for the daily water quality assessor and government practitioner.



## 5. UNDERSTANDING THE FLUVIAL SEDIMENT SYSTEM

The fluvial sediment system is a heterogeneous mixture of two phases (matrices): 1. flowing water ('fluvial': from the Latin word 'fluvialis' meaning 'of the river', 'flowing surface water'), and 2. solid material ('sediment': from the Latin word 'sedere' meaning 'to settle,' or 'sit').

The water phase is a solution composed of water (H<sub>2</sub>O) and dissolved material (e.g. Ca, Mg, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, oxygen gas, dissolved organic carbon etc.), while the solid sediment phase is in fact a mixture of phases (e.g. minerals such as clays, organic matter, iron oxyhydroxide colloids, etc.). Since HSs in the fluvial sediment system can be found both in the water phase (dissolved) or in the solid phase (sediment-bound), and can exchange between these two phases (partitioning), sediment quality assessment requires the understanding of both the water and solid sediment behaviour and their interaction. Moreover, HSs can reach the biota receptors (exposure) through both the water and the solid sediment, which underlines the importance of the understanding of the fluvial sediment system as a whole. The understanding of the fluvial water and sediment phases in their interaction is also dictated by the WFD as the current EQS values (for organic HSs) refer to the total HS concentration in the water column (river water plus suspended sediment).

**Fluvial sediment** has 3 types according to its transportation and deposition mode (**Figure 1**):

- **bottom sediment**, deposited from the water flowing in the river channel as:
  - river bed sediment,
  - bed load sediment,

- **suspended sediment** (also called suspended solids; or suspended particulate matter: **SPM**), carried in the water flowing in the river channel,
- **overbank sediment** (also called floodplain sediment for large rivers), deposited over the river bank in the inundated area during flood events.

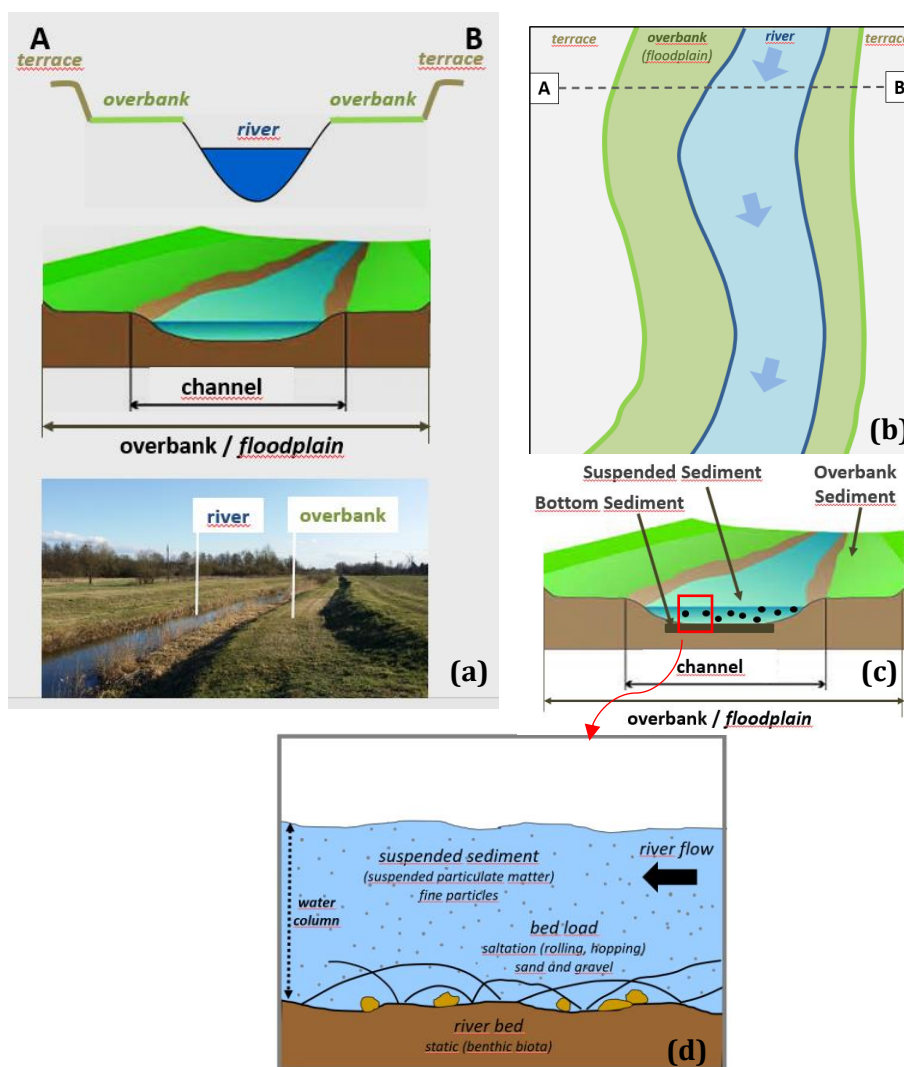
The term ‘sediment’ and the three sediment types are not defined in the WFD documents.

ISO 6107-2:2006 defines **bottom sediment** as “solid material deposited by settling from suspension onto the bottom of bodies of water, both moving and static”. River bed sediment is the relatively static sediment where benthic (sediment dwelling) biota lives (**Figure 1**). Bed load sediment is the relatively fast moving uppermost (few centimetre) part of the sediment consisted of moving sand and gravel, thus in this sediment biota cannot dwell. Note that in the bottom sediment as a compartment for HSs is composed of two matrices: 1. solid sediment particulate matter and 2. pore (interstitial) water.

According to ISO 5667-17:2008, **suspended solids** (suspended sediment) are “solids with a diameter greater than 0.45 µm that are suspended in water” and bulk suspended solids are “solids that can be removed from water by filtration, settling or centrifuging under specified conditions” (ISO 5667-17:2008). The suspended sediment is usually fine-grained (silt and clay). Note that in the water column as a compartment for HSs is composed of two matrices: 1. solid suspended particulate matter and 2. river water.

Bottom (river bed and bed load) sediment and suspended sediment are also called channel sediments because they occur in the river channel located between the two river banks, where the river is found most of the time, during the predominant low-flow conditions (**Figure 1**). From the **risk assessment (sediment quality evaluation)** point of view it is important that bottom (river bed and bed load) sediment and suspended sediment are almost permanently in contact with the river water and thus with the aquatic (pelagic and benthic) biota, too.

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS



**Figure 1.** The fluvial sediment system: sediment regimes and sediment types. (a) Cross-section view of the fluvial system and its main parts: the river channel, the actively (regularly) flooded overbank or floodplain area and the river terrace as the old and inactive overbank or floodplain area. A-B indicated the cross-section line in Figure 1b. (b) The planer view of the fluvial system and its main parts: river channel, overbank or floodplain area and river terrace. Blue arrows show river flow direction. A-B indicates the cross-section shown in Figure 1a. (c) The three types of fluvial sediment (bottom sediment, suspended sediment and overbank sediment) in association with the corresponding two main parts of the fluvial system (river channel: bottom sediment and suspended sediment; overbank area: overbank/floodplain sediment). (d) River channel sediments: bottom sediment: 1. river bed sediment where benthic biota dwells and 2. moving bed load sediment; suspended sediment which is a part of the water column (water + suspended sediment).

**Overbank sediment** deposition in a fluvial environment takes place outside the river channel, over the inundated area, during high-flow (also called overbank flow, or flood event) conditions. Thus, overbank sediment is in fact **event-based suspended sediment** deposited overland during the short spells of flood events (**Figure 4**). From the **risk assessment (sediment quality evaluation)** point of view it is important that overbank (floodplain) sediment is almost permanently out of contact with the river water, it is subaerially exposed on the land surface and thus it is essentially not in contact with the aquatic (pelagic and benthic) biota. In fact, between the short high-flow (flood) events **soil formation** takes place (see FAO fluvisols soil class).

The significance of overbank sediments for sediment quality evaluation lies in the following:

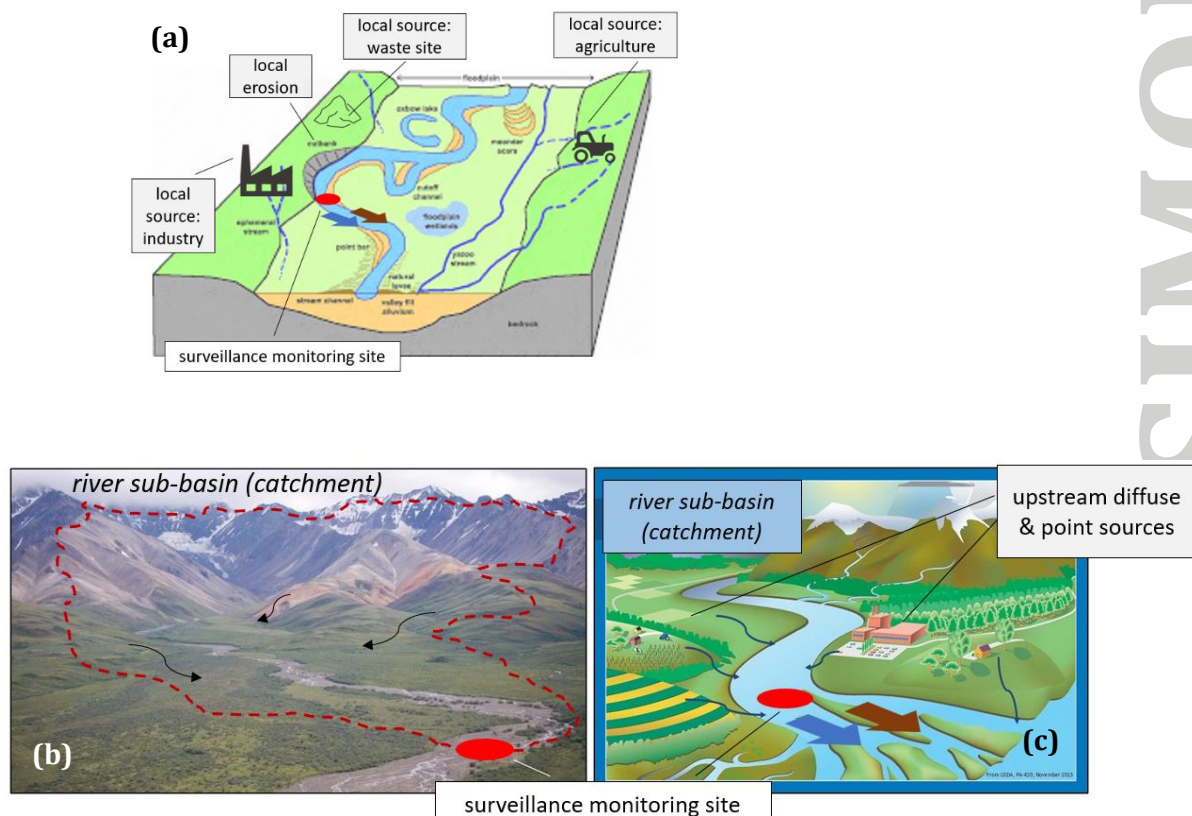
- overbank sediment is deposited during high-flow events induced by catchment-wide run-off event (rain or melting snow) that carries soil particles eroded from the whole catchment area thus overbank sediment better **represents the whole catchment** (river sub-basin) than bottom sediment or suspended sediment which are confined to the river channels;
- accumulated overbank sediment layers are suitable to evaluate **sediment quality trend** and past contamination records (**Figure 4**);
- overbank sediment is suitable for defining the **background concentration** for the naturally occurring inorganic substances (metals): the local background value could be defined as a compound concentration of the deeper, natural, preindustrial fluvial sediments at the sampling site. It is important that former floodplains ('inactive floodplains'; river terraces) that may preserve longer sediment quality history are of high importance for sediment quality trend assessment.

In terms of material balance for the solid sediment particles and associated HSS at a surveillance monitoring site, the sediment input originates from local sources and from upstream sources in the catchment area (**Figure 2**). In low-flow conditions, local sediment source is soil erosion (river bank erosion) and upstream sediment source is predominantly river channel sediment. In high-flow (flood) conditions sediment sources are dominated by precipitation-induced soil erosion and wash-off both locally and in the upstream catchment area.

At the site, bed load and suspended sediment flow through the site moved by the flowing river water (input/output: throughflow) (**Figure 2**). River bed sediment and overbank (floodplain) sediment are deposited at the site (accumulation). If the hydrological regime of the river at the site changes (e.g. a

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

depositional site becomes erosive) or during high-flow (flood) events, the deposited river bed and overbank (floodplain) sediment can be remobilised and transported downstream from the site as sediment output.

