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Transnationally harmonized sediment sampling protocol for HSs in DRB's surface waters proposal

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1. Introduction

Sediments are a sink as well as a source of HSs in an aquatic environment. The HSs in sediments may represent risk to the environment and consequently they should be monitored. Monitoring of HSs includes sampling, chemical analyses and risk assessment of the sediments. The aim of this protocol is providing a proposal for sampling strategy of sediments in accordance with Water Framework Directive (WFD) which includes general consideration about different type of sediments deposited in river system, list of HSs for monitoring in sediment according to requirements of the Directive 2013/39/EU on environmental quality standards (EQS) in the field of water policy which amending Directives 2000/60/EC and 2008/105/EC, selection of sediment sampling stations, sediment collection, sampling equipment and transport of samples.

Over the years, monitoring has been carried out on the concentration of pollutants dissolved in water and in small degree in sediments. The environmental significance of sediment in water quality management was recognised recently. Chemical and physical analysis of sediments could serve as a tool for the monitoring of contaminants releases to a river or lake system. Sediments are used to locate historical or current sources of the pollution.

The Water Framework Directive, EQS Directives (2013/39/EU and 2008/105/EC) and CIS Guidance Documents 7, 19, 25, 27 recognised the general term *sediments*. This term was used to describe any kind of sediments deposited in river bed, floodplain or carried by water. Generally, four types of sediment: stream, bottom, floodplain and suspended sediment in a river systems and lakes are distinguished in various scientific studies. These sediments are deposited in the different areas of the river, and they are genetically, physically and chemically distinctive. The appropriate monitoring of HSs in sediment should take into account all these sediment types in order to investigate comprehensively in sediment-associated contaminants.

2. Definition and type of sediments for monitoring

The deposition of drainage sediment in a river environment takes place at the river bed (bottom sediments), at the river sides (bottom or stream sediments), on the river bank (floodplain sediment) and the particulate carried out in water (suspended sediment or suspended solids).

The Water Framework Directive and CIS Guidance Document No. 19, 25 and 27 are not specified different type of sediment. The general term - sediment is used in relation to the concentrations of the priority substances in surface water, sediments or biota.

There are series 5667 of the ISO standards prescribed for the sampling of water, but only two of them are focused on standard procedures for the collection of the sediments. ISO 5667-12:2017 Water quality -- Sampling -- Part 12: Guidance on sampling of bottom sediments from rivers, lakes and estuarine areas and ISO 5667-17:2008 Water quality -- Sampling -- Part 17: Guidance on sampling of bulk suspended solids (reviewed and confirmed in 2017). There are no nationally or internationally prescribed standards for the collection of different types of drainage sediment (stream/bottom, floodplain and suspended sediment).

ISO 6107-2:2006 standard defines the **bottom sediment** as "*solid material deposited by settling from suspension onto the bottom of bodies of water, both moving and static*". Bottom sediments consist of suspended material that has been transported by water and deposited on the river bed. These sediments comprise particulate matter terrestrial origin and substances precipitated from chemical and biological processes. Apart from geogenic origin of the particles is anthropogenic input through atmospheric deposition, runoff from land, or direct discharge into the water. Organic contaminants, metals, nutrients, sludge, industrial waste and other man-made material deposited in water become associated with particulates. These particulates then settle down and accumulate in the bottom sediments.

The **bottom and stream sediments** should be considered as synonyms in this protocol. The researcher use the term bottom sediment for the sediment settled down in bigger rivers or lakes and term stream sediments in small rivers for deposited fine material at the side of the river bed. Stream sediments are like bottom sediments deposited fine fraction of bed load material (silt, clay, sand). According to Geochemical Atlas of Europe - FOREGS stream sediment represent the small drainage basin (< 100 km^2). These sediments should be collected above streams confluence with the main channel of the large drainage basin (Salminen et al., 2005). Stream sediment is susceptible to anthropogenic contamination and represent situation of the upstream drainage basin.

According to the ISO 5667-17:2008 **suspended solids** are "solids with a diameter greater than 0,45µm 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".

The fine grained fraction (silt and clay) is transported in rivers in suspension, which concentration is mostly dependent on the rock and soil