Interreg
EUROPEAN UNION
Danube Transnational Programme
SIMONA

SIMONA OUTPUT T3.1.

SEDIMENT QUALITY EVALUATION PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

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

30/11/2021

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

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Please cite this protocol as: Katalin Mária DUDÁS, Gyozo JORDAN and The SIMONA Project Team. 2021. Sediment quality evaluation protocol for hazardous substances in surface waters. EU Interreg Danube Transnational Programme 71p.

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1. PURPOSE

The purpose of this document is to give practical guidance and provide methods for sediment quality monitoring data evaluation in compliance with the EU Water Framework Directive (EU WFD) (EC 2000) with focus on the use in the Danube Basin Countries. The aim of the document is to serve the trans-national harmonised evaluation of sediment quality among 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 (long-term regular monitoring);
- single monitoring site (sampling station);
- single water body;
- hazardous substances listed in the EU WFD Annex X and EQS Directive (priority substances and priority hazardous substances);
- 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 hazardous substance (HS) concentrations;
- developing toxicity tests related to EQS values for sediment quality evaluation is outside of the scope.three sediment quality evaluation methods are presented: (1) comparison of the measured HS concentration to corresponding national quality standard (QS) values, (2) comparison of the measured HS concentration to international EQS values, and (3) conversion of QS value available for one media (e.g. dissolved in the water) to sediment-bound QS values based on the WFD CIS documents.

3. BASIC TERMS

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

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

Fluvial sediment is meant here as solid material transported (moved and deposited) by river as bottom/stream sediment (river bed and bed load), suspended sediment, and overbank or floodplain- sediment (Šorša and The SIMONA Project Team, 2019).

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 2000). Surveillance monitoring is different from the other two types of monitoring: Operational Monitoring and Investigative Monitoring. In the context of the SIMONA project, surveillance monitoring refers to long-term and regular 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 investigated 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 the investigated medium which should not be exceeded in order to protect the relevant receptors connected to the investigated 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% of the environmental standard (i.e. LOQ≤30% 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 methods (Šorša and The SIMONA Project Team, 2019; Jordan and The SIMONA Project Team, 2021,) and laboratory methods (Čaić Janković, A., Šorša, A. and The SIMONA Project Team, 2019) 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_2O) and dissolved material (e.g. Ca, Mg, NO_3^-, HCO_3^-, 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 partition between these two phases, 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.

Further details on the sediment types can be found in SIMONA Sampling Protocol (Šorša and The SIMONA Project Team, 2019)

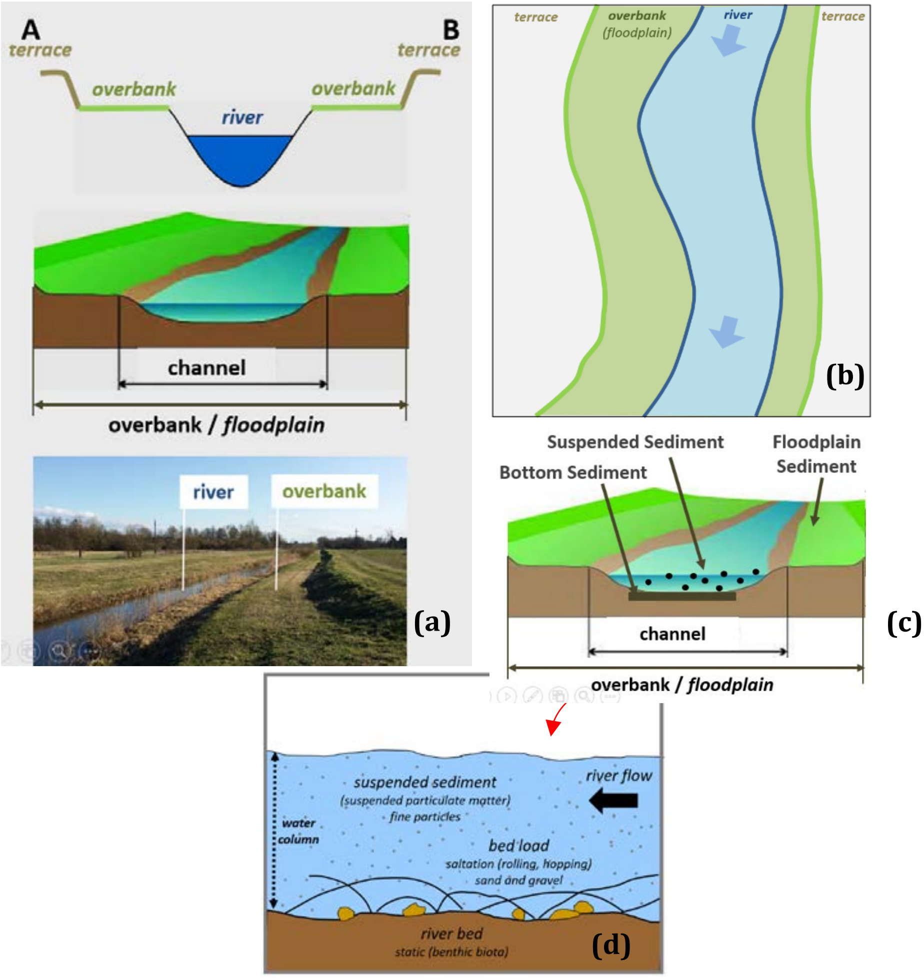


Figure 1. The fluvial sediment system: sediment regimes and sediment types. (a) Cross-section view of the fluvial system and its main parts: the river channel, the actively (regularly) flooded overbank or floodplain area and the river terrace as the old and inactive overbank (floodplain) area. (b) The 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. (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 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 6)**. 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 the FAO fluvisols soil class).

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

- overbank sediment is suspended sediment 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 low-flow 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 6**);
- overbank sediment is suitable for defining the natural **background concentration** for the naturally occurring inorganic substances (metals): the local natural background value could be defined as a compound concentration of the deeper, natural, preindustrial fluvial sediments at the monitoring (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 monitoring site, bed load and suspended sediment flows through the site moved by the flowing river water (throughflow: input/output balance) (**Figure 2**). River bed sediment and overbank sediment are deposited at the site (accumulation). If the hydrological regime of the river at the site changes in the long term (e.g. a depositional site becomes erosive) or during high-flow (flood) events in the short term, the deposited river bed and overbank sediment can be remobilised and transported downstream from the site as sediment output from the monitoring site. Floodplains (overbank areas of large rivers) tend to be predominantly depositional areas.

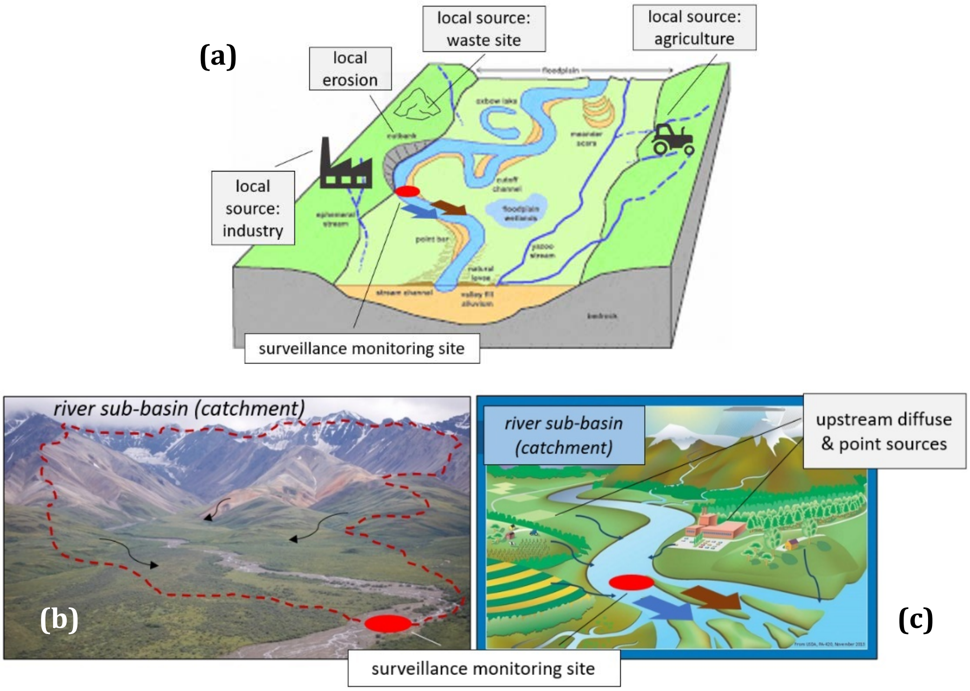


Figure 2. The fluvial sediment system: local scale and catchment scale aspects. Red dot: surveillance monitoring site. Thin arrows: transport of sediment, water and associated HSs. Blue arrow: water and dissolved HS transport. Brown arrow: sediment and sediment-bound HSs transport. (a) Local sources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

It is noted that particle-bound contamination can reach the monitoring site by atmospheric deposition, too.

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**). Note that it is assumed that there is no piped or channelled waste water input or water extraction within a surveillance monitoring site. 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 in the catchment. At the monitoring 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, while the only 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**).

The interaction of groundwater and surface water at the monitoring site occurs in the **hyporheic zone** which includes the bottom sediment (**Figure 4**). The hyporheic zone is critical from the sediment quality point of view because pore water is a major HS exposure route to the benthic biota which is the sediment quality assessment endpoint in WFD. Moreover, due to the hyporheic zone interactions, bottom sediment can reflect the very local effects of ground water inflow including local contamination input.