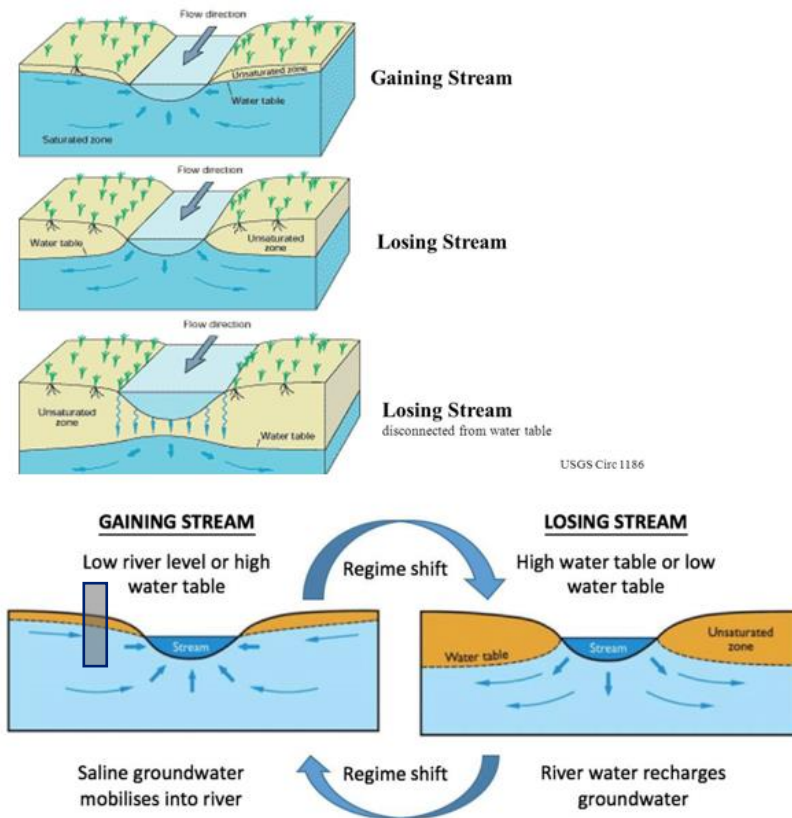


**Figure 2.** The fluvial sediment system: local scale and catchment scale aspects. Red dot: surveillance monitoring site. Thin arrows: transport of sediment, water and associated HSs. Blue arrow: water and dissolved HS transport. Brown arrow: sediment and sediment-bound HSs transport. (a) Local sources of sediment and associated contamination sources at the monitoring site. (b) The catchment draining water and sediment to the monitoring site. Dashed red line: catchment boundary. (c) The catchment showing point and diffuse HS sources transported to the monitoring site by draining water and sediment.

In terms of material balance of the water and associated dissolved HSs at a surveillance monitoring site, water input originates from local groundwater flow and from upstream surface water flow from the catchment area (**Figure 3**). In low-flow conditions, water is purely of **groundwater** origin in the whole catchment. In high-flow (flood) conditions, precipitation and related surface run-off water may dominate water input at the monitoring site. At the site, surface



water can be gained from local groundwater inflow ('gaining stream'), or surface water can be lost by outflow into the groundwater ('losing stream') (**Figure 3**). This has important implications for the bottom sediment pore water composition: pore water composition is dominated by groundwater at gaining stream sites (which the overwhelming situation for rivers), while the dominant source of bottom sediment pore water is surface water at losing stream sites. The direction of groundwater versus surface water filtration through the bottom sediment can be reversed if the hydrological regime of the river at the site changes (e.g. river incision) or during high-flow (flood) events (**Figure 3**).

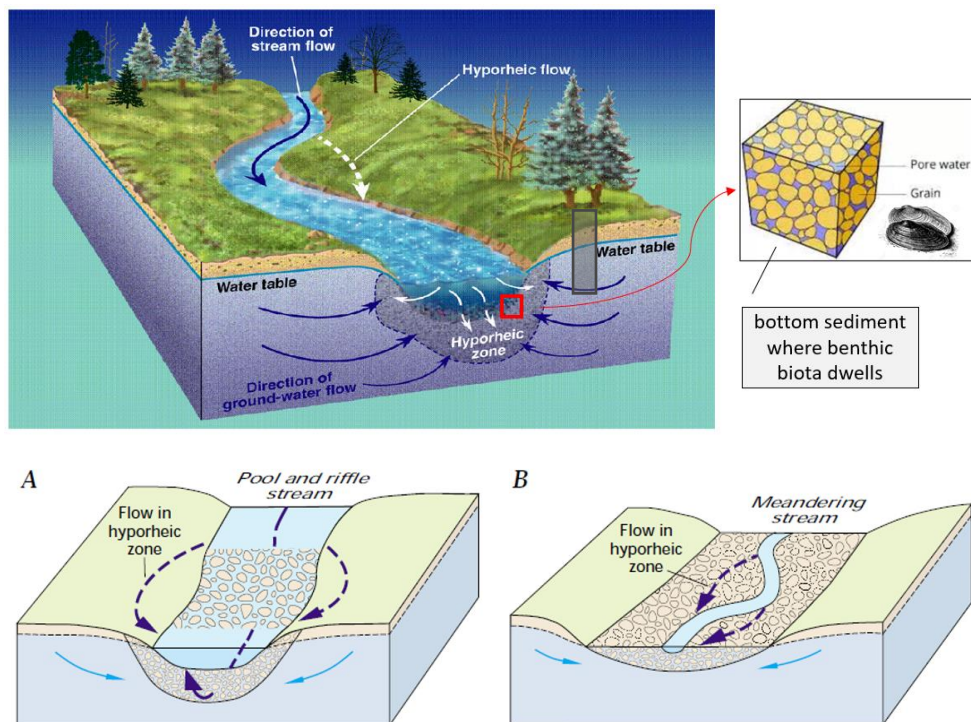


**Figure 3.** The fluvial system water balance at the monitoring site. The origin of bottom sediment pore water from groundwater vs surface water is emphasised. Note that the groundwater–surface water flow direction can be reversed (bottom figure). Grey rectangle indicated a groundwater monitoring well.

The interaction of groundwater and surface water at the surveillance monitoring site occurs in the hyporcheic zone which also contains the bottom sediment (**Figure 4**). This is critical from the sediment quality point of view because pore water is a major

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

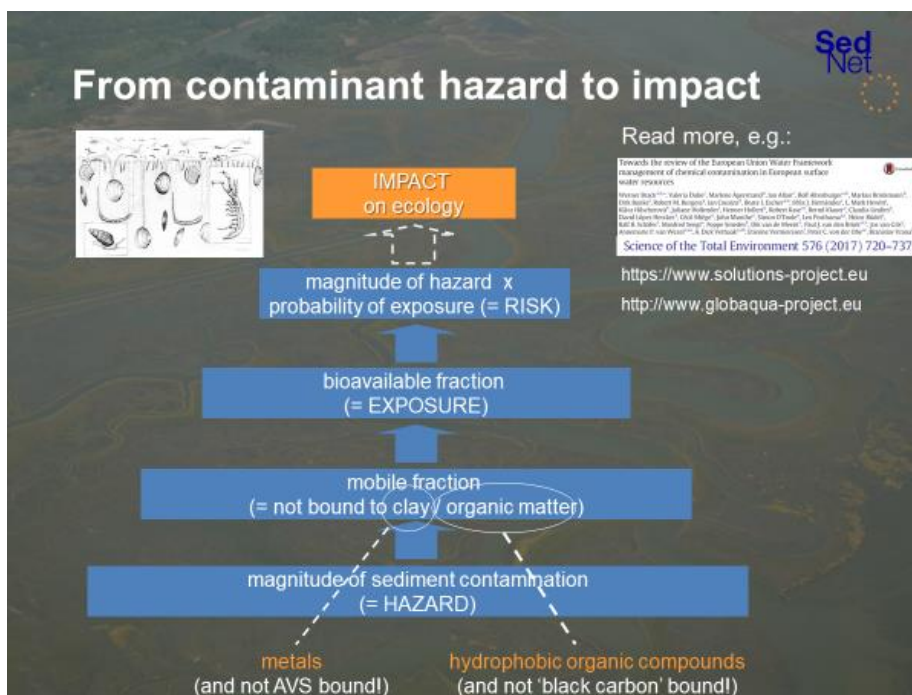
HS exposure route to the benthic biota which is the sediment quality assessment end-point in WFD. Moreover, due to the hyporheic zone interactions, bottom sediment can reflect the very local effects of underground water inflow including local contamination input.



**Figure 4.** The hyporheic zone: the location of river water and groundwater interaction including the bottom sediment where benthic biota dwells. Top: location of bottom sediment in the hyporheic zone where benthic biota dwells. Bottom: River water flow under ground in the hyporheic zone.

## 6. UNDERSTANDING SEDIMENT QUALITY EVALUATION

Research on European as well as global rivers, and sediment-related ecotoxicological studies in general, have demonstrated that **sediment associated contaminants can have adverse effects on sediment-dwelling organisms and thus on ecology**. Depending on the magnitude of concentrations of contaminants, mixtures of contaminants and their species-specific bioavailability as well as toxicity, exposure to these contaminants will impact ecology (**Figure 5**).



**Figure 5.** The relationship of hazard, exposure and impact in the fluvial sediment system. For example, the abundance of **certain species may decrease** while other, more susceptible species **may disappear completely**, ultimately resulting in a **decreased biodiversity**. These changes in populations of **species causes also indirect food-web effects**. A decreased abundance results in a **decrease in food availability** for the respective predators, which can also be pelagic species living in the water column. [CIS sed. guidance draft]



If substances are released from sediment to the water column, they **may impact pelagic organisms such as zoo- and phytoplankton and fish**. Furthermore, the **direct uptake** of chemicals **via (pore-)water or ingestion of contaminated sediment particles** may lead to bioaccumulation of the chemicals within the organism which may at a certain level impact that organism. Bioaccumulation may be further exacerbated through the **consumption of 'contaminated organisms'** as the level of contamination can thus increase in organisms with each step in the food-chain. This **food-chain transfer (biomagnification)** may ultimately result in **effects on reproduction or health of fish-eating birds and mammals** such as cormorants and otters. It is important to note that due to **effects on sediment-dwelling species and contaminant bioaccumulation within these organisms**, contaminated sediment may also contribute to disruption of the whole aquatic ecosystem because of the benthic-pelagic coupling, i.e. benthic and pelagic food webs are interlinked and part of one aquatic food web. In addition, consumption of severely contaminated fish (e.g. eel) or consumption of meat or milk from livestock raised on flood plains, covered with (contaminated) suspended matter during flooding events including remobilised contaminated sediment, could **also have an impact on human health**. There are examples of **floodplains where use by livestock has been restricted** (Salomons and Brils, 2004) and this implies **potential impacts of contaminated sediment on** (terrestrial) ecology in **floodplains** as well.

The ecological status assessment is based on several biological quality elements (BQE) and this assessment is supported by several hydro-morphological and physicochemical quality elements. When considering these various elements, it may appear that severe and specific chemical contamination could affect two of the BQE, i.e. the one describing the composition and health of the benthic invertebrate community, and phytobenthos as possibly the second one. While **chemical contamination may have other indirect effects**, such as on the health of certain pelagic species, it will be **difficult to quantify the effect of sediment associated contaminants** as compared to the contaminants dissolved in the water column. A further complication is of course that contaminants move through rivers, while sediment remains largely in place. What should be compared to what? In conclusion, **sediment associated contaminants can affect some of the BQE but its overall impact on ecological status of the water body may turn out to be minor**.

## 7. EVALUATION OF OVERBANK (FLOODPLAIN) SEDIMENT QUALITY

### 7.1 PRINCIPAL CONSIDERATIONS

The WFD does not require the evaluation of overbank sediment quality for water body status assessment. Thus, overbank sediment quality evaluated is not mandatory. The WFD does not mention the overbank or floodplain areas but it requires the characterisation of the structure of the **'riparian zone'** under the hydromorphological elements, including the consideration of 'substrate conditions' which can be interpreted as the soil and sediment in this zone. The WFD does not define riparian zones, the EEA Copernicus program says that "riparian zones represent transitional areas occurring between land and freshwater ecosystems, characterised by distinctive hydrology, soil and biotic conditions and **strongly influenced by the stream water**. They provide a wide range of riparian functions (e.g. chemical filtration, flood control, bank stabilization, aquatic life and riparian wildlife support, etc.) and ecosystem services." Riparian zones could be thus identified with the overbank or floodplain areas, although quite indirectly only. For overbank (floodplain) sediment the notation 'FS' is used after the term 'floodplain sediment', according to the conventions of environmental geochemistry practice.

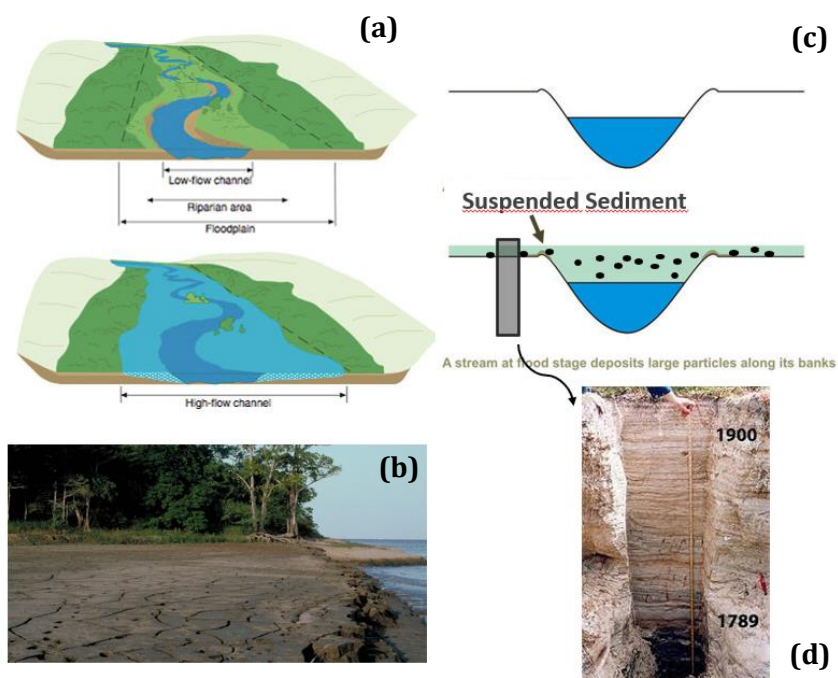
Since overbank (floodplain) sediment, even the uppermost top layers freshly deposited during the last high-flow (flood) event, (1) is not in contact with the river water and thus it is not exposed to aquatic (pelagic and benthic) biota and (2) it is not in chemical equilibrium with the river water column, and, in addition, (3) this sediment is exposed subaerially on the land surface for soil formation (**Figure 6**), the HS concentration measured in overbank sediment

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

should be evaluated against **soil QS limit values ( $QS_{\text{soil}}$ )**. For the same reasons, overbank (floodplain) sediment quality at **deep sediment layers** should also be evaluated against soil QS limit values. In other words, overbank sediment is event-based suspended sediment that becomes soil immediately after deposition from flood water.

For the above reasons, suspended sediment sampled using sediment trap such as passive sediment box or collected using on-site **suspended sediment sampling during flood event in the overbank (floodplain) area** and the collected suspended sediment is expected to deposit during/after the flood event on the land surface should be also evaluated against **soil QS limit values**, despite it was collected from river water suspension as suspended sediment.

Note that many soil limit values derived by statistical procedures and not by evidence-based ecotoxicological data. **Soil limit values  $QS_{\text{soil}}$  derived from evidence-based ecotoxicological data are preferred** for overbank (floodplain) sediment quality evaluation under the EU WFD implementation.



**Figure 6.** The overbank sediment system. (a) River water area cover under low flow and high flow conditions. The area covered by river water during high flow is called the overbank or floodplain area. (b) Typical overbank sediment deposited during flood (high flow) event. (c) Overbank sediment is in fact suspended sediment deposited

during high flow (flood) events. Grey bar indicated the overbank sediment vertical profile shown in Figure 2d. (d) Typical overbank sediment vertical profile deposited during high flow (flood) event in the past 200 years as shown by the dates.

It is important that the **HS concentration measured in the collected overbank (floodplain) sediment sample ( $C_{FS}$ ) is representative for the soil QS limit value used for sediment quality evaluation (comparison of  $C_{HS-FS}$  and  $QS_{soil}$  if  $C_{FS} < QS_{soil}$ )**. Thus, sampling, sample preparation, laboratory analysis and reporting procedures should match exactly those used for the soil QS limit value:

- **sampling** (sampling method, e.g. undisturbed or grab sample; sampling depth, e.g. topsoil depth 0-5cm; etc.),
- **sample preparation** (drying temperature for dry weight measurement, e.g. 40C° or 105C°; analysed fraction, e.g. <2mm; etc.),
- **sample analysis** (sample digestion, e.g. aqua regia or nitric acid-peroxide; deionised water leaching; etc.),
- **reporting** (measured concentration values are reported and/or converted to the units of the QS; mg/kg dry weight or wet weight; µg/L vs mg/L; etc.).

This requires the detailed understanding of the representativity of the used  $QS_{soil}$  value, by studying its derivation such as the toxicity tests on which the QS value is based on.

## 7.2 PRACTICAL EVALUATION

### STEP 1. If soil QS limit value is available (in your country's legislation):

1.1 Assure that the HS concentration measured in the collected overbank sediment sample ( $C_{HS-FS}$ ) is representative for the soil QS limit value to be used for the overbank sediment quality evaluation (comparison of  $C_{HS-FS}$  and soil QS limit value whether  $C_{HS-FS} < QS_{soil}$ ).

**AND**

1.2 Compare the **HS concentration measured in the collected overbank sediment sample ( $C_{FS}$ ) to the soil QS limit value**: if  $C_{FS} < QS_{soil}$  then the sampled overbank sediment is not risky with respect to the evaluated HS.

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

NOTE: Soil QS limit values are readily available in most countries, although, there are no relevant EU-level soil contamination QS concentration values at present. Soil limit values  $QS_{soil}$  derived from evidence-based ecotoxicological data are preferred, therefore, if possible, give preference to this kind of  $QS_{soil}$ .

### **STEP 2. If soil QS limit value is not available (in your country's legislation):**

2.1 Establish (e.g. adopt) soil QS limit values in your country's legislation. Give preference to soil limit values  $QS_{soil}$  derived from evidence-based ecotoxicological data. If soil QS limit values become available in your country's legislation, implement STEP 1 above.

**OR**

2.2 Do not evaluate overbank (floodplain) sediment quality. (WFD does not require the evaluation of overbank sediment quality.) Archive the measured HS concentration values for 1. latter evaluation when soil QS limit values become available or 2. other uses such as site contamination indicators (e.g. by comparing the measured HS concentration to recognised soil QS limit value such as those in the 'Dutch List'), or such as scientific investigation.

## **7.3 RECOMMENDATION FOR TRANSNATIONAL MONITORING**

It is recommended to

- **review** the available national soil QS limit values in terms of
  - **list of HS** (preferably covering the EU EQS Directive HS list),
  - concentration values, with respect to ecotoxicology evidence,
  - **representative matrix** (sampling: undisturbed sample of 0-5cm topsoil, composite sample, etc.; sample preparation: drying temperature of 40C°, analysed fraction of <2mm, etc.; analysis: digestion with nitric acid-peroxide, deionised water leaching, etc.; reporting: units of measured concentration values, etc.),
- **develop** methods for sediment quality evaluation (comparison of national  $QS_{soil}$  limit values and measured  $C_{FS}$  concentrations).

## 8. EVALUATION OF SUSPENDED SEDIMENT QUALITY

### 8.1 PRINCIPAL CONSIDERATIONS

For suspended sediment the notation 'SPM' is used after the term '**suspended particulate matter**', according to the WFD documents notation. Suspended sediment together with the sediment-bound HS is differentiated from water and the water-dissolved HS operationally by using filtration through the  $0.45\mu\text{m}$  filter: the solid residue trapped on the filter top is the particulate suspended sediment which also contains the sediment-bound HS, and the filtrate passing through the filter is the water and the dissolved HS. Technically, suspended sediment and water can be separated by centrifuging, too.

River water, containing the suspended particulate matter, comprises the '**water column**'. Water column, as an environmental compartment, is therefore a heterogeneous mixture of liquid water and solid suspended sediment. For risk assessment (sediment quality evaluation), therefore, HS concentration can be measured and presented in three different ways according to the three matrices:

- **Dissolved HS,  $C_{\text{water, dissolved}}$**  (dissolved in river water):  
*Measured in the  $<0.45\mu\text{m}$  filtrate, or in the separate of centrifuging,*
- **Solid particle-bound HS,  $C_{\text{susp}}$**  (absorbed or adsorbed to solid suspended sediment):  
*Measured in the  $\geq 0.45\mu\text{m}$  filter residue, or in the residue of centrifuging,*
- **Total HS,  $C_{\text{water, total}}$**  (dissolved and particle-bound together in the mixture of the water column):  
*Measured in the total water column.*

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

Accordingly, quality standards can be given as

- Dissolved HS concentration ( $\mu\text{g/L}$ ) ( $QS_{\text{water, dissolved}}$ ),
- Total HS concentration ( $\mu\text{g/L}$ ) ( $QS_{\text{water, total}}$ ),
- Particle-bound HS concentration ( $\mu\text{g/kg}$ ) ( $QS_{\text{susp}}$ ).

The WFD, for example, gives HS concentration QS limit values as follows (EC 2008):

“The water QS laid down [...] are expressed as **total concentrations in the whole water** sample [ $QS_{\text{water, total}}$ ]. By way of derogation from the first subparagraph, in the case of cadmium, lead, mercury and nickel (hereinafter “**metals**”), **the water EQS refer to the dissolved concentration** [ $QS_{\text{water, dissolved}}$ ], i.e. the dissolved phase of a water sample obtained by filtration through a  $0.45 \mu\text{m}$  filter or any equivalent pre-treatment, or, where specifically indicated, to the bioavailable concentration.”

According to the WFD, suspended sediment is part of the water column and it is discussed under water quality. Therefore, evaluation of suspended sediment quality (i.e. comparison of HS concentration in the suspended sediment to the relevant QS limit value) has to consider the chemical interaction between the suspended sediment particulate matter and water. If equilibrium of HS sorption and desorption between the suspended sediment particles and water can be assumed, then HS-specific partitioning coefficient between suspended sediment and water can be used indirectly to estimate the HS concentration in any of the water column matrices (dissolved in water, particle-bound in solid suspended sediment, total in water column: dissolved plus particle-bound). Accordingly, consider the following mass balance equation:

$$C_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right] = C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right] + C_{\text{susp, water}} \left[ \frac{\text{mg}}{\text{L}} \right]$$

Due to the assumed equilibrium for HS between suspended sediment particles and water, the partitioning of HS (the ratio of concentrations) between these two matrices (phases) is constant:

$$K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] = \frac{C_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right]}{C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right]},$$

from which



$$C_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right],$$

or  $C_{\text{susp, solid}}$  expressed as (converted to) particle-bound HS concentration per unit volume of water:

$$C_{\text{susp, water}} \left[ \frac{\text{mg}}{\text{L}} \right] = (K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}) \cdot C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right],$$

thus

$$C_{\text{water, total}} = C_{\text{water, dissolved}} + (K_{\text{p, susp}} \cdot C_{\text{SPM}}) \cdot C_{\text{water, dissolved}},$$

and

$$C_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right] = C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right] (1 + K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}).$$

If  $K_{\text{p, susp}}$  is unknown, then using the relationship

$$K_{\text{p, susp}} = f_{\text{oc, susp}} \cdot K_{\text{OC}},$$

the equation becomes

$$C_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right] = C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right] (1 + f_{\text{oc, susp}} \cdot K_{\text{OC}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}).$$

or rearranged as

$$C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right] = C_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot \frac{1}{1 + f_{\text{oc, susp}} \cdot K_{\text{OC}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}}.$$

This means that the total water column HS concentration can be estimated from the measured dissolved HS concentration, and vice versa: the dissolved HS concentration can be estimated from the measured total water column HS concentration, if equilibrium exists for HS between suspended sediment particles (particle-bound HS) and water (dissolved HS) or, in other words, the partitioning of HS (the ratio of concentrations) between these two matrices (phases) is constant.