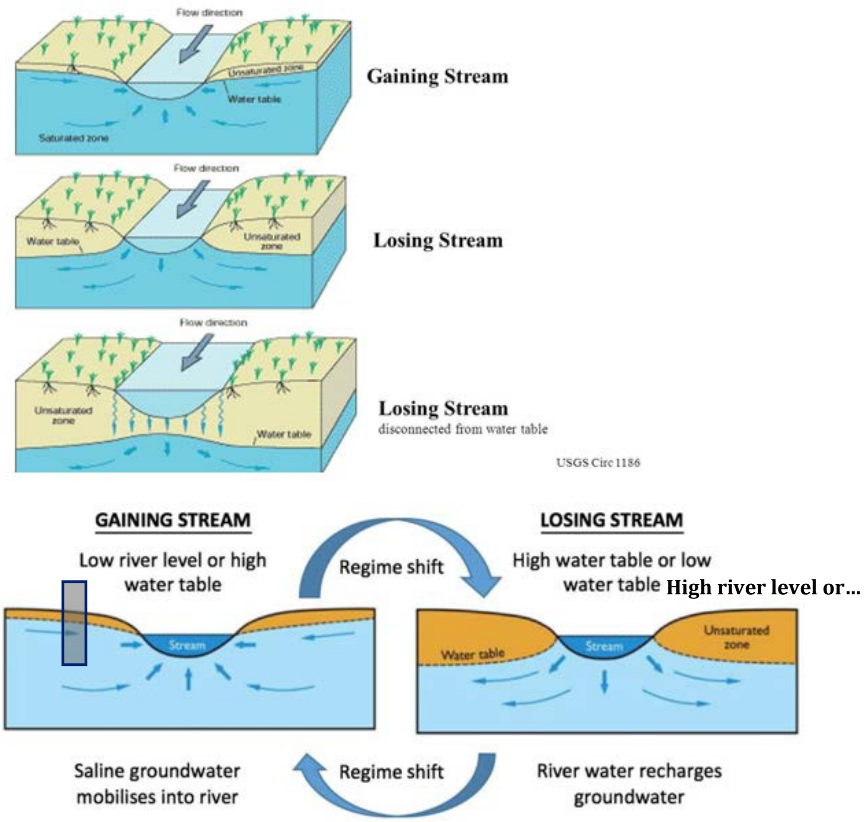


Figure 3. The fluvial system water balance at the monitoring site. The origin of bottom sediment pore water from groundwater vs surface water is emphasised. Note that the groundwater–surface water flow direction can be reversed (bottom figure). Grey rectangle indicate a groundwater monitoring well.

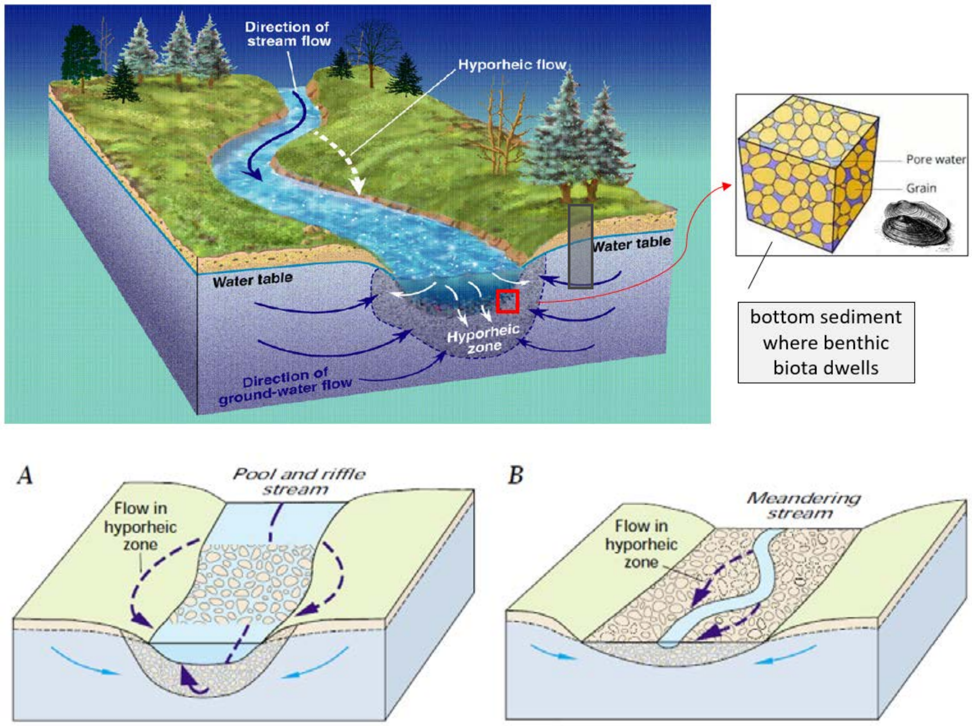


Figure 4. The hyporheic zone is the location of river water and groundwater interaction including the bottom sediment where benthic biota dwells. Top: location of bottom sediment in the hyporheic zone where benthic biota dwells. Bottom: River water flow underground in the hyporheic zone.

6. UNDERSTANDING SEDIMENT QUALITY EVALUATION

6.1 CONTAMINATION RISK ASSESSMENT

Risk assessment (RA), defined in its broadest sense, deals with the probability of any adverse effects.

Contamination risk is the combined effect of the probability of contamination and the significance of toxic impacts. This is studied through the pathway from (1) hazard description, through (2) dose/response (toxicity) analysis, (3) contaminant transport, (4) exposure assessment, to (5) risk characterisation and (6) risk management (van Leuwen and Hermens 1996; US EPA 2007) (Fig. 5).

Although risk assessment is not directly related to one economic activity, RAs are concerned with the risk involved at a specific site, at a specific time and due to specific causes. Contamination risk is the combined effect of the probability of contamination and the significance of toxic impacts. This is studied through the pathway from (1) hazard description, through (2) dose/response (toxicity) analysis, (3) contaminant transport, (4) exposure assessment, to (5) risk characterisation and (6) risk management (van Leuwen and Hermens 1996; US EPA 2007) (Fig. 5).

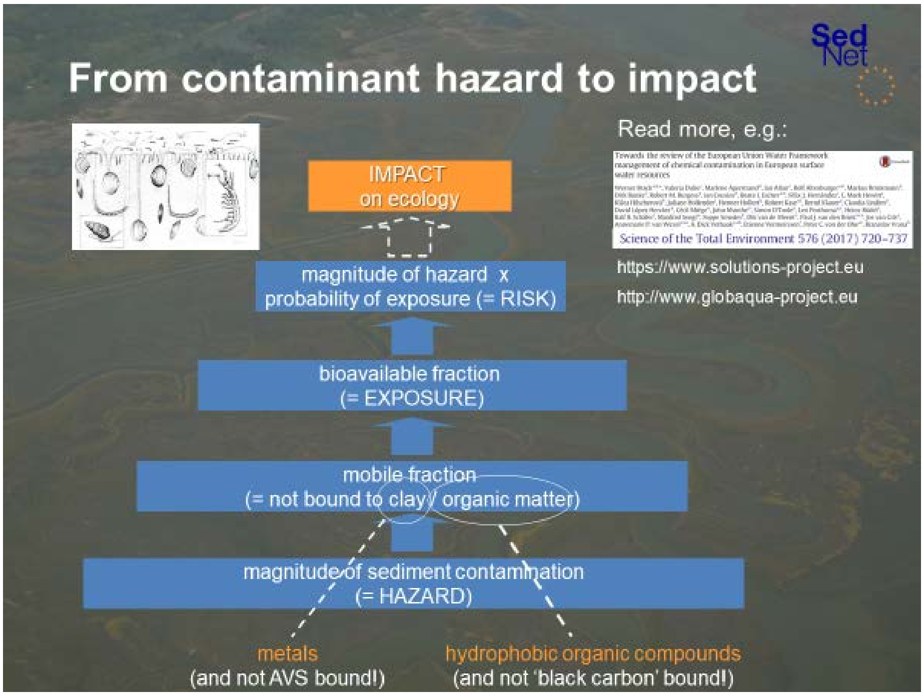
The source–pathway–receptor chain for contamination risk assessment

(1) preliminary screening and site selection, (2) source–pathway–receptor model and (3) risk ranking system.

Contamination RA is defined as the probability of adverse effects to humans and ecosystem resulting from exposure to environmental pollutants (Kolluru et al. 1996; Fergusson 1998; US EPA 1989, 1998; Di Sante et al. 2009; Fan et al. 2010). RA is concerned with the risk involved at a specific site, at a specific time and due to specific causes. RA includes the steps of (1) hazard description, (2) dose/response (toxicity) analysis, (3) contaminant transport, (4) exposure assessment, (5) risk characterization and (6) risk management (Van Leuwen and Hermens 1996; U.S. EPA 2002, 2007). Contamination risk exists for a site only if all the source, pathway and receptor components are present. While human health risk assessment studies the probability of impact on a single organism (U.S. EPA 1989; Gazdag and Sipter 2008), ecological risk assessment studies the impact on organisms (U.S. EPA 1998; Yi et al. 2011). In the case of mine waste sites, for example, this means that a hazardous waste should be present such as an ore tailings pond, contamination transport should be enabled by air, surface- and groundwater or direct contact to reach sensitive receptors such as settlements, protected ecosystems or agricultural lands.