If the C concentration of HS is replaced with the predefined QS limit value of the HS, then this equation can be used for transferring the QS limit value defined for one matrix (e.g.  $QS_{\text{water, dissolved}}$ ) by ecotoxicological tests to estimate the QS limit value for the other matrix (e.g.  $QS_{\text{water, total}}$ ), and vice versa, still assuming that the two matrices (phases) are in chemical equilibrium with respect to the HS:

$$QS_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right] = QS_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right] (1 + f_{\text{oc, susp}} \cdot K_{\text{OC}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}).$$



## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

OR

$$QS_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right] = QS_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot \frac{1}{1 + f_{\text{oc, susp}} \cdot K_{\text{OC}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}}$$

where:

- $C_{\text{susp, solid}}$  : suspended sediment particle-bound HS concentration in unit weight of solid suspended sediment ( $\text{mg} \cdot \text{kg}^{-1}$ );
- $C_{\text{susp, solid}}$  : suspended sediment particle-bound HS concentration in unit mass of solid suspended sediment ( $\text{mg} \cdot \text{kg}^{-1}$ );
- $C_{\text{susp, water}}$  : suspended sediment particle-bound HS concentration in unit volume of river water ( $\text{mg} \cdot \text{L}^{-1}$ );
- $C_{\text{water, dissolved}}$  : dissolved HS concentration in river water ( $\text{mg} \cdot \text{L}^{-1}$ );
- $C_{\text{water, total}}$  : total (dissolved + particle-bound) HS concentration in river water ( $\text{mg} \cdot \text{L}^{-1}$ );
- $QS_{\text{susp, solid}}$  : quality standard for suspended sediment particle-bound HS concentration in unit mass of solid suspended sediment ( $\text{mg} \cdot \text{kg}^{-1}$ );
- $QS_{\text{susp, water}}$  : quality standard for the suspended sediment particle-bound HS concentration in unit volume of river water ( $\text{mg} \cdot \text{L}^{-1}$ );
- $QS_{\text{water, dissolved}}$  : quality standard for dissolved HS concentration in water, mostly directly derived from the toxicity or bioaccumulation tests;
- $QS_{\text{water, total}}$  : quality standard for total HS concentration in water column, mostly directly derived from the toxicity or bioaccumulation tests;
- $K_{\text{p, susp}}$  : partition coefficient of HS between suspended matter and dissolved in water;  $K_{\text{p, susp}}$  value might be estimated as the product of the  $K_{\text{oc}}$  value for the substance and the organic carbon content ( $f_{\text{oc}}$ );
- $K_{\text{oc}}$  : substance-specific organic carbon-water partition coefficient, which is independent of site-specific conditions (see Appendix 1 for  $K_{\text{oc}}$  values);
- $f_{\text{oc, susp}}$  : weight fraction of organic carbon in the suspended sediment;  $f_{\text{oc, susp}}$  value can be derived (1) from measurement in the suspended sediment, or (2) from the EU default value (EU default from EC 2003 is  $f_{\text{oc, susp}} = 0.1$ );
- $C_{\text{SPM}}$  : concentration of suspended matter; for several water types like large rivers the SPM content is reasonably constant, and a default value has been proposed for this type of river (EU default is  $C_{\text{SPM}} = 15 \text{ mg} \cdot \text{L}^{-1}$  for freshwater);
- $10^{-6}$  : the conversion factor from mg into kg.

Using one of the initial equation above, the suspended sediment particle-bound HS concentration can be estimated from the measured dissolved HS concentration:

$$C_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right],$$

and, in the same way, the QS limit value for the suspended sediment particle-bound HS concentration can also be estimated from dissolved QS limit value directly derived from toxicity or bioaccumulation tests:

$$QS_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot QS_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right].$$

Finally, the suspended sediment particle-bound HS concentration can also be estimated from the measured total HS concentration:

$$C_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot \frac{C_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right]}{1 + K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}}.$$

and, in the same way, the QS limit value for the suspended sediment particle-bound HS concentration can also be estimated from total QS limit value directly derived from toxicity or bioaccumulation tests:

$$QS_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot \frac{QS_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right]}{1 + f_{\text{oc, susp}} \cdot K_{\text{OC}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}}.$$

In practice this means that the available  $QS_{\text{water, total}}$ , such as the EQS values in the EU EGS directive (EC 2008), can be used to derive an estimated  $QS_{\text{susp, solid}}$  limit value. This estimated QS limit value then compared to the measured suspended solid HS concentration in order to evaluate if the suspended sediment is at risk by having HS concentration above the corresponding estimated suspended sediment QS value.

Suspended sediment QS limit values are not available in most of the countries and there are no relevant EU-level suspended sediment QS concentration values at present. (The currently available EU-level QS values refer to total water column concentrations for the organic HSs and refer to the dissolved concentrations for metals; EC 2008). Suspended sediment EQS limit value estimation

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

could be avoided if suspended sediment QS values existed based on reliable toxicity tests.

It is important that the HS concentration measured in the collected suspended sediment sample ( $C_{\text{susp, solid}}$ ) which is used for sediment quality evaluation (comparison of  $C_{\text{susp, solid}}$  and  $QS_{\text{susp, solid}}$  whether  $C_{\text{susp, solid}} < QS_{\text{susp, solid}}$ ) is **representative** for the suspended sediment  $QS_{\text{susp, solid}}$  limit value (either directly available from toxicity tests or estimated from water  $QS_{\text{water, dissolved}}$  or  $QS_{\text{water, total}}$  limit values). Thus, sampling, sample preparation, laboratory analysis and reporting procedures should match exactly those used for the suspended sediment  $QS_{\text{susp, solid}}$  limit value:

- **sampling** (sampling method, e.g. on-site total water column grab sampling or passive sediment box sampling; sampling depth, e.g. vertical composite or single depth sample; etc.),
- **sample preparation** (separation from water phase, e.g. filtering through 0.45  $\mu\text{m}$  filter or centrifuging; drying temperature for dry weight measurement, e.g. 40C° or 105C°; etc.),
- **sample analysis** (sample digestion, e.g. aqua regia or nitric acid-peroxide; etc.),
- **reporting** (measured concentration values are reported and/or converted to the units of the QS, e.g. mg/kg dry weight or mg/L;  $\mu\text{g/L}$  vs mg/L; etc.).

This requires the detailed understanding of the representativity of the used QS value, by studying its derivation such as the toxicity tests on which the QS value is based on.

## 8.2 PRACTICAL EVALUATION

**STEP 1.** Check the  $K_p$  and/or the  $K_{oc}$  (or  $K_{ow}$ ) value in Appendix 2 for the HSs listed in the EU EQS Directive.

**STEP 2.** Carry out the evaluation (comparison of HS concentration in bottom sediment to the QS limit value) of suspended sediment quality only for those substance which have a  $\log K_{oc}$  or  **$\log K_{ow}$  of  $\geq 3$**  value (hydrophobic substances that tend to be associated with sediment). For substances having a  $\log K_{oc}$  or

**logK<sub>ow</sub> of <3** value, evaluation should be limited to the water (dissolved or total) concentration.

**STEP 3. If suspended sediment  $QS_{\text{susp, solid}}$  limit value is available (in your country's legislation):**

3.1 Make sure that the HS concentration measured in the collected suspended sediment sample ( $C_{\text{susp, solid}}$ ) is representative for the suspended sediment QS limit value used for sediment quality evaluation (comparison of  $C_{\text{susp, solid}}$  and suspended sediment QS limit value whether  $C_{\text{susp, solid}} < QS_{\text{susp, solid}}$ ).

**AND**

3.2 Compare the **HS concentration measured in the collected suspended sediment sample ( $C_{\text{susp, solid}}$ ) to the suspended sediment QS limit value.**

If  $C_{\text{susp, solid}} < QS_{\text{susp, solid}}$  then the sampled suspended sediment is not risky with respect to the evaluated HS.

NOTE: Suspended sediment QS limit values are not available in most of the countries and there are no relevant EU-level suspended sediment contamination QS concentration values at present. The currently available EU-level EQS values refer to total concentration in the water column for organic substances and to dissolved concentration for metals (EC 2008). Note that QS limit values based on ecotoxicological tests are preferred.

**STEP 4. If suspended sediment QS limit value is not available (in your country's legislation) and HS concentration is measured in suspended sediment:**

4.1 Establish (e.g. adopt) suspended sediment QS limit values in your country's legislation. If suspended sediment QS limit values become available in your country's legislation, implement STEP 3 above.

NOTE: Note that QS limit values based on ecotoxicological tests are preferred.

**OR**

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

4.2 Estimate the suspended sediment QS limit value as a surrogate standard with calculation using the EU water EQS limit value. It represents the total concentration in the water column for organic substances ( $QS_{\text{water, total}}$ ) and the dissolved concentration for metals ( $QS_{\text{water, dissolved}}$ ) in units of  $\mu\text{g/L}$  (EC 2018). using the equations below:

$$QS_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot \frac{QS_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right]}{1 + K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}}$$

OR

$$K_{\text{p, susp}} = f_{\text{oc, susp}} \cdot K_{\text{oc}}$$

then

$$QS_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot \frac{QS_{\text{water, total}} \left[ \frac{\text{mg}}{\text{L}} \right]}{1 + f_{\text{oc, susp}} \cdot K_{\text{oc}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot C_{\text{SPM}} \left[ \frac{\text{mg}}{\text{L}} \right] \cdot 10^{-6}}$$

OR

$$QS_{\text{susp, solid}} \left[ \frac{\text{mg}}{\text{kg}} \right] = K_{\text{p, susp}} \left[ \frac{\text{L}}{\text{kg}} \right] \cdot QS_{\text{water, dissolved}} \left[ \frac{\text{mg}}{\text{L}} \right]$$

See parameter explanation above.

AND

4.3 Derive input parameters as follows:

- $QS_{\text{water, total}}$  and  $QS_{\text{water, dissolved}}$  : copy the relevant EQS value for the HS annual average AA-EQS, Inland surface waters'; note the unit of  $\mu\text{g/L}$  (also see Appendix 3 of this document), or copy it from the relevant list of QS values presented in national legislation;
- $C_{\text{SPM}}$  : its value can be derived (1) from measurement in the suspended sediment samples, or (2) from the EU default value  $C_{\text{SPM}} = 15 \text{ mg}\cdot\text{L}^{-1}$  for freshwater;
- $K_{\text{p, susp}}$ : take this substance-specific partition coefficient value from any valid experimental source (e.g.  $K_{\text{p, susp}}$  defined experimentally specifically to the site

using representative samples of the site). If  $K_{p, \text{susp}}$  is not available, estimate it as the product of  $f_{oc, \text{susp}}$  and  $K_{oc}$ .

- $f_{oc, \text{susp}}$ : its value can be derived (1) from measurement in the suspended sediment samples, or (2) from the EU default value  $f_{oc, \text{susp}} = 0.01$  (ECHA, 2008).
- $K_{oc}$ : copy the value relevant for the given HS from literature (see Appendix 1 for  $K_{oc}$  values);

## AND

4.4 Compare the **HS concentration measured in the collected suspended sediment sample ( $C_{\text{susp}, \text{solid}}$ ) to the estimated suspended sediment QS limit value ( $QS_{\text{susp}, \text{solid}}$ )**. If  $C_{\text{susp}, \text{solid}} < QS_{\text{susp}, \text{solid}}$  then the sampled suspended sediment is not risky with respect to the evaluated HS.

NOTE: For the measurement of HS concentration in the collected suspended sediment sample ( $C_{\text{susp}, \text{solid}}$ ), the solid suspended sediment phase (containing HS associated with sediment) has to be separated from the liquid water phase (containing HS dissolved in water) either by (1) using filtration through the  $0.45\mu\text{m}$  filter and analysing the filtrate trapped on the filter top, or (2) using centrifuging. Separation of the suspended sediment phase from the water phase and subsequent chemical analysis is not a trivial task including problems of limited sample quantity and improper phase separation.

**STEP 5. Optionally, it is useful for the evaluation of site-specific HS contamination to compare measured and estimated (calculated) HS suspended sediment concentrations.**

6.1 Compare the estimated  $C_{\text{susp}, \text{solid}}$  (*estimated*) value calculated according to the above equation:

$$C_{\text{susp}, \text{solid}}(\textit{estimated}) \Leftarrow C_{\text{water}, \text{dissolved}}$$

$$C_{\text{susp}, \text{solid}}(\textit{estimated}) \Leftarrow C_{\text{water}, \text{total}}$$

to the measured  $C_{\text{susp}, \text{solid}}$  (*measured*) value obtained from laboratory analysis of the  $0.45\mu\text{m}$  suspended sediment filtrate or by centrifuging, by calculating the relative error (difference) between the measured and estimated concentrations:

$$ERROR [\%] = \frac{C_{\text{susp,solid}}(\text{measured}) - C_{\text{susp,solid}}(\text{estimated})}{C_{\text{susp,solid}}(\text{measured}) + C_{\text{susp,solid}}(\text{estimated})} \cdot 100$$

If this value is  $\leq 5\%$  then the relative error between the measured and estimated (modelled) values is  $\leq 10\%$  (the denominator is the average of the two values). If the difference is  $> 10\%$  then investigate and adjust the input parameters used for the estimation (see the equations above;  $K_{p, \text{susp}}$  value, or the constituting  $f_{oc}$  and  $K_{oc}$  values; or the  $C_{SPM}$  value), assuming that measured  $C_{\text{susp, solid}}(\text{measured})$  concentration value is accurate.

### **8.3 RECOMMENDATION FOR TRANSNATIONAL MONITORING**

It is recommended to

- **review** the available national suspended sediment EQS limit values in terms of
  - **list of HS** (preferably covering the EU EQS Directive HS list),
  - concentration values,
  - **representative matrix** (sampling: passive membrane sampling for total HS water column concentration, grab sampling for total HS water column concentration, passive sediment trap box sampling, etc.; sample preparation: filtering through 0.45  $\mu\text{m}$  filter or centrifuging; drying temperature for dry weight measurement, e.g. 40C° or 105C°; etc.; analysis: digestion with nitric acid-peroxide, etc.; reporting: units of measured concentration values, etc.),
- **develop** methods for the comparison of national EQS<sub>SPM</sub> limit values and measured  $C_{\text{HS-SPM}}$  concentrations.

## 9. EVALUATION OF BOTTOM SEDIMENT QUALITY

### 9.1 PRINCIPAL CONSIDERATIONS

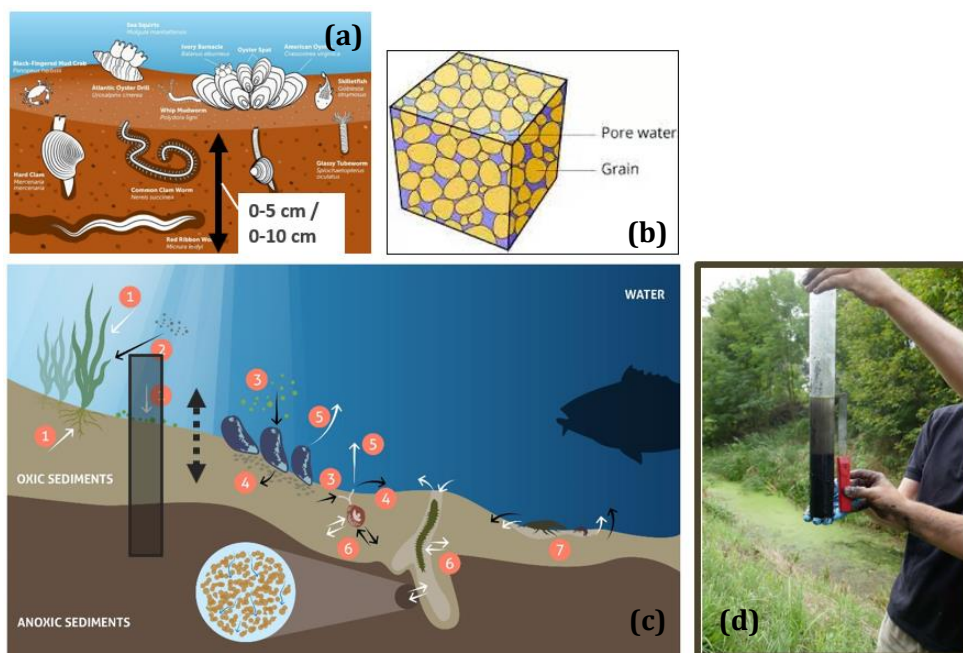
WFD uses the term ‘sediment’ exclusively for bottom sediment (river bed) in order to distinguish this compartment from the water column compartment. (Suspended sediment is called ‘suspended particulate matter’ and it is considered as a part of the water column compartment, and floodplain sediment is not considered at all).

According to WFD documents, bottom sediment (river bed), as an environmental compartment, is also a mixture of two matrices (phases): (1) solid sediment (particulate matter) and (2) liquid pore water (**Figure 7b**).

In the solid sediment phase, organic carbon (OC) content plays the dominant role in the absorption of nonionic organic HSs, and also for metals and metal compounds. In the pore water dissolved organic carbon (DOC) content plays the dominant role in the absorption of nonionic organic HSs. Solid sediment together with the sediment-bound HS is differentiated from water and the water-dissolved HS operationally by using filtration through the 0.45µm filter: the solid residue trapped on the filter top is the particulate suspended sediment which also contains the sediment-bound HS, and the filtrate passing through the filter is the water and the dissolved HS. Technically, suspended sediment and water can be separated by centrifuging, too.



## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS



**Figure 7.** The bottom sediment system. (a) The benthic (sediment dwelling) biota lives in the uppermost oxic sediment layers (0-5cm, 0-10cm). (b) 3D cartoon showing the relationship of solid sediment (grains) and pore water. Pore water is assumed to be in chemical equilibrium with solid sediment. (c) Cartoon showing the possible layering of the top oxic sediments over the lower lying anoxic sediments. Arrow emphasises the physical equilibrium with the water column (e.g. by exchange of oxygen, dissolved substances, etc.). (d) Field sampled river bottom sediment. Note the uppermost oxic layer (brown colour) and the lower anoxic layer rich in organic matter (black colour). Compare the sediment core sample photo to the theoretical core location in figure (c).

Fate estimates based on “partitioning” are limited to distribution of a substance in molecular form. For substances that will also be distributed in the environment as particles (caused by abrasion/weathering of anthropogenic materials), extrapolation based on partitioning may not be relevant. In such a case, the partitioning method may underestimate exposure of sediment environments and overestimate the exposure of water. There are no estimation methods available for particle distribution so this has to be dealt with on a case-by-case basis.

Each of the compartments sediment, and suspended matter is described as consisting of two phases: solids and water. The bulk density of each compartment is thus defined by the fraction and bulk density of each phase. Both the fractions solids and water, and the total bulk density are used in subsequent

calculations. This implies that the bulk density of a compartment cannot be changed independently of the fractions of the separate phases and vice versa. The bulk densities of the compartments sediment and suspended matter are defined by the fractions of the separate phases:

$$RHO_{comp} = F_{solid_{comp}} \cdot RHO_{solid} + F_{water_{comp}} \cdot RHO_{water}$$

Explanation of symbols

$F_{x_{comp}}$	fraction of phase x in compartment comp	$[m^3 \cdot m^{-3}]$	Table R.16-8
$RHO_x$	density of phase x	$[kg \cdot m^{-3}]$	Table R.16-8
$RHO_{comp}$	wet bulk density of compartment comp	$[kg \cdot m^{-3}]$	

Application of the formulas above for the values mentioned leads to the following bulk densities of each standard environmental compartment:

Total bulk density of the environmental compartments

$RHO_{susp}$	Bulk density of (wet) suspended matter	$[kg \cdot m^{-3}]$	1,150
$RHO_{sed}$	Bulk density of (wet) sediment	$[kg \cdot m^{-3}]$	1,300

Adsorption/desorption (solids-water partitioning) to/from solid surfaces is the main partitioning process that drives distribution in surface waters and sediments. The adsorption of a substance to sediment and suspended matter can be obtained from experimental data or estimated.

The solid-water partition coefficient ( $K_p$ ) in each compartment (sediment, suspended matter) can be calculated from the  $K_{oc}$  value, and the fraction of organic carbon in the compartment. Initially, the fraction of organic carbon in the standard environment should be used, as given in Table 1.

$$K_{p_{comp}} = F_{oc_{comp}} \cdot K_{oc} \quad \text{with } comp \in \{sed, susp\}$$

Explanation of symbols

$K_{oc}$	partition coefficient organic carbon-water	$[l \cdot kg^{-1}]$	data set
$F_{oc_{comp}}$	weight fraction of organic carbon in compartment comp	$[kg \cdot kg^{-1}]$	Table R.16-8
$K_{p_{susp}}$	partition coefficient solid-water in suspended matter	$[l \cdot kg^{-1}]$	
$K_{p_{sed}}$	partition coefficient solid-water in sediment	$[l \cdot kg^{-1}]$	

$K_p$  is expressed as the concentration of the substance sorbed to solids (in  $mg_{chem} \cdot kg_{solid}^{-1}$ ) divided by the concentration dissolved in porewater ( $mg_{chem} \cdot l_{water}^{-1}$ ). The dimensionless form of  $K_p$ , or the total compartment-water

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

partitioning coefficient in  $(\text{mg}\cdot\text{m}_{\text{comp}}^{-3})/(\text{mg}\cdot\text{m}_{\text{water}}^{-3})$ , can be derived from the definition of the sediment in the two phases:

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

$$K_{\text{comp-water}} = F_{\text{water comp}} + F_{\text{solid comp}} \cdot \frac{K_{\text{p comp}}}{1000} \cdot \text{RHOSolid}$$

Explanation of symbols			
$F_{\text{water comp}}$	fraction water in compartment <i>comp</i>	$[\text{m}^3\cdot\text{m}^{-3}]$	Table R.16-8
$F_{\text{solid comp}}$	fraction solids in compartment <i>comp</i>	$[\text{m}^3\cdot\text{m}^{-3}]$	Table R.16-8
$F_{\text{air comp}}$	fraction air in compartment <i>comp</i> (only relevant for soil)	$[\text{m}^3\cdot\text{m}^{-3}]$	Table R.16-8
$\text{RHOSolid}$	density of the solid phase	$[\text{kg}\cdot\text{m}^{-3}]$	2,500
$K_{\text{p comp}}$	solids-water part. coeff. in compartment <i>comp</i>	$[\text{l}\cdot\text{kg}^{-1}]$	Equation R.16-6
$K_{\text{air-water}}$	air-water partitioning coefficient	$[-]$	Equation R.16-5
$K_{\text{soil-water}}$	soil-water partitioning coefficient	$[\text{m}^3\cdot\text{m}^{-3}]$	
$K_{\text{susp-water}}$	suspended matter-water partitioning coefficient	$[\text{m}^3\cdot\text{m}^{-3}]$	
$K_{\text{sed-water}}$	sediment-water partitioning coefficient	$[\text{m}^3\cdot\text{m}^{-3}]$	

Table 1. Default values for environmental compartments

CHARACTERISATION OF ENVIRONMENTAL COMPARTMENTS			
Parameter	Symbol	Unit	Value
<b>General</b>			
Density of the solid phase	RHOSolid	$[\text{kg}_{\text{solid}} \cdot \text{m}_{\text{solid}}^{-3}]$	2 500
Density of the water phase	RHOWater	$[\text{kg}_{\text{water}} \cdot \text{m}_{\text{water}}^{-3}]$	1 000
Density of air	RHOair	$[\text{kg}_{\text{air}} \cdot \text{m}_{\text{air}}^{-3}]$	1.3
Temperature (12°C)	TEMP	[K]	285
<b>Surface water</b>			
Concentration of suspended matter (dry weight)	SUSP <sub>water</sub>	$[\text{mg}_{\text{solid}} \cdot \text{l}_{\text{water}}^{-1}]$	15
<b>Suspended matter</b>			
Volume fraction solids in susp. matter	Fsolid <sub>susp</sub>	$[\text{m}_{\text{solid}}^3 \cdot \text{m}_{\text{susp}}^{-3}]$	0.1
Volume fraction water in susp. matter	Fwater <sub>susp</sub>	$[\text{m}_{\text{water}}^3 \cdot \text{m}_{\text{susp}}^{-3}]$	0.9
Weight fraction organic carbon in susp. solids	Foc <sub>susp</sub>	$[\text{kg}_{\text{oc}} \cdot \text{kg}_{\text{solid}}^{-1}]$	0.1
<b>Sediment</b>			
Volume fraction solids in sediment	Fsolid <sub>sed</sub>	$[\text{m}_{\text{solid}}^3 \cdot \text{m}_{\text{sed}}^{-3}]$	0.2
Volume fraction water in sediment	Fwater <sub>sed</sub>	$[\text{m}_{\text{water}}^3 \cdot \text{m}_{\text{sed}}^{-3}]$	0.8
Weight fraction organic carbon sediment solids	Foc <sub>sed</sub>	$[\text{kg}_{\text{oc}} \cdot \text{kg}_{\text{solid}}^{-1}]$	0.05

## 9.2 PRACTICAL EVALUATION

**STEP 1.** Check the  $K_{\text{sed-water}}$  and/or the  $K_{\text{oc}}$  (or  $K_{\text{ow}}$ ) value in Appendix 1 for the HSs listed in the EU EQS Directive.

**STEP 2.** Carry out the evaluation (comparison to EQS limit value) of bottom sediment quality only for those substance which have a  $\log K_{\text{oc}}$  or **log  $K_{\text{ow}}$  of  $\geq 3$**  value (hydrophobic substances that tend to be associated with sediment). For substances having a  $\log K_{\text{oc}}$  or **log  $K_{\text{ow}}$  of  $< 3$**  value, evaluation should be limited to the water dissolved concentration.

**STEP 3. If bottom sediment EQS<sub>BS</sub> limit value is available (in your country's legislation):**

3.1 Assure that the HS concentration measured in the collected bottom sediment sample ( $C_{\text{HS-BS}}$ ) is representative for the bottom sediment EQS limit

**SEDIMENT QUALITY SAMPLING PROTOCOL  
FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS**

value used for sediment quality evaluation (comparison of  $C_{HS-BS}$  and bottom sediment EQS limit value whether  $C_{HS-BS} < EQS_{BS}$ ).