6.2 SEDIMENT QUALITY

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 ecosystems. Depending on the concentrations of contaminants, mixtures of contaminants and their species-specific bioavailability as well as toxicity, exposure to the sediment-bound contaminants will impact organisms and ecosystems (**Figure 5**).



From contaminant hazard to impact

IMPACT on ecology

magnitude of hazard x probability of exposure (= RISK)

bioavailable fraction (= EXPOSURE)

mobile fraction (= not bound to clay / organic matter)

magnitude of sediment contamination (= HAZARD)

metals (and not AVS bound!)

hydrophobic organic compounds (and not 'black carbon' bound!)

Read more, e.g.:

Towards the review of the European Union Water Framework management of chemical contamination in European surface water resources

Science of the Total Environment 576 (2017) 720–737

https://www.solutions-project.eu

http://www.globaqua-project.eu

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 may also cause indirect food-web effects. A decreased abundance results in a decrease in food availability for the respective benthic or pelagic predators. If sediment-associated hazardous substances are released from sediment to the water column, they may impact pelagic organisms such as zoo- and phytoplankton and fish, or they may impact benthic biota by direct uptake of chemicals via porewater.

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' and 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 are 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 floodplains covered with contaminated suspended matter during flood events could also have an impact on human health. There are examples of floodplains where the consumption of livestock has been restricted (Salomons and Brils, 2004). This implies potential impacts of contaminated sediment on terrestrial ecosystems in floodplains as well.

The ecological status assessment is based on several biological quality elements (BQEs) and this assessment is supported by several hydro-morphological and physico-chemical 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 sediment contamination may have indirect effects such as impact on the health of certain pelagic species, it is difficult to quantify the effect of sediment associated contaminants as compared to the contaminants dissolved in the water column. In conclusion, sediment chemical status assessment is essentially hazard assessment, while the ecological status assessment is essentially impact assessment. Sediment associated contaminants can affect some of the BQEs but their overall impact on the ecological status of the water body and on the health of organisms along the food chain may turn out to be minor.

6.2 EVALUATION OF SEDIMENT QUALITY

Evaluation means contamination (hazardous substance; HS) risk assessment, and sediment quality means potential toxicity of sediment associated contamination to the receptor pelagic or benthic biota. Thus, **sediment quality evaluation** is the assessment of the risk posed by sediment associated hazardous substances to the receptor biota endpoint.

In practice, the evaluation of sediment quality monitoring data under legislative conditions means the comparison of the hazardous substance (HS) concentration measured in the sediment (C^{HS}) to the relevant environmental limit value, called quality standard (QS^{HS}) in the WFD:

$$C^{HS}_{sediment\ compartment} \leq QS^{HS}_{sediment\ compartment}$$

If the HS concentration measured in the sediment sample ($C^{HS}_{sed\ comp}$) is less than or equal to the relevant QS ($QS^{HS}_{sed\ comp}$) then the sediment is not regarded polluted with respect to the studied HS and thus it poses no significant risk to the biota, ecosystem or human health. In this case, if the water body status assessment is based on sediment quality, and concentration of all the WFD HSs (shown in the EU EQS Directive priority substances and priority hazardous substances list) are below the relevant QS values, the water body is designed being in good status. Here 'relevant' means that the HS concentration is measured in the same sediment compartment (e.g. HS dissolved in water, total water column, solid matter dry weight, etc.) as the QS value refers to. For sediment quality evaluation the following aspects have to be thoroughly considered:

- the studied sediment compartment such as dissolved HS concentration in pore water or total HS concentration in the <63µm fraction **must match the sediment compartment** that the used QS value refers to; this means that the QS value is 'relevant' to the measured HS concentration,
- the used QS value should be **based on toxicological tests** and studies because the basis of sediment quality evaluation is the toxicity to the biota endpoint in the WFD.

Certain sediment quality QS systems such as the Elbe River (**REF**) or the US EPA (**REF**) systems are based on toxicological tests, while other limit value system such as the Dutch List (**REF**) are based on statistical data analysis.

SIMONA uses 3 sediment quality assessment methods:

1. **comparison** of measured HS concentration to existing relevant **national environmental limit** value (QS value),
2. **comparison** of measured HS concentration to existing relevant **international environmental limit** value (QS value),
3. **conversion** of existing QS value to a QS value relevant to the sediment compartment for which the sediment quality evaluation is performed or in which the HS concentration is measured, using the QS transformation equations presented in the WFD CIS document; this method requires other input parameters such grain size or sediment bulk density data, and has 2 sub-cases:
    A. using standard parameters for the conversion equations such as regional or European average grain size or sediment bulk density data, OR
    B. using site specific parameters such as grain size or sediment bulk density measured in the monitoring site.

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 evaluation is not mandatory. The WFD does not mention the overbank areas or floodplains but it requires the characterisation of the structure of the '**riparian zone**' under the 'hydromorphological elements' evaluation item, 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." Thus, riparian zones can be identified with the overbank or floodplain areas, although quite indirectly only.

Overbank (floodplain) sediment, even the uppermost top layers of the sediment 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, (2) is not in chemical equilibrium with the river water column, and, in addition, (3) is exposed subaerially on the land surface for soil formation (**Figure 6**). Therefore, the HS concentration measured in overbank sediment should be evaluated against **soil QS limit values (QS_{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 eventually becomes soil after deposition from flood water.

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

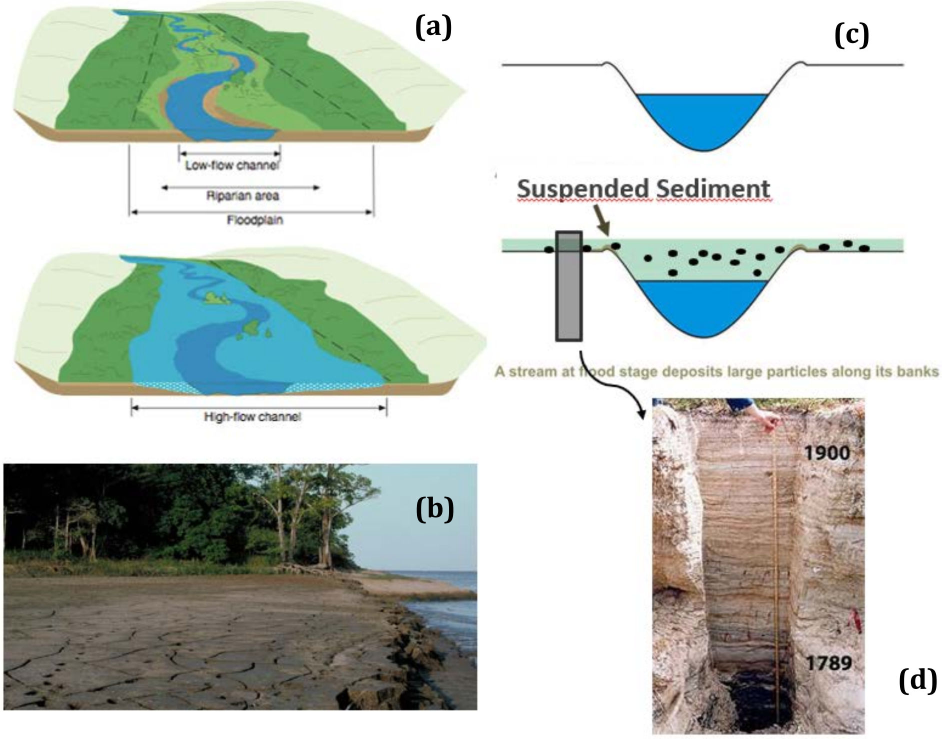


Figure 6. The overbank sediment system. (a) Area cover by river water under low flow and high flow conditions. The area covered by river water during high flow is called the overbank or floodplain area. (b) Typical overbank sediment deposited during flood (high flow) event. (c) Overbank sediment is in fact suspended sediment deposited during high flow (flood) events. Grey bar indicates the location of the overbank sediment vertical profile shown in Figure 2d. (d) Typical overbank sediment vertical profile deposited during high flow (flood) events in the past 200 years as shown by the dates.

In high mountain areas where there is no overbank (floodplain) sediment deposited, this sediment type cannot be sampled, analysed and therefore evaluated.

It is important that the **HS concentration measured in the collected overbank (floodplain) sediment sample (C_{OS}) is representative for the soil QS limit value used for sediment quality evaluation.** This means that the sampling, sample preparation, laboratory analysis, quality control and quality assurance, and reporting procedures should match exactly those used for the derivation of the soil QS_{soil} limit value:

- **sampling** (sampling method: e.g. undisturbed or grab sample; sampling depth such as topsoil from 0-5cm depth; etc.),

- **sample preparation** (sample drying temperature: e.g. 40C° or 105C°; analysed fraction, e.g. <2mm or <63µm; etc.),
- **sample analysis** (sample digestion: e.g. aqua regia or nitric acid-peroxide; mobile HS fraction defined by deionised water leaching; etc.),
- **reporting** (LOQ values; 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_{soil} value is based on.

7.2 PRACTICAL EVALUATION

STEP 1. If soil QS limit values are available in your country's legislation for the substances listed among the priority substances and priority hazardous substances in the EU EQS Directive :

1.1 Make sure that the HS concentration measured in the collected overbank sediment sample (C_{OS}) is representative for the soil QS_{soil} limit value used for the overbank sediment quality evaluation. This shall be done by matching the HS concentration measurement to the sampling, laboratory analysis and data quality procedures and requirements of the soil QS_{soil} limit value standards, in addition to other specifications such as the soil type relevant to the QS_{soil} and other limitations of applicability of the QS value such as grain size.

AND

1.2 Compare the **HS concentration measured in the collected overbank sediment sample (C_{OS}) to the soil QS_{soil} limit value:** if

$$\boxed{C_{OS} \leq QS_{soil}}$$

then the **sampled overbank sediment is in good status** with respect to the evaluated HS.

NOTE: Soil QS_{soil} limit values are readily available in most countries, although, there are no relevant EU-level soil contamination QS_{soil} concentration values at present. Soil limit values QS_{soil} derived from evidence-based ecotoxicological data should be preferred for overbank sediment quality evaluation in relation to the WFD.

STEP 2. If soil QS limit values are not available in your country's legislation for the substances listed among the priority substances and priority hazardous substances in the EU EQS Directive :

2.1 Establish soil QS_{soil} limit values in your country's legislation. Give preference to soil limit values QS_{soil} derived from evidence-based ecotoxicological data. QS_{soil} limit values can be established by

2.1.1 developing independent national soil QS_{soil} limit values,

OR

2.1.2 adopting existing internationally recognised soil QS_{soil} limit values.

If soil QS_{soil} 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_{soil} limit values become available or for 2. other uses such as site contamination **indicative evaluation** by comparing the measured HS concentration to internationally recognised soil QS_{soil} limit value such as that in the 'Dutch List'), or for scientific investigation purposes.

7.3 RECOMMENDATION FOR TRANSNATIONAL MONITORING

It is recommended to

- **review** the national soil QS_{soil} limit values available in the Danube Basin countries in terms of
    - **list of hazardous substances** covering the EU EQS Directive priority substances and priority hazardous substances list,
    - if the available QS_{soil} limit values are **based on ecotoxicological evidence**,
    - levels of concentration values,
    - **representative matrix and speciation** (sampling: undisturbed sample of 0-5cm topsoil, composite sample, etc.; sample preparation: drying at

temperature of 40C° analysed fraction of <63µm, etc.; laboratory analysis: digestion with nitric acid-peroxide, leaching with deionised water, etc.; reporting: LOQ values, units of measured concentrations, etc.),

- **develop** methods for sediment quality evaluation (comparison of measured C_{OS} concentrations to the national QS_{soil} limit values.
- due to the uncertainties about the representativity of overbank (floodplain) sediment samples and to the technical difficulties of sediment sampling during flood event, suspended sediment in the overbank (floodplain) area could be best sampled using sediment traps such as the Joint Danube Survey (JDS) passive sediment box placed on the overbank area. Suspended sediment collected over the overbank (floodplain) area during flood event should be evaluated against soil QS_{soil} limit values, despite the fact that it was collected from river water suspension as suspended sediment.

8. EVALUATION OF SUSPENDED SEDIMENT QUALITY

8.1 PRINCIPAL CONSIDERATIONS

Suspended sediment is called ‘**suspended particulate matter**’ (SPM) in the WFD. Suspended sediment together with the sediment-bound hazardous substances is separated from water and the water-dissolved HSs operationally by using filtration through the 0.45µm filter: the solid residue trapped on the filter is the suspended particulate matter 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 <0.45µm filtrate, or in the separate of centrifuging,
- **Solid particle-bound HS,** $C_{\text{susp, solid}}$ (absorbed in or adsorbed to the solid suspended sediment particles):
  measured in the ≥0.45µm 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.

Accordingly, quality standards can be given as

- **$QS_{water,\ dissolved}$**: Dissolved HS concentration (μg/L),
- **$QS_{susp,\ solid}$**: Solid particle-bound HS concentration (mg/kg),
- **$QS_{water,\ total}$**: Total HS concentration (μg/L).

The WFDprovides HS concentration QS limit values as follows (EC 2008):

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

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 measured 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 the suspended sediment and the water phases can be used 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:

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

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:

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

from which

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

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

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

thus

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

and

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

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

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

or rearranged as

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

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 the given 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 concentration of HS is replaced by the relevant predefined QS limit value, 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:

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

or

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

where:

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

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[1] For more information see: https://www.ecetoc.org/report/estimated-partitioning-property-data/computational-methods/log-koc/

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 $QS_{\text{water, dissolved}}$ limit value directly derived from toxicity or bioaccumulation tests:

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

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 $QS_{\text{susp, solid}}$ 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:

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

In practice this means that the available $QS_{\text{water, total}}$, such as the EQS values in the EU EQS Directive (EC 2008), can be used to derive an estimated $QS_{\text{susp, solid}}$ limit value. This estimated QS limit value is then compared to the measured suspended solid HS concentration in order to evaluate if the suspended sediment is at risk of 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 the total water column concentrations for the organic HSs and refer to the dissolved concentrations for metals; EC 2008). Suspended sediment EQS limit value estimation 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 ($C_{susp,\ solid}$) which is used for sediment quality evaluation (comparison of $C_{susp,\ solid}$ and $QS_{susp,\ solid}$ weather $C_{susp,\ solid} < QS_{susp,\ solid}$) is **representative** for the suspended sediment $QS_{susp,\ solid}$ limit value (either directly available from toxicity tests or estimated from water $QS_{water,\ dissolved}$ or $QS_{water,\ total}$ limit values). Thus, sampling, sample preparation, laboratory analysis and reporting procedures should match exactly those used for the suspended sediment $QS_{susp,\ solid}$ 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 µm filter or centrifuging; drying temperature, 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; µg/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 suspended 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 ≥ 3** value (hydrophobic substances that tend to be associated with sediment). For substances having a $\log K_{OC}$ or **$\log K_{OW}$ of <3** value, evaluation should be limited to the water (dissolved or total) concentration.

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

3.1 Make sure that the HS concentration measured in the collected suspended sediment sample ($C_{susp,\ solid}$) is representative for the suspended sediment

QS limit value used for sediment quality evaluation (comparison of $C_{susp,\ solid}$ and suspended sediment QS limit value weather $C_{susp,\ solid} < QS_{susp,\ solid}$).
AND

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

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 ($QS_{water,\ total}$) and the dissolved concentration for metals ($QS_{water,\ dissolved}$) in units of μg/L (EC 2018), using the equations below:

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

OR

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

then

$$\mathrm{QS}_{\text{susp, solid}}\left[\frac{\mathrm{mg}}{\mathrm{kg}}\right] = \mathrm{K}_{\text{p, susp}}\left[\frac{\mathrm{L}}{\mathrm{kg}}\right] \cdot \frac{\mathbf{QS}_{\textbf{water,total}}\left[\frac{\mathrm{mg}}{\mathrm{L}}\right]}{1 + \mathrm{f}_{\mathrm{oc,susp}} \cdot \mathrm{K}_{\mathrm{OC}}\left[\frac{\mathrm{L}}{\mathrm{kg}}\right] \cdot \mathrm{C}_{\mathrm{SPM}}\left[\frac{\mathrm{mg}}{\mathrm{L}}\right] \cdot 10^{-6}}.$$

OR

$$\boxed{\mathrm{QS}_{\text{susp, solid}}\left[\frac{\mathrm{mg}}{\mathrm{kg}}\right] = \mathrm{K}_{\text{p, susp}}\left[\frac{\mathrm{L}}{\mathrm{kg}}\right] \cdot \mathbf{QS}_{\textbf{water, dissolved}}\left[\frac{\mathrm{mg}}{\mathrm{L}}\right].}$$

See parameter explanation above.

AND

4.3 Derive input parameters as follows:

- **$\mathbf{QS}_{\textbf{water, total}}$** and **$\mathbf{QS}_{\textbf{water, dissolved}}$** : copy the relevant EQS value for the HS annual average AA-EQS 'Inland surface waters'; note the unit of μg/L (also see **Appendix 3** of this document), or copy it from the relevant list of QS values presented in national legislation;
- **$\mathbf{C}_{\mathbf{SPM}}$** : its value can be derived (1) from measurement in the suspended sediment samples, or (2) from the **EU default value $\mathbf{C}_{\mathbf{SPM}} = 15\ \mathbf{mg{\cdot}L^{-1}}$** for freshwater;
- **$\mathbf{K}_{\textbf{p, susp}}$**: take this substance-specific partition coefficient value from any valid experimental source (e.g. $\mathrm{K}_{\text{p, susp}}$ defined experimentally specifically to the site using representative samples of the site). If **$\mathbf{K}_{\textbf{p, susp}}$** is not available, estimate it as the product of $\mathrm{f}_{\text{oc, susp}}$ and K_{oc}.
- **$\mathbf{f}_{\textbf{oc, susp}}$**: its value can be derived (1) from measurement in the suspended sediment samples, or (2) from the **EU default value $\mathbf{f}_{\textbf{oc, susp}} = 0.01$** (ECHA, 2008).
- **$\mathbf{K}_{\mathbf{oc}}$**: 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 ($\mathbf{C}_{\textbf{susp, solid}}$) to the estimated suspended sediment QS limit value (**$\mathrm{QS}_{\text{susp, solid}}$**)**. If $\mathrm{C}_{\text{susp, solid}} < \mathrm{QS}_{\text{susp, solid}}$ 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 ($\mathrm{C}_{\text{susp, solid}}$), 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 0.45µm 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 $\mathbf{C_{susp,\,solid}}$ **(estimated)** value calculated according to the above equation:

$$C_{susp,\,solid}(\text{estimated}) \Leftarrow C_{water,\,dissolved} \quad \textbf{OR} \quad C_{susp,\,solid}(\text{estimated}) \Leftarrow C_{water,\,total}$$

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

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

If this value is ≤5% then the relative error between the measured and estimated (modelled) values is ≤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; $K_{p,\,susp}$ value, or the constituting f_{oc} and K_{oc} values; or the C_{SPM} value), assuming that measured $C_{susp,\,solid}$(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 PS/PHS 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 µm 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_{SPM} limit values and measured C_{susp} 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, as well as of 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 separated 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.