**AND**

- 3.2 Compare the **HS concentration measured in the collected bottom sediment sample ( $C_{HS-BS}$ ) to the bottom sediment EQS limit value**. If  $C_{HS-BS} < EQS_{BS}$  then the sampled bottom sediment is not risky with respect to the evaluated HS.

**STEP 4. If bottom sediment EQS limit value is not available (in your country's legislation) and HS concentration is measured in bottom sediment:**

- 4.1 Establish (e.g. adopt) bottom sediment EQS limit values in your country's legislation. If bottom sediment EQS limit values become available in your country's legislation, implement STEP 3 above.

**OR**

- 4.2 Estimate the bottom sediment EQS limit value ( $EQS_{BS}$ ) as a surrogate standard with calculation using the EU water EQS limit value (water concentration,  $\mu\text{g/L}$ ) using the equation below (EC 2018):

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

$$EQS_{BS} [\text{mg/kg dw}] = EQS_{BS} [\text{mg/kg ww}] \cdot CONV_{\text{sed}}$$

$$CONV_{\text{sed}} = RHO_{\text{sed}} / F_{\text{solid, sed}} \cdot RHO_{\text{solid}}$$

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

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

where:

- $EQS_{BS}$ : estimated environmental quality standard for water referring to the HS concentration in bottom sediment according to the EU TGD (EU, 2003),
- $EQS_{\text{water}}$ : environmental quality standard for water referring to the HS concentration,

- $K_{\text{sed-water}}$  [ $\text{m}^3$  pore water/ $\text{m}^3$  sediment]: substance- and site-specific partition coefficient for bottom sediment–pore water
- $\text{RHO}_{\text{sed}}$  [ $\text{kg}$  wet sediment / $\text{m}^3$  wet sediment]: bulk density of wet sediment,
- 1000: conversion factor from  $\text{m}^3$  to litre,
- for estimate conversion factor ( $\text{CONV}_{\text{sed}}$ ) between wet and dry weight:
  - $F_{\text{solid, sed}}$  [ $\text{kg}$  solid content of sediment / $\text{kg}$  wet sediment]: fraction solids in bottom sediment,
  - $\text{RHO}_{\text{solid}}$ : density of the solid phase of the bottom sediment.

## AND

4.3 Derive input parameters as follows:

- **EQS<sub>water</sub>**: simply copy the value from the EQS values listed in Directive 2013/39/EU in Annex II, column (4) ‘AA-EQS (Annual Average EQS, Inland surface waters’ (also see Appendix 3 of this document; note the unit of  $\mu\text{g}/\text{L}$ ).
- $K_{\text{sed-water}}$ : derive this value (1) from measurement in the bottom sediment, or (2) from long-term region- or site-specific measurements in the bottom sediment, or (3) from the EU default values from Appendix 1.
- $\text{RHO}_{\text{sed}}$ : value of the bulk density of wet sediment, can be derived (1) from current measurement in the bottom wet sediment, or (2) from long-term region- or site-specific measurements in the bottom sediment, or (3) from the EU default value = 1300.
- $F_{\text{solid, sed}}$ : value of the fraction solids in sediment can be derived (1) from measurement in the bottom wet sediment, or (2) from long-term region- or site-specific measurements in the bottom sediment, or (3) from the EU default value = 0.2.
- $\text{RHO}_{\text{solid}}$ : value of density of the solid phase of the bottom sediment can be estimate (1) from literatures based on the type bottom sediment, or (2) from the EU default value = 2500.

## AND

4.4 If  $K_{\text{sed-water}}$  value is not available for the substance at site, and measured HS concentration is available for the total sediment and pore water, use the equation below:

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

where:

- $C_{\text{porew sed}}$  is the measured concentration in pore water of sediment [ $\text{mg HS} / \text{m}^3$  pore water],

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

- $C_{\text{total sed}}$  is the measured concentration in wet sediment [mg HS / m<sup>3</sup> wet sediment].

**OR**

5.10 If  $K_{\text{sed-water}}$  value is not available for the substance, and measured HS concentration is not available for the total sediment and pore water, use the equation below:

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

where:

- $F_{\text{solid sed}}$  fraction solids in wet sediment, see above,
- $F_{\text{water sed}}$  fraction pore water in wet sediment
- $K_{\text{p sed}}$  partition coefficient solids-pore water in sediment
- $RHO_{\text{solid}}$  density of the solid phase, see above.

Further  $K_{\text{p sed}}$  can be estimated using the equation below:

$$K_{\text{p sed}} = f_{\text{oc, sed}} \cdot K_{\text{oc}}$$

where:

- $F_{\text{oc, sed}}$ : weight fraction of organic carbon in the bottom sediment;  $F_{\text{oc, sed}}$  value can be derived (1) from current measurement in the bottom wet sediment, or (2) from long-term region- or site-specific measurements in the bottom sediment, or (3) from the EU default value of 0.05.
- $K_{\text{oc}}$ : substance-specific organic carbon-water partition coefficient, which not depends on site-specific conditions, values are found in literatures; (proposed values see in Appendix 1).

**AND**

4.5 Compare the **HS concentration measured in the collected bottom sediment sample ( $C_{\text{HS-BS}}$ ) to the estimated bottom sediment EQS limit value.** If  $C_{\text{HS-BS}} < EQS_{\text{BS}}$  then the sampled bottom sediment is not risky with respect to the evaluated HS.

**STEP 5. Optionally, it is interesting and useful for the evaluation of site-specific HS contamination to compare measured and estimated (calculated) HS bottom sediment concentrations.**

6.1 Compare the estimated  $C_{\text{HS-sediment, ww}}(\textit{estimated})$  value calculated according to the equation to the measured  $C_{\text{HS-sediment, ww}}(\textit{measured})$  by calculating the relative error (difference) between the measured and estimated concentrations:

$$\textit{ERROR} [\%] = \frac{C_{\text{HS-sediment, ww}}(\textit{measured}) - C_{\text{HS-sediment, ww}}(\textit{estimated})}{C_{\text{HS-sediment, ww}}(\textit{measured}) + C_{\text{HS-sediment, ww}}(\textit{estimated})}$$

If this value is  $\leq 5\%$  then the relative error between the measured and estimated (modelled) values is  $\leq 10\%$  (the denominator is the average of the two values). If the difference is  $> 10\%$  then investigate and adjust the measured and estimated input parameters, assuming that measured  $C_{\text{HS-sediment, ww}}$  concentration value is accurate.

## 9.3 RECOMMENDATION FOR TRANSNATIONAL MONITORING

It is recommended to

- **review** the available national bottom sediment EQS limit values in terms of
  - **list of HS** (preferably covering the EU EQS Directive HS list),
  - concentration values,
  - **representative matrix** (sampling: grab sampling for total HS bottom sediment concentration, passive sediment trap box sampling, etc.; sample preparation: filtering through 0.45  $\mu\text{m}$  filter or centrifuging; drying temperature for dry weight measurement, e.g. 40C° or 105C°; etc.; analysis: digestion with nitric acid-peroxide, etc.; reporting: units of measured concentration values, etc.),
- **develop** methods for the comparison of national  $Q_{\text{HS-sediment, ww}}$  limit values and measured  $C_{\text{HS-sediment, ww}}$  concentrations.



## 10. SELECTION OF HAZARDOUS SUBSTANCES FOR SEDIMENT QUALITY EVALUATION

### 10.1 PRINCIPAL CONSIDERATIONS

The most hazardous – for waters and related ecological system – HSs are identified as Priority Substances (PSs) or Priority Hazardous Substances (PHSs) by WFD Annex X. HSs are listed according to the requirements of the Directive 2013/39/EU on environmental quality standards (EQS) in the field of water policy which amend Directives 2000/60/EC and 2008/105/EC. Additionally, 4 heavy metals (arsenic, chromium, copper and zinc) and their compounds were added to this list for Danube River Basin (ICPDR, 2003), based on their relevancy in the Danube Basin, such as high percentage of usage (Appendix 2).

According to the WFD, Member States should arrange **monitoring of the priority HSs** that tend to accumulate in sediment and/or biota, giving particular consideration to the substances numbered in the Directive 2013/39/EU.

Not all HS should be monitored in sediments. The criteria for the selection of the HSs to be monitored from the EQS Directive (2013/39/EU) for sediment and biota is their **insolubility in water, tendency to associate with solid sediment**. Some chemical species become bonded (absorbed or adsorbed) in preference to small mineral particles and organic matter while some are dominantly found dissolved in the water phase in the river water column or in the bottom sediment pore water (ISO 5667-12:2017).

The Guidance Document No. 27 (Updated version 2018) prescribes: “The criteria for triggering an assessment are consistent with those under REACH Regulation (EC) No 1907/2006 (ECHA, 2008, Chapter R.7b). In general, substances with an organic carbon adsorption coefficient ( $K_{oc}$ ) of  $<500 - 1000 \text{ L}\cdot\text{kg}^{-1}$  are not likely to be sorbed to sediment. Consequently, a  $\log K_{oc}$  or  **$\log K_{ow}$  of  $\geq 3$**  is used as a trigger value for sediment effects assessment. Some substances can occur in sediments even though they do not meet these criteria so, in addition, evidence of high toxicity to aquatic organisms or sediment-dwelling organisms or evidence of accumulation in sediments from monitoring, would also trigger derivation of a sediment EQS”.

In addition, the HSs which are present in known emissions or in potential emission sources such as industrial sites (point sources; e.g. for PAHs) or agricultural areas (diffuse sources; e.g. pesticides) posing potential contamination risk on the given river water body, should be also added to the list of HSs monitored in river sediment.

## 10.2 PRACTICAL EVALUATION

**STEP 1.** Check the the  $K_{oc}$  (or  $K_{ow}$ ) value in Appendix 1 for the HSs listed in the EU EQS Directive.

**STEP 2.** Carry out the evaluation of sediment quality only for those substance which have a  $\log K_{oc}$  or  **$\log K_{ow}$  of  $\geq 3$**  value.

## 11. TREND ASSESSMENT FOR SEDIMENT QUALITY

### 11.1 PRINCIPAL CONSIDERATIONS

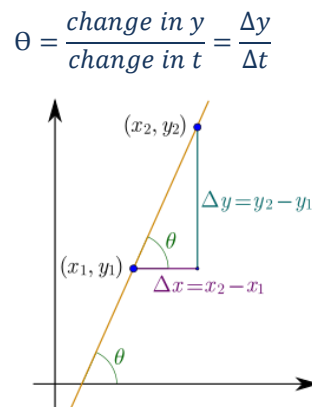
According to the WFD surface water surveillance monitoring is required, among others, for the assessment of **long-term changes** in **natural** conditions and for the assessment of long-term changes due to **anthropogenic** activity. Identification of significant trend of HSs is a major goal of surveillance monitoring. Member States should monitor sediment at an adequate frequency to provide sufficient data for a reliable long-term trend analysis of those priority substances that tend to accumulate in sediment. According to WFD guide documents, for the purpose of trend monitoring, sediment, or alternatively SPM, and biota are the most suitable matrices for many substances because they integrate, in time and space, the pollution in a specific water body; the changes of pollution in these compartments are not as fast as in the water column and long-term comparisons can be made. In addition, then monitoring for temporal trends, sound statistical analysis will require several data points in time (EC 2010). In conclusion, sediment quality trend assessment at a surveillance monitoring site has to consider the following:

- what is 'change' (natural and anthropogenic),
- what is 'significant' change,
- what is 'long-term' change,
- what is trend,
- how to detect trend.

## 1. What is change: deterministic definition

By definition, 'change' in the value of a measured parameter is the difference between the parameter values measured between two successive observations (**Figure 8.**):  $\Delta y = y_2 - y_1$ , where  $y_2$  and  $y_1$  are measured at times  $t_2$  and  $t_1$ , respectively ( $t_1 < t_2$ ). If  $\Delta y$  is positive ( $\Delta y > 0$ ,  $y_2 > y_1$ ) then the  $y$  parameter value increases, if  $\Delta y$  is negative ( $\Delta y < 0$ ,  $y_2 < y_1$ ) then the  $y$  parameter value decreases, and if  $\Delta y = 0$  ( $y_2 = y_1$ ) then  $y$  parameter does not change, it is constant.

The rate of change ( $\theta$ ) is the change in parameter value ( $\Delta y$ ) within unit time ( $\Delta t$ ):



**Figure 8.** Change between the parameter ( $y$ ) values of two successive observations is  $\Delta y$ .  $X$  is time ( $t$ ) in the case of temporal monitoring.  $\theta$  denotes the rate of change ( $\Delta y/\Delta t$ ): the change in parameter value  $y$  within unit time ( $\Delta t$ ).