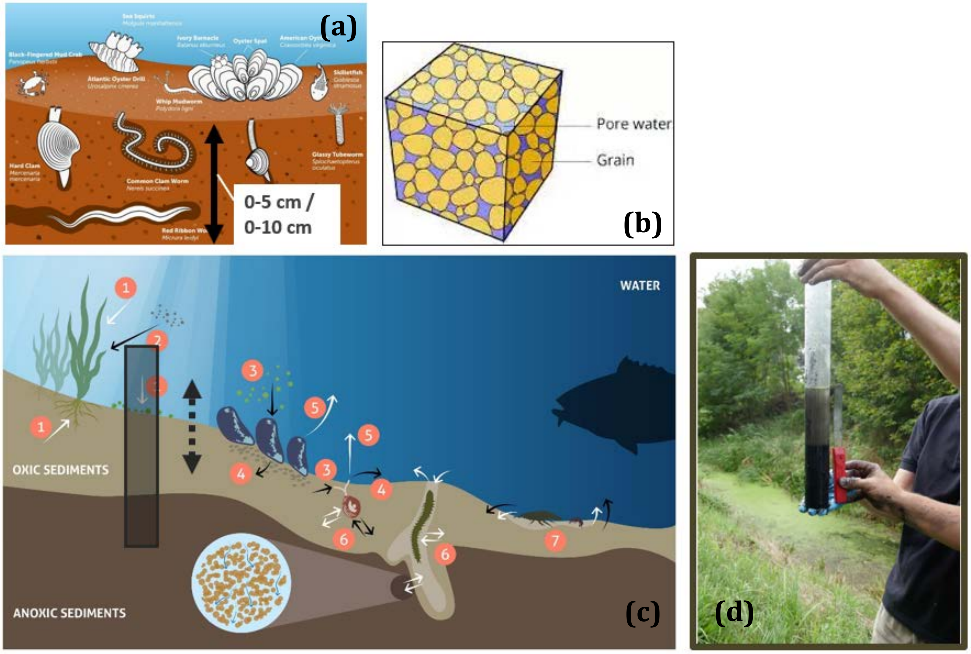


Figure 7. The bottom sediment system. (a) The benthic (sediment dwelling) biota lives in the uppermost oxic sediment layers (0-5cm, 0-10cm). (b) 3D cartoon showing the relationship of solid sediment (grains) and pore water. Pore water is assumed to be in chemical equilibrium with solid sediment. (c) Cartoon showing the possible layering of the top oxic sediments over the lower lying anoxic sediments. The dashed 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 the bulk density of each phase. The fractions of the solids and water phases, and the total bulk density are both 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:

- $\mathbf{F_{solid,comp}}$: fraction of phase solid in compartment comp [$m^3\cdot m^{-3}$];
- $\mathbf{RHO_{solid}}$: density of phase solid [$kg\cdot m^{-3}$];
- $\mathbf{F_{water,comp}}$: fraction of phase water in compartment comp [$m^3\cdot m^{-3}$];
- $\mathbf{RHO_{water}}$: density of phase water [$kg\cdot m^{-3}$];
- $\mathbf{RHO_{comp}}$: 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:

- $\mathbf{RHO_{susp}}$: bulk density of wet suspended matter [$kg\cdot m^{-3}$], default value is 1150;
- $\mathbf{RHO_{sed}}$: bulk density of wet sediment [$kg\cdot m^{-3}$], default value is 1300;

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.

$$K_{p,comp}=F_{OC,comp}\cdot K_{OC} \quad \text{with comp} \in \{\text{sed, susp}\}$$

Explanation of symbols:

- $\mathbf{K_{OC}}$: partition coefficient between organic carbon and water [$L\cdot kg^{-1}$];
- $\mathbf{F_{OC,comp}}$: weight fraction of organic carbon in compartment comp[$kg\cdot kg^{-3}$];
- $\mathbf{K_{p,susp}}$: partition coefficient between solid and water in suspended matter [$L\cdot kg^{-1}$];
- $\mathbf{K_{p,sed}}$: partition coefficient between solid and 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 partitioning coefficient in $(mg{\cdot}m_{comp}{}^{-3})/(mg{\cdot}m_{water}{}^{-3})$, can be derived from the definition of the sediment in the two phases:

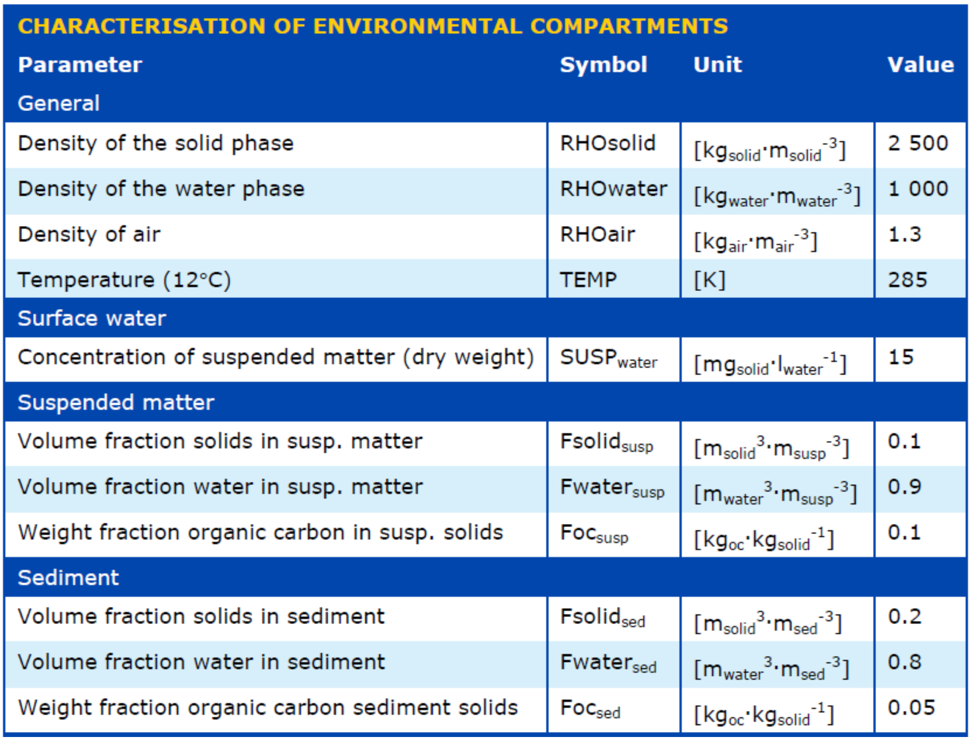
$$K_{comp,water} = \frac{C_{total,\ comp}}{C_{porewater,\ comp}}$$

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

Explanation of symbols:

- **$F_{water,comp}$**: fraction water in compartment comp $[m^3{\cdot}m^{-3}]$;
- **$F_{solid,comp}$**: fraction solids in compartment comp $[m^3{\cdot}m^{-3}]$;
- **$F_{air,comp}$**: fraction air in compartment comp $[m^3{\cdot}m^{-3}]$, only relevant for soil;
- **RHO_{solid}**: density of the solid phase $[kg{\cdot}m^{-3}]$, default value is 2500;
- **$K_{p,comp}$**: partitioning coefficient between solids and water in compartment comp $[L{\cdot}kg^{-1}]$,
- **$K_{soil\text{-}water}$**: soil-water partitioning coefficient $[m^3{\cdot}m^{-3}]$;
- **$K_{susp\text{-}water}$**: suspended matter-water partitioning coefficient $[m^3{\cdot}m^{-3}]$;
- **$K_{sed\text{-}water}$**: sediment-water partitioning coefficient $[m^3{\cdot}m^{-3}]$;
- **$K_{air\text{-}water}$**: air-water partitioning coefficient $[m^3{\cdot}m^{-3}]$;

Table 1. Default values for environmental compartments



CHARACTERISATION OF ENVIRONMENTAL COMPARTMENTS			
Parameter	**Symbol**	**Unit**	**Value**
General			
Density of the solid phase	RHOsolid	$[kg_{solid}{\cdot}m_{solid}{}^{-3}]$	2 500
Density of the water phase	RHOwater	$[kg_{water}{\cdot}m_{water}{}^{-3}]$	1 000
Density of air	RHOair	$[kg_{air}{\cdot}m_{air}{}^{-3}]$	1.3
Temperature (12°C)	TEMP	[K]	285
Surface water			
Concentration of suspended matter (dry weight)	$SUSP_{water}$	$[mg_{solid}{\cdot}l_{water}{}^{-1}]$	15
Suspended matter			
Volume fraction solids in susp. matter	$Fsolid_{susp}$	$[m_{solid}{}^{3}{\cdot}m_{susp}{}^{-3}]$	0.1
Volume fraction water in susp. matter	$Fwater_{susp}$	$[m_{water}{}^{3}{\cdot}m_{susp}{}^{-3}]$	0.9
Weight fraction organic carbon in susp. solids	Foc_{susp}	$[kg_{oc}{\cdot}kg_{solid}{}^{-1}]$	0.1
Sediment			
Volume fraction solids in sediment	$Fsolid_{sed}$	$[m_{solid}{}^{3}{\cdot}m_{sed}{}^{-3}]$	0.2
Volume fraction water in sediment	$Fwater_{sed}$	$[m_{water}{}^{3}{\cdot}m_{sed}{}^{-3}]$	0.8
Weight fraction organic carbon sediment solids	Foc_{sed}	$[kg_{oc}{\cdot}kg_{solid}{}^{-1}]$	0.05

9.2 PRACTICAL EVALUATION

STEP 1. Check the $K_{sed\text{-}water}$ and/or 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 (comparison to EQS limit value) of bottom sediment quality only for those substance which have a log K_{OC} or **log K_{OW} of ≥3** value (hydrophobic substances that tend to be associated with sediment). For substances having a log K_{OC} or **log K_{OW} of <3** value, evaluation should be limited to the water dissolved concentration.

STEP 3. If bottom sediment EQS_{BS} limit values are available (in your country's legislation):

3.1 Assure that the HS concentration measured in the collected bottom sediment sample ($C_{HS\text{-}BS}$) is representative for the bottom sediment EQS limit value used for sediment quality evaluation (comparison of $C_{HS\text{-}BS}$ and bottom sediment EQS limit value weather $C_{HS\text{-}BS} < EQS_{BS}$).
AND

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

STEP 4. If bottom sediment EQS limit values are 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, µg/L) using the equation below (EC 2018):

$$EQS_{BS}\ [\text{mg/kg ww}] = \frac{K_{\text{sed-water}}}{RHO_{\text{sed}}} \cdot EQS_{\text{water}} \cdot 1000$$

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

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

$$\mathrm{CONV_{sed}} = \mathrm{RHO_{sed}} \, / \, (\mathrm{F_{solid,\,sed}} \cdot \mathrm{RHO_{solid}})$$

$$QS_{\mathrm{sediment,EqP,dw}} = CONV\mathrm{sed} \times QS_{\mathrm{sediment,EqP,ww}}$$

where:

- **EQS$_{BS}$**: estimated environmental quality standard for water referring to the HS concentration in bottom sediment according to the EU TGD (EU, 2018),
- **EQS$_{water}$**: environmental quality standard for water referring to the HS concentration,
- **K$_{sed\text{-}water}$** [m^3 pore water/m^3 sediment]: substance- and site-specific partition coefficient for bottom sediment–pore water
- **RHO$_{sed}$** [kg wet sediment /m^3 wet sediment]: bulk density of wet sediment,
- **1000**: conversion factor from m^3 to litre,
- for estimating the conversion factor (**CONV$_{sed}$**) between wet and dry weight:
    - **F$_{solid,\,sed}$** [m^3 solid content of sediment / m^3 wet sediment]: fraction solids in bottom sediment,
    - **RHO$_{solid}$**: [kg solid content of sediment /m^3 solid content of sediment] density of the solid phase of the bottom sediment.

AND

4.3 Derive input parameters as follows:

- **EQS$_{water}$**: 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 µg/L).
- **K$_{sed\text{-}water}$**: 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**.
- **RHO$_{sed}$**: 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$_{solid,\,sed}$**: 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**.

- **RHO$_{\text{solid}}$**: (1) value can be derived from current measurement in the bottom wet sediment, or (2) from long-term region- or site-specific measurements (or can be estimate from literatures) in the bottom sediment, or (3) **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:

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

where:

- **C$_{\text{porew,sed}}$** is the measured concentration in pore water of sediment [mg HS / m^3 pore water],
- **C$_{\text{total,sed}}$** is the measured concentration in wet sediment [mg HS / m^3 wet sediment].

OR

4.5 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:

$$K_{\text{sed-water}} = F\text{water}_{\text{sed}} + F\text{solid}_{\text{sed}} \times \frac{K\text{p}_{\text{sed}}}{1000} \times RHO\text{solid}$$

where:

- **F$_{\text{solid.sed}}$** fraction solids in wet sediment, see above,
- **F$_{\text{water.sed}}$** fraction pore water in wet sediment; value 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 = 0.8.
- **K$_{\text{p.sed}}$** partition coefficient solids-pore water in sediment
- **RHO$_{\text{solid}}$** density of the solid phase, see above.

Further K$_{\text{psed}}$ can be estimated using the equation below:

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

where:

- **$F_{oc, sed}$**: weight fraction of organic carbon in the bottom sediment; Foc_{oc} 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_{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

4.6 Compare the **HS concentration measured in the collected bottom sediment sample ($C_{HS\text{-}BS}$) to the estimated bottom sediment EQS limit value**. If $C_{HS\text{-}BS} < EQS_{BS}$ 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.

5.1 Compare the estimated $C_{HS\text{-}sediment,\ ww}$(estimated) value calculated according to the equation to the measured $C_{HS\text{-}sediment,\ ww}$(measured) by calculating the relative error as the ratio of the difference between the measured and estimated concentrations to their average, expressed in percent:

$$\text{RELATIVE ERROR [\%]} = \frac{C_{HS\text{-}sed,\ ww}(\text{measured}) - C_{HS\text{-}sed,\ ww}(\text{estimated})}{\frac{C_{HS\text{-}sed,\ ww}(\text{measured}) + C_{HS\text{-}sed,\ ww}(\text{estimated})}{2}} \cdot 100$$

If 10% relative error is acceptable, as usual, then if this value is below 5 it means that the relative error between the measured and estimated (modelled) values is ≤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 $C_{HS\text{-}sediment,\ ww}$ 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 PS/PHS 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 µm 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 $QS_{\text{HS-sediment, ww}}$ 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). In the selection and evaluation of HS, especially for metals, the geochemical background of the catchment must be taken into account.

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 $L\cdot kg^{-1}$ are not likely to be sorbed to sediment. Consequently, a log K_{OC} or **log K_{OW} of ≥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 ≥3** value.

11. TREND ASSESSMENT FOR SEDIMENT QUALITY

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 trends 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 trend analysis of those priority substances that tend to accumulate in sediment. The adequate sampling frequency is defined by the Nyquist frequency as discussed in the latter sections. According to WFD guidance documents, for the purpose of trend monitoring, bottom 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, when monitoring for temporal trends, sound statistical analysis will require several data points per year (EC 2010). In conclusion, sediment quality trend assessment at a surveillance monitoring site has to consider the following:

- what is ‘change’ (in natural and anthropogenic HS),
- what is ‘significant’ change,
- what is trend,
- how to detect and characterise trend.

11.1 WHAT IS CHANGE?

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 Δy is positive ($\Delta y > 0$, $y_2 > y_1$) then the y parameter value increases, if Δy 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** (Θ) is the change in parameter value (Δy) within unit time (Δt):

$$\Theta = \frac{\text{change in y}}{\text{change in t}} = \frac{\Delta y}{\Delta t}$$

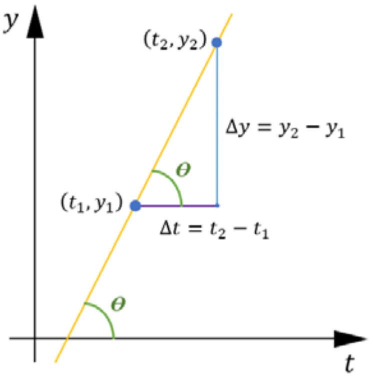


Figure 8. Change between the parameter (y) values of two successive observations is Δy which occurred within Δt time interval during monitoring. θ denotes the rate of change (Δy/Δt): the change in parameter value y within unit time (Δt).

11.2 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 signs + or – such as

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

or with 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 %:

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

11.3 WHAT IS SIGNIFICANT CHANGE: UNCERTAINTY, CONFIDENCE, AND THEIR CHARACTERISATION

Scientifically, significant change or significant difference between two measured values is any difference larger than the uncertainty of these two values. In other words, if these two values can be regarded different with a certain level of certainty (confidence).

All measured sediment quality parameters have inherent uncertainty. If the uncertainty of the measured values is characterised then it is possible to state if these values are significantly different or not.

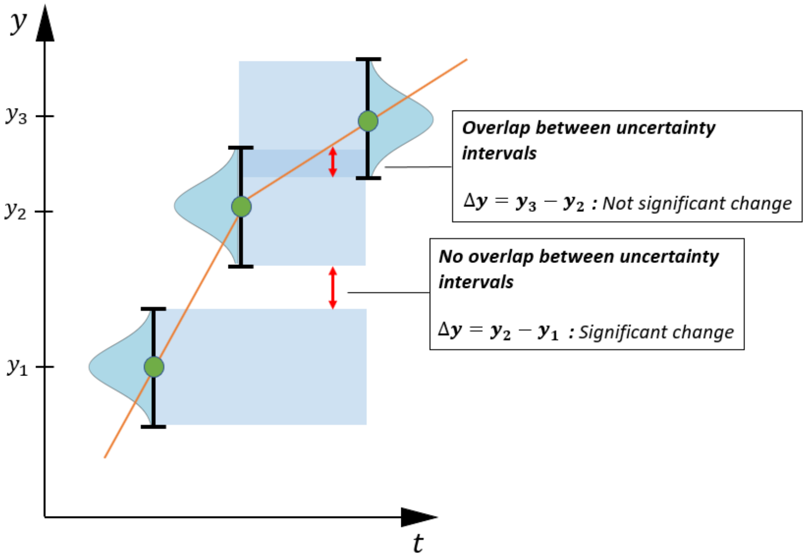


Figure 9. Significant change. Change between successive monitoring data is significant if the corresponding uncertainty intervals ('confidence intervals'; error bars) do not overlap at a defined confidence level (e.g. 95% confidence level).