## 2. The magnitude of change: absolute and relative change

Using the notation above, the absolute change is the difference between successive measurements:

$$\Delta y = y_2 - y_1.$$

The **absolute change** can be given with signed + or - such as

+ $\Delta y$  (increase) or - $\Delta y$  (decrease),

or in absolute value:

$$|\Delta y|.$$

The **relative change** is the fraction (ratio) of the absolute change and a reference value, such as the first ( $t_1$ ) measurement ( $y_1$ ), often given as %:

$$\text{Relative change} = \frac{|\Delta y|}{y_1} \text{ or } \frac{|\Delta y|}{y_1} \cdot 100 (\%)$$

### 3. What is uncertainty and confidence, and how to measure

**Deterministic uncertainty** can be defined

1. by measurement resolution (the smallest quantity that can be resolved):

$$\text{Uncertainty} = \pm \text{smallest unit},$$

so measurement and its uncertainty is given as

$$\text{Data} = \text{measured value} \pm \text{smallest unit}.$$

This is typically the case for measurements with digital devices such as field and laboratory digital scales and pH, EC, Dissolved Oxygen or redox potential devices (**Figure 9**).



**Figure 9.** Uncertainty of measurement in case digital devices - examples. Digital scale (left) and digital pH meter (right).

or

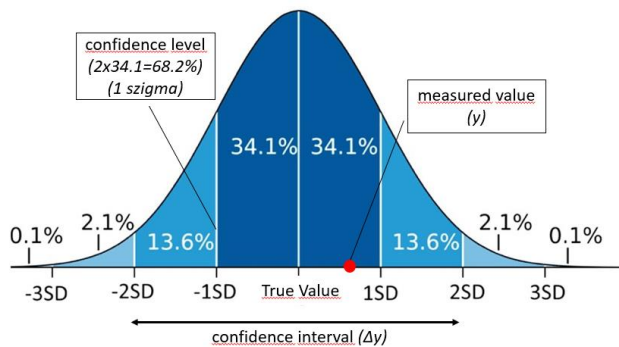
2. by the half of the range between the minimum and maximum values of repeated measurements:

$$\text{Uncertainty} = \pm \frac{1}{2} (\text{Maximum} - \text{Minimum}).$$

so measurement and its uncertainty is given as

$$Data = measured\ value \pm \frac{1}{2}(Maximum - Minimum)$$

**Stochastic uncertainty** is defined by the randomness of the measurement. It is characterised with the uncertainty interval (just like in the deterministic case) called the confidence interval but the probability of having the true value of the measurement is also given, which is called confidence level, most often given as percentage or simply as multiples of the standard deviation (SD) (**Figure 10.**).



**Figure 10.** Stochastic uncertainty is given in terms of the confidence interval (uncertainty,  $\Delta y$ ) and the confidence level associated with the confidence interval. SD: Standard deviation.

The true value is either known from some sources (e.g. concentration in standard material) or it is estimated as the mean from repeated measurements by calculating the average:

$$Average, \bar{x} = \frac{\sum_{i=1}^n y_i}{n}$$

where  $y_i$  is the  $i$ th repeated measurement and  $n$  is the number of measurements.

**Statistical uncertainty** is defined as

$$Uncertainty = \pm c \cdot SD,$$

so measurement and its uncertainty is given as

$$Data = average\ value \pm c \cdot SD,$$

where  $c$  is a constant and  $SD$  is the standard deviation given as

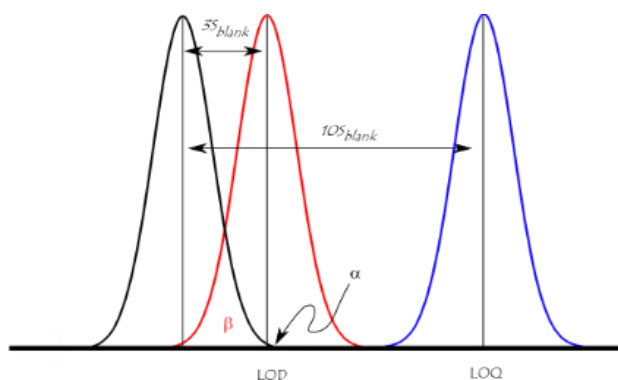
$$\text{Standard deviation, } SD = \sqrt{\frac{1}{n-1} \sum_1^n (x_i - \bar{x})}$$

This is typically the case for the determination of limit of detection (LOD) and limit of quantification (LOQ) of a certain compound such as a HS using a certain analytical method: the repeated measurement of a blank material (which does not contain the studied compound) is used to estimate the confidence interval in terms of multiples of standard deviation (**Figure 11.**):

- *Uncertainty, **LOD*** =  $\pm 3 \cdot SD$ , where  $3 \cdot SD$  corresponds to 99.73% confidence,
- *Uncertainty, **LOQ*** =  $\pm 10 \cdot SD$ , where  $10 \cdot SD$  corresponds to 99.9% confidence.

Since blank is used, the true value is 0 concentration unit. For example, deionized water (DW) is used as a blank for chemical element analysis because the true concentration value of the chemical element is assumed zero:

$$\text{LOQ} = \text{true value} \pm c \cdot SD = 0 \pm 10 \cdot SD = \pm 10 \cdot SD,$$



**Figure 11.** Statistical uncertainty shown by the limit of detection (LOD) and limit of quantification (LOQ).

Note that the LOD and LOQ values are confidence intervals (concentration values) defining confidence levels (percent probability that the measured concentration in the blank falls within the Zero–LOD/LOQ interval).



## 5. Total uncertainty of data

The uncertainty of data is not limited to the measurement uncertainty (random variation or scatter of repeated measurements, calculated as the standard deviation SD) but it also comes from random sampling error and from the uncertainty of the HS concentration due to its natural random variability. These uncertainties are independent from each other; therefore, the total uncertainty (random variation) is the sum of each uncertainty:

$$\begin{aligned} \text{Total uncertainty, } SD_{total} &= \text{Uncertainty}_{\text{sampling}} + \text{Uncertainty}_{\text{measurement}} + \text{Uncertainty}_{\text{natural}} \\ &= SD_{\text{sampling}} + SD_{\text{measurement}} + SD_{\text{natural}} \end{aligned}$$

All the uncertainties can be described as the measurement uncertainty discussed above. Note that natural uncertainty cannot be controlled and it is in fact assessed by the estimation of total uncertainty minus sampling and measurement uncertainty. If sampling and/or measurement uncertainty are not known or considered then it is assumed that all the uncertainties (variation) come from the natural variation of, for example, the studied HS.

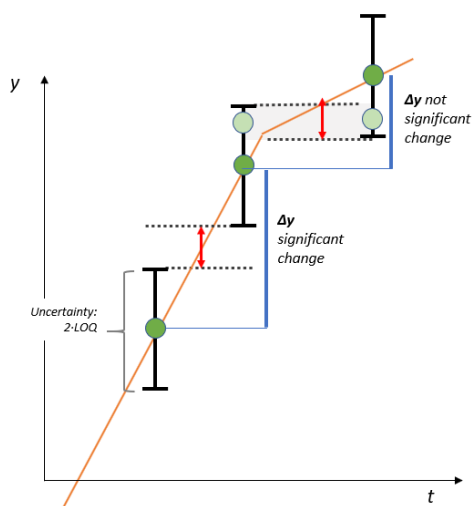
## 6. Significant change between two monitoring data points

According to the WFD documents, what constitutes a meaningful (significant) change will depend on the objectives of the assessment.

From the monitoring data point of view, since measurements always have uncertainty (error) it is obvious that any change (difference) within the measurement uncertainty is not significant (**Figure 12.**):

$$\text{Significant change: } \Delta y \geq LOQ .$$

Note that in water quality monitoring practice the quantitative uncertainty is rarely known, thus, error bars can be rarely drawn around the datapoints. Among the uncertainties it is the LOQ value which is widely available due to the WFD requirements, but most likely it shows only the minimum uncertainty associated with a monitoring data value.

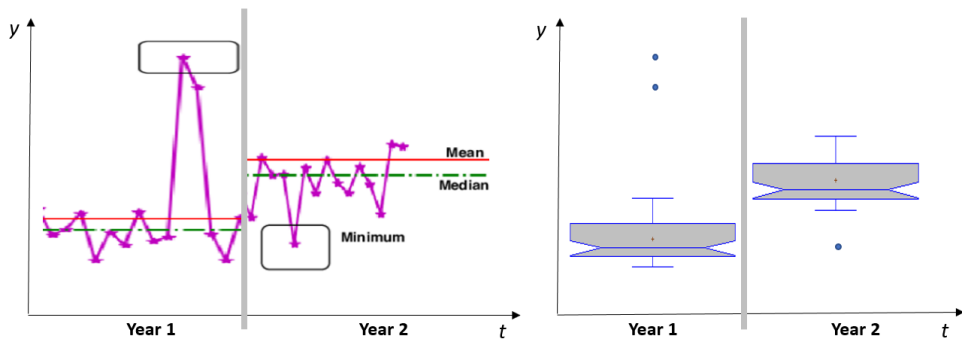


**Figure 12.** The change (difference;  $\Delta y$ , red arrow) between the two successive measurements is significant between the first two points because their error bars (uncertainty intervals; measurement resolution: LOQ) do not overlap. However, the change between the next two points ( $\Delta y$ , red arrow) is not significant because their error bars overlap. This means that there is chance that the two measurements are equal, as shown by the light green dots.

## 7. Significant change between two monitoring time intervals

The WFD prescribes the comparison of annual aggregated HS values if there is a significant change (increase) between the overall concentrations of two successive years. This is important for sediment quality assessment because surveillance monitoring results are expected to be evaluated against the WFD annual average EGS (AA-EQS) values which are based on chronic toxicity tests.

The comparison of the means of two annual series of measurements is simply done by the statistical Student's t-test using any statistical software. If the test rejects the assumption that the two means are equal, usually we set the confidence level at 95%, then there is a (statistically) significant difference between the two annual averages. This can be conveniently visualised with box plots (**Figure 13.**):



**Figure 13.** Left: Surveillance monitoring time series of two successive years. Note the increase of the central value (both the average; green dashed line and the median; red solid line). Note the high and low outlier values emphasised with the empty frames. Right: Box plots of measured data for the two successive years. Red dot: average; blue line: median; Upper and lower box boundaries: upper quartile and lower quartile, respectively; whiskers: define outliers as data points lying more than 1.5 times the inter-quartile range (box width) above or below the box. Note the high and low outlier values.

Note that the mean (and the standard deviation) calculated from data are sensitive to outlying values as shown in **Figure 13**. This means that a few high outlying values can increase the mean so that it does not characterise the majority of data. Therefore, as suggested by the WFD documents, the annual medians should be calculated and compared using the Mann-Whitney (Wilcoxon) W-test using any statistical software. The interpretation of the test result in terms of significant differences of the annual median values. Note that the term ‘annual average’ refers to the ‘overall yearly’ concentration, therefore, the median (or any appropriate central value) can be used for its characterisation.