Ways to state uncertainty

Let us call the result of measurement 'MEASUREMENT VALUE', and the error of the measurement 'UNCERTAINTY', then True Value of measurement is given as

True Value = MEASUREMENT VALUE ± UNCERTAINTY

There are 3 ways to state uncertainty:

- **absolute uncertainty**: UNCERTAINTY

- **fractional uncertainty**: UNCERTAINTY / MEASUREMENT VALUE
- **percent uncertainty**: UNCERTAINTY / MEASUREMENT VALUE · 100 (%)

EXAMPLE: Ways to state uncertainty

If the measurement result is given as 1563 ± 5 g, then

- the **absolute** uncertainty is 5 g
- the **fractional** uncertainty is 5/1563 = 0.003
- the **percent** uncertainty is 5/1563 · 100 = 0.3%

Deterministic uncertainty can be defined

1. for **single measurement,** by the measurement resolution (the smallest quantity that can be resolved):

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

so, the true value of the measured parameter can be estimated as

True value=measured value±smallest measurement unit

This means that the true value is somewhere within the interval

(measured value-uncertainty; measured value+uncertainty)

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 10**).

Figure 10. Uncertainty of measurement in the case of digital devices. Digital scale (left) and digital pH meter (right).

or

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

$$\text{Uncertainty}=\pm\frac{1}{2}(\text{maximum-minimum}).$$

The best estimate of the true value is given by the average of the repeated measurements:

$$\text{Best estimate of the true value}=\text{average},\ \bar{x}=\frac{1}{n}\sum_{i=1}^{n}y_i$$

where y_i is the ith repeated measurement value and n is the number of repeated measurements. Thus, the true value of the measured parameter can be estimated as

$$\mathbf{True\ value=average\pm\frac{1}{2}(maximum\text{-}minimum)}$$

This means that the true value is somewhere within the interval

(average-uncertainty; average+uncertainty)

In deterministic uncertainty, the probability of having the true value within the measured value/best estimate ± uncertainty is not specified. It is assumed that the true value falls within this interval with 100% probability (100% confidence). This means that any number of repeated measurement values are available, all will fall within the uncertainty interval. In this case, uncertainty is characterised by 2 numbers:

- measured value or the best estimate, and
- uncertainty.

The limitation of deterministic uncertainty is that it may give to big uncertainty interval. Also, in practice, we are often satisfied if the uncertainty interval (boundaries) is less confident, let’s say only 95% or even 90% confidence. This means that only the 95% (or 90%) of the repeated measurement values is expected to fall within the uncertainty interval.

Stochastic uncertainty is defined by the random distribution of the measured values. 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 within this interval is also given (this probability is called ‘confidence level’). In this case, uncertainty is characterised by 3 numbers:

- - best estimate, and
- - uncertainty,
- - confidence level.

Statistical uncertainty is most often given as multiples of the standard deviation (SD) (**Figure 11.**):

$$\text{Uncertainty}=\pm c\cdot \text{SD},$$

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

$$\text{Standard deviation, SD}=\sqrt{\frac{1}{n-1}\sum\nolimits_1^n (x_i-\overline{x})}.$$

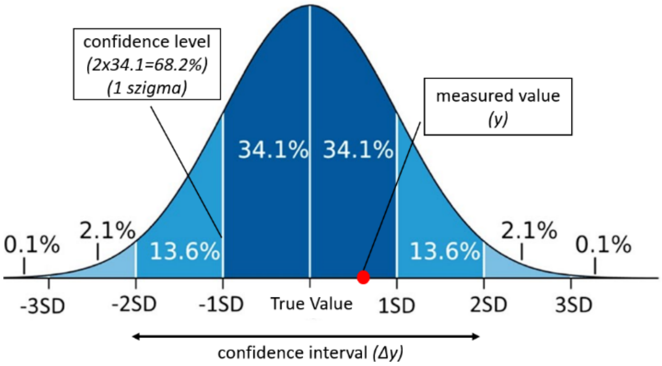


Figure 11. Stochastic uncertainty is given in terms of the confidence interval (uncertainty interval) and the confidence level associated with the confidence interval. SD: Standard deviation.

The true value is either known from some sources (e.g. concentration in standard material) or the best estimate of the true value is given by the average of the repeated measurements:

$$\text{Best estimate of the true value=average, } \bar{x}=\frac{1}{n}\sum_{i=1}^{n} y_i$$

where y_i is the ith repeated measurement value and n is the number of repeated measurements.

Thus, the true value of the measured parameter can be estimated as

$$\textbf{True value=average value} \pm c \cdot \textbf{SD},$$

This means that the true value is somewhere within the interval

(average-uncertainty; average+uncertainty).

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 12.**):

- $\textbf{LOD} = \pm 3 \cdot \mathrm{SD}$, where 3·SD corresponds to 99.73% confidence level,
- $\textbf{LOQ} = \pm 10 \cdot \mathrm{SD}$, where 10·SD corresponds to 99.9% confidence level.

For a blank material, the true value is zero. 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:

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

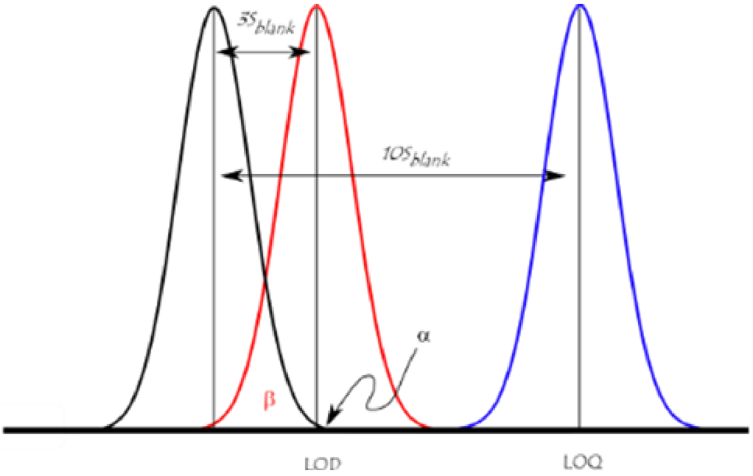


Figure 12. Statistical uncertainty shown by the limit of detection (LOD) and limit of quantification (LOQ).

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).

11.4 TOTAL UNCERTAINTY OF MONITORING 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 natural random variability of the HS concentration. These uncertainties are independent from each other; therefore, the total uncertainty (random variation) is the sum of each uncertainty:

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

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.

11.5 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 LOQ is not significant (**Figure 13.**):

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

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.

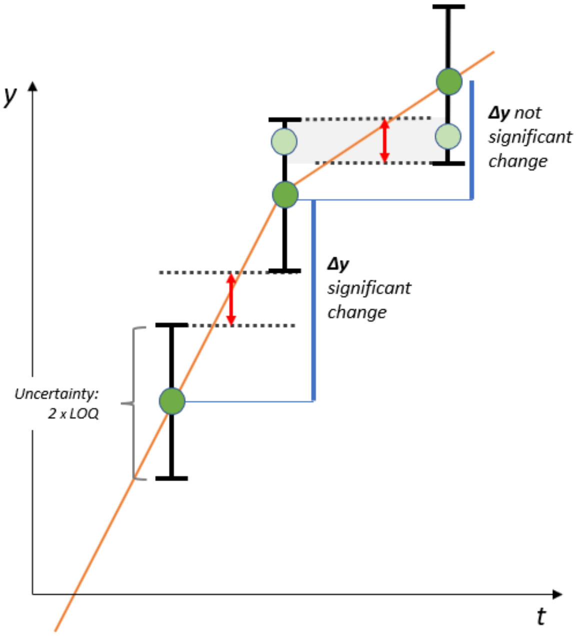


Figure 13. The change (difference; Δy, blue line) between the two successive measurements is significant between the first two points because their error bars (uncertainty intervals; measurement resolution: LOQ) do not overlap. However, the change between the next two points (Δy, blue line) is not significant because their error bars overlap (see red arrow). This means that there is chance that the two measurements are equal, as shown by the light green dots.

11.6 SIGNIFICANT CHANGE ALONG SUCCESSIVE MONITORING DATA POINTS: TREND ASSESSMENT

Three or more successive significant changes (increase or decrease) is called monotonous trend of three or more time-units. For example, if the sampling is monthly then three successive significant positive changes is called 'three months monotonously increasing trend'. The trend can be characterised by

1. Total rate of change given as

$$\text{Total rate of change} = \frac{\Delta Y}{\Delta T} \quad ,$$

or by

2. Least squares regression line (see below).

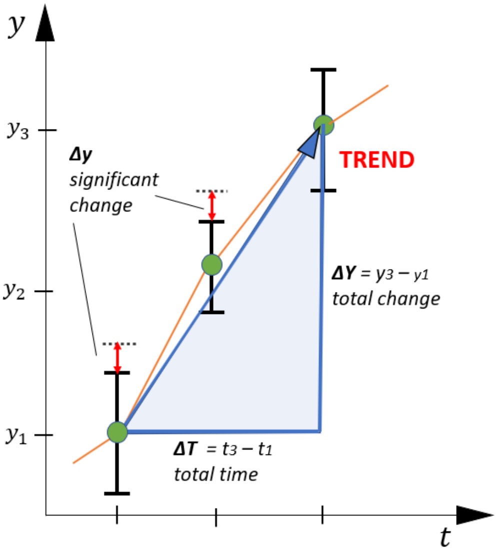


Figure 14. Trend along successive monitoring data points. The trend line is characterised the easiest by its slope: ΔY/ΔT (total change per total elapsed time).

11.7 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. This test compares two means from the measured data (called the empirical mean or the mean of the sample, each estimated by the averages) calculated and uses the standard deviations (SD) also calculated from the measured data (called the empirical standard deviation or standard deviation of sample).

If the test rejects the assumption that the two means are equal, e.g. at the usual 95% confidence level, then there is a (statistically) significant difference between the two annual averages. This can be conveniently visualised with box plots (**Figure 15.**):

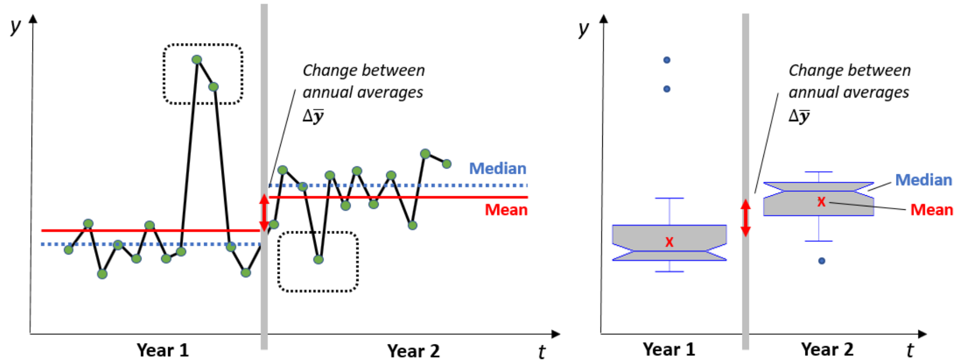


Figure 15. Left: Surveillance monitoring monthly time series of two successive years. Note the increase of the central value (both the median - blue dotted line and the mean - red solid line). Note the high and low outlier values emphasised with the empty dotted line frames. Red arrows indicate the difference between the annual averages. Right: Box plots of measured data for the two successive years. Red cross: average; blue line: median; Upper and lower box boundaries: upper quartile and lower quartile, respectively; whiskers: maximum and minimum values without outliers; outliers defined as data points lying more than 1.5 times the interquartile range (box width) above or below the box. Note the high and low outlier values. Red arrows indicate the difference between the annual averages.

Note that the mean (and the standard deviation) calculated from data are sensitive to outlying values as shown in **Figure 15**. This means that a few high outlying values can considerably increase or decrease 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 standard statistical software. The W-test result will show whether there are 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.

11.8 SIGNIFICANT CHANGE ALONG SUCCESSIVE MONITORING TIME INTERVALS: TREND ASSESSMENT

Three or more successive significant changes (increase or decrease) among the yearly means is called monotonous trend of three or more yearly means. The trend can be characterised by

1. total rate of change of yearly means (see Figure 14) given as

$$\text{Total rate of change of yearly means} = \frac{\Delta\bar{Y}}{\Delta\bar{X}} \quad ,$$

or by

2. lLeast squares regression line (see below).

11.9 SIGNIFICANT CHANGE ALONG SUCCESSIVE MONITORING DATA POINTS: LONG-TERM TREND ASSESSMENT

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 (**Figure 16**). Recognition and characterisation of such pattern in surveillance monitoring data is a subject of time series analysis (TSA). A time series consists of a set of sequential numeric data taken at equally spaced intervals usually over a period of time.

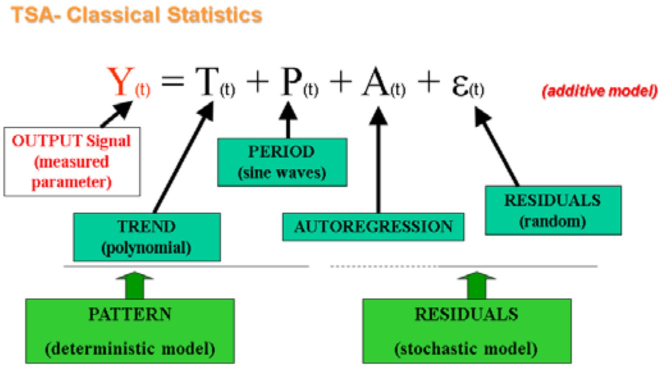


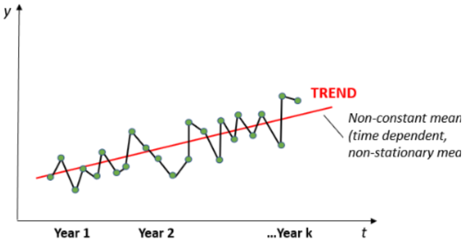
Figure 16. The basic components of classical monitoring time series analysis shown in the common additive model: trend (described with polynomial functions, mostly linear function), periodicity such as seasonality or diurnal cycles (described with sine waves), autoregressive component (correlation between successive data points; 'memory effect') and random noise (gaussian white noise).

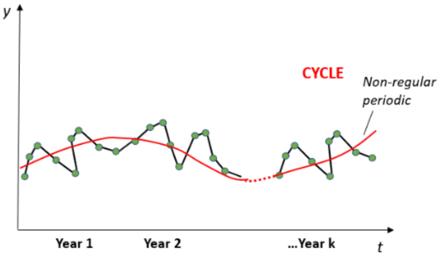
In practical surveillance monitoring observed data series may have further characteristics such as cycle and events (outliers or transients). The latter is particularly important because flood events or pollution events may provide the major load of HS contaminated sediment onto the biota receptors in the monitored surface water body.

Therefore, the surveillance sediment quality monitoring data series (measured HS concentration c(t)) is best represented as follows:

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

where measured HS concentration c(t) is additively decomposed into trend (T(t)), cycle (C(t)), periodicity (P(t)), autoregression (A(t)), white noise residuals (ε(t)) and events (outliers or transients; E(t)) (**Figure 16**).





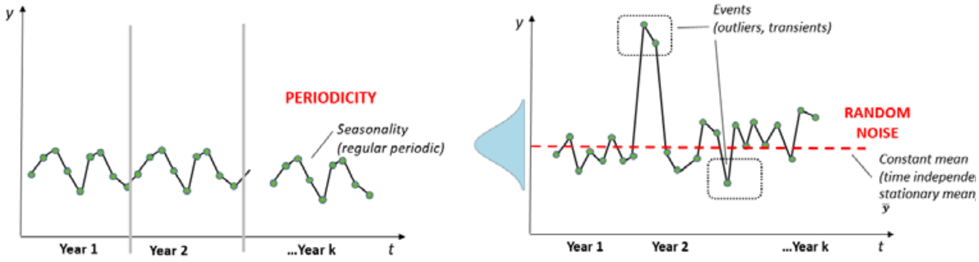


Figure 17. The various components of sediment quality monitoring time series: Trend, Cycle, Periodicity (e.g. seasonal, diurnal), Autoregressive component (memory effect) and random noise. Note that 'transients' such as outliers occur and are found in the random component.

Based on the above considerations, a complete and consistent procedure for the time series analysis of surveillance monitoring data is provided below. This example assumes regular monitoring data, preferably monthly sampling, which is available for several years.

First, a 3RSSH type nonlinear moving median smoother algorithm is used (it fits on 3 successive data points) (Tukey, 1977). 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, extreme high HS values of flood events, which are less representative for trend observation). The 3RSSH algorithm starts with a 3-point window moving median calculation then Resmooth (R) and Split (S) algorithm is applied twice. This process separates the series into 'smooth' (S1(t)) carrying pattern (cycle, trend, periodicity) and 'rough' or 'residual' (R1(t)) containing auto-correlation, noise and outliers:

$$\begin{aligned} c(t) &= S_1(t) + R_1(t), \\ S_1(t) &= T(t) + C(t) + P(t), \\ R_1(t) &= A(t) + E(t) + \varepsilon(t). \end{aligned}$$

All features or periods of time shorter than 3 time-units (3 months in case of monthly data) join the rough (R1(t); residuals) eliminating random noise and the outliers from the smooth (S1(t); pattern). 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' (R1(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 such as trend and periodicity. Autocorrelation is not studied for WFD surveillance monitoring data. Finally, the statistical distribution of the outlier-free noise is described by the standard summary statistics: the central value (mean estimated as the arithmetic average which is tested in turn if it equals to zero), and the variability (standard deviation).

Second, the ‘smooth’ (S1(t)) is processed to model trend, cycle and periodicity. In order to capture the seasonal periodicity in the 3RSSH smoothed data, the cycle and trend components are removed with a moving average smoother having the length of one year (12 months in the case of monthly data, i.e. 12+1=13 data points; the smoother has to have odd number of data points). In this way the 3RSSH ‘smooth’ (S1(t)) is further separated into a smooth containing the cycle and trend components (S2(t)) and a rough containing the seasonal periodicity (R2(t)):

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

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

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

Periodicity is analysed by a 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 are identified, periodicity is modelled by fitting sine waves to the data series (R2(t)) using 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 (S2(t)), the trend component is modelled by a simple linear least-squares regression line to S2(t). **This is the trend of the surveillance monitoring data series which was the main objective of the whole time series analysis.** In addition, 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 HS contamination trend can also be studied in the historic records of overbank (floodplain) sediment.

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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:
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