## 8. Significant change along several monitoring data points: trend assessment of long-term change

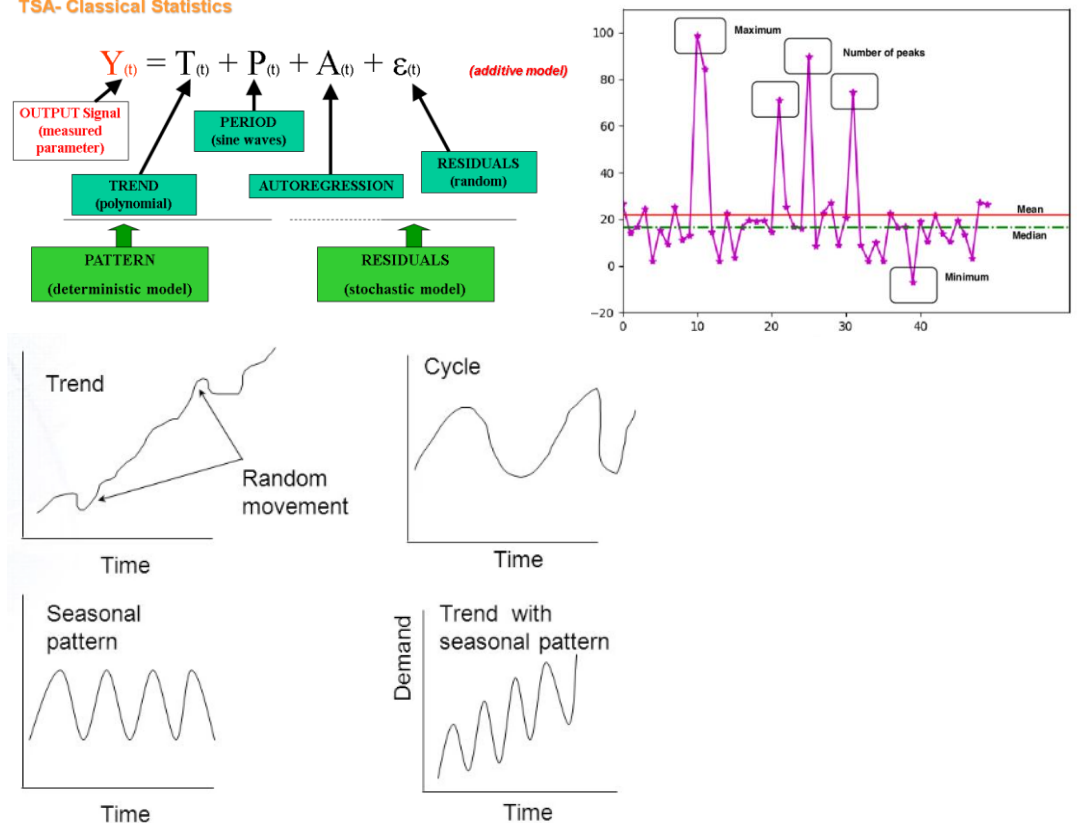
According to the WFD, trend in the HS monitoring data has to be assessed, although the term ‘trend’ is not defined. Trend is the systematic change of measured data values in time. The WFD documents recognise the importance of 1. data frequency in relation to trend assessment, 2. seasonal effects, and 3. random changes. Recognition and characterisation of such pattern in surveillance monitoring data is a subject of time series analysis (TSA). A time series consists

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

of a set of sequential numeric data taken at equally spaced intervals usually over a period of time. Time series analysis defines pattern according to an additive decomposition of the surveillance monitoring measurement series into trend ( $T(t)$ ), cycle ( $C(t)$ ), periodicity ( $P(t)$ ), autocorrelation ( $A(t)$ ), white noise residuals ( $\varepsilon(t)$ ) and events (outliers or transients;  $E(t)$ ) (**Figure 14.**):

$$c(t) = T(t) + C(t) + P(t) + A(t) + E(t) + \varepsilon(t).$$

### TSA- Classical Statistics



**Figure 14.** The various components of monitoring time series: Cycle, Trend, Periodicity (e.g. seasonal, diurnal), Autoregressive (memory effect) and random noise. Note that 'transients' such as outliers also occur and are found in the random component.

## 11.2 PRACTICAL EVALUATION

A complete and consistent procedure for the time series analysis of surveillance monitoring data is provided below.

First, a 3RSSH type nonlinear moving median smoother algorithm was used (it fits on 5 successive data points). WFD documents also suggest that the median of a year should be used to observe the trend, as it is less sensitive to the outliers (this eliminates, for example, findings made at times of high water, which are less representative for trend observation). This algorithm starts with a 5 point window moving median calculation then Re-smooth and Split algorithm is applied. This process separates the series into 'smooth' ( $S_1(t)$ ) carrying pattern (cycle, trend, periodicity) and 'rough' or 'residual' ( $R_1(t)$ ) containing auto-correlation, noise and outliers:

$$c(t) = S_1(t) + R_1(t),$$

$$S_1(t) = T(t) + C(t) + P(t),$$

$$R_1(t) = A(t) + E(t) + \varepsilon(t).$$

All features or period of time shorter than 5 time units (5 months in case of monthly data) join the rough (residuals) eliminating random noise and the effect of outliers. The residuals are stationary (constant in the mean) and represent the natural variability of the measured parameter, in addition to the stochastic and the sampling uncertainties. First, the above obtained 'rough' ( $R_1(t)$ ) is processed and outliers are defined by the previously described inner-fence criteria and subsequently removed. The outlier-free series is then subject to tests for randomness of median, sign and Box-Pierce tests to check if no pattern remains in the noise as trend, periodicity and autocorrelation, respectively using tests for randomness. Autocorrelation is not studied for WFD surveillance monitoring data. Finally, the statistical distribution of the outlier-free noise is described by the above mentioned summary statistics.

Second, the 'smooth' ( $S_1(t)$ ) is processed to model trend, cycle and periodicity. In order to capture the seasonal periodicity in the 5RSSH smoothed data, can be made stationary by removing the cycle and trend components with a moving average smoother having the length of one year. In this way the 5RSSH

## SEDIMENT QUALITY SAMPLING PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

'smooth' ( $S_1(t)$ ) is further separated into another smooth containing the cycle and trend components ( $S_2(t)$ ) and another rough containing the seasonal periodicity ( $R_2(t)$ ):

$$S_1(t) = S_2(t) + R_2(t),$$

$$S_2(t) = T(t) + C(t),$$

$$R_2(t) = P(t).$$

Periodicity is analyzed by the periodogram showing the power at each Fourier frequency. The periodogram shows the data in the frequency domain by considering how much variability exists at different frequencies. Once the frequencies in the data is identified, periodicity is modeled with sine waves fit to each monthly week data series with the least-squares method. The best fit is indicated by the smallest root-mean-square error (RMSE) value. The amplitude of the calculated sine waves may reveal seasonal differences. From the one-year long moving average smoothed data, the trend component is modeled by a simple linear least-squares regression line to  $S_2(t)$ . After subtracting the trend line from the smoothed series, the pure cycle component ( $C(t)$ ) is obtained.

It is noted that according to the Nyquist frequency theorem (Makridakis et al., 1998), the studied frequencies should be represented by more than two observation points in each time period. This means that for capturing the annual seasonal variation at least 3 samples per year shall be collected. WFD documents suggest that sampling of suspended solids for trend analysis should be carried out at least 4 times a year, although monthly sampling should be the goal. It is noted that trend can also be studied in the historic records of overbank (floodplain) sediment.

## REFERENCES

- Albanese, S., De Vivo, B., Lima, A., Cicchella, D. 2007. Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Italy). *Journal of Geochemical Exploration* 93, 21-34.
- Audry, S., Schäfer, J., Blanc, G., Jouanneau, J.-M. 2004. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environmental Pollution* 132, 413-426.
- DIN 4188-1:1977 Screening surfaces, wire screens for test sieves, dimensions. German Institute for Standardisation.
- EC 2000. 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. p. 1-72.
- EC 2008. 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. p. 84-97.
- EC 2003. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document No. 7. Monitoring under the Water Framework Directive. Luxembourg: Office for Official Publications of the European Communities.
- EC 2007. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document No. 15 Guidance on Groundwater Monitoring Luxembourg: Office for Official Publications of the European Communities.
- EC 2009. 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 Luxembourg: Office for Official Publications of the European Communities.



**SEDIMENT QUALITY EVALUATION PROTOCOL  
FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS - PROPOSAL**

- EC 2010. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document No. 25 Guidance on chemical monitoring of sediment and biota under the Water Framework Directive Luxembourg: Office for Official Publications of the European Communities.
- EC 2018. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Technical Guidance for deriving Environmental Quality Standards, Guidance Document No. 27 Updated version 2018.
- EPA 2001. Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual. Office of Science & Technology Office of Water U.S. Environmental Protection Agency Washington, DC, USA 20460. 208 p.
- Fabian, K., Reimann, C., de Caritat, P. 2017. Quantifying Diffuse Contamination: Method and Application to Pb in Soil. *Environmental Science & Technology* 51 (12), 6719-6726.
- Fraunhofer Institute 2002. Towards the Derivation of Quality Standards for Priority Substances in the Context of the Water Framework Directive: Final Report of the Study: Identification of Quality Standards for Priority Substances in the Field of Water Policy. EAF(3)-06/06/FHI. Fraunhofer-Institute Environmental Chemistry and Ecotoxicology, Germany. 124p.
- Hawkes, H.E., Webb, J.S. 1962. *Geochemistry in Mineral Exploration*. Harper & Row, New York.
- Horowitz, A.J. 1991. *A Primer on Sediment-Trace Element Chemistry*, USA, CRC Press; 2 ed., 136p.
- ICPDR 2003. List of Priority Substances for the Danube River Basin. International Commission for the Protection of the Danube River, 4p.
- ICPDR 2018. Water Quality in the Danube River Basin – 2016. In: Liska, I. (Ed.) TNMN – Yearbook 2016. ICPDR – International Commission for the Protection of the Danube River, Vienna, Austria, 61p.
- ISO 5667-1:2006 Water quality – Sampling – Part 1: Guidance on the design of sampling programmes and sampling techniques. International Organization for Standardization.
- ISO 5667-6:2014 Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams International Organization for Standardization.
- ISO 5667-12:2017 Water quality – Sampling – Part 12: Guidance on sampling of bottom sediments from rivers, lakes and estuarine areas. International Organization for Standardization.
- ISO 5667-15:2009 Water quality – Sampling – Part 15: Guidance on the preservation and handling of sludge and sediment samples (reviewed and confirmed in 2015). International Organization for Standardization.

- ISO 5667-17:2008 Water quality – Sampling – Part 17: Guidance on sampling of bulk suspended solids (reviewed and confirmed in 2017). International Organization for Standardization.
- ISO 6107-2:2006 Water quality — Vocabulary — Part 2. International Organization for Standardization.
- ISO 7027-1:2016 Water quality — Determination of turbidity — Part 1. Quantitative methods. International Organization for Standardization.
- Lin, J.G., Chen, S.Y., Su, C.R. 2003. Assessment of Sediment Toxicity by Metal Speciation in Different Particle-Size Fractions of River Sediment. *Water Science and Technology* 47, 233-241.
- Long, E.R., Robertson, A., Wolfe, D.A., Hameedi, J., Sloane, G.M. 1996. Estimates of the spatial extent of sediment toxicity in major U.S. estuaries. *Environmental Science and Technology* 30, 3585-3592.
- OSPAR 2018. CEMP Guidelines for Monitoring Contaminants in Sediments (revised 2018). OSPAR Agreement 2002–16, OSPAR Commission, 118 p.
- Reimann, C., Garrett, R.G. 2005: Geochemical background - Concept and reality. *Science of the Total Environment*, 350 (1-3), 12-27.
- Reimann, C., Filzmoser, P., Garrett, R.G. 2005. Background and threshold: critical comparison of methods of determination. *Science of the Total Environment* 346, 1-16.
- Reimann, C., Filzmoser, P., Garrett, R.G., Dutter, R. 2008. *Statistical Data Analysis Explained*. John Wiley & Sons, Ltd, London. 343p.
- Reimann, C., Fabian, K., Birke, M., Filzmoser, P., Demetriades, A., Negrel, P., Oorts, K., Matschullat, J., de Caritat, P., The GEMAS Project Team 2018. GEMAS: Establishing geochemical background and threshold for 53 chemical elements in European agricultural soil. *Applied Geochemistry* 8 (B) 302-318.
- Salminen, R. (Ed.), Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. 2005. *Geochemical Atlas of Europe. Part 1 – Background Information, Methodology and Maps*. Geological Survey of Finland, Espoo, Finland, 526p. <http://www.gtk.fi/publ/foregsatlas/>).

## CONTACT DETAILS

### Contact to project leader partner:

Geological Survey of Slovenia, Department for Mineral Resources and Environmental Geochemistry  
Dimiceva ulica 14, SI-1000 Ljubljana  
Tel: +386 (0)1 2809 764 | Fax: +386 (0)1 2809 753  
[www.geo-zs.si](http://www.geo-zs.si)

Project manager: dr. Meta Dobnikar, SI-GEOZS  
Mob: +386 31 739 882 | [meta.dobnikar@geo-zs.si](mailto:meta.dobnikar@geo-zs.si)

### Contact to authors:

Gyozo Jordan (SIMONA Scientific coordinator), HU-MATE  
Mob: +36 30 728 4060 | [gyozojordan@gmail.com](mailto:gyozojordan@gmail.com)

Katalin Mária Dudás, HU-MATE  
Mob: +3620 333 5177 | [kata.9.dudas@gmail.com](mailto:kata.9.dudas@gmail.com)

## OTHER INFORMATION

### Project title:

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

### Partnership of the project SIMONA:

The SIMONA partnership has 16 full partners (10 ERDF, 4 IPA and 2 ENI) and 12 associated partners (ASPs) from 13 Countries, which is a balanced and strong representation of almost the whole Danube River Basin.

### Project duration:

01/06/2018 - 30/11/2021

### Project co-funded by the European Union (ERDF, IPA and ENI)

For further information on the project, partnership and the Danube Transnational Programme:  
[www.interreg-danube.eu/simona](http://www.interreg-danube.eu/simona)



**FIND SIMONA PROTOCOLS ON THE WEBSITE!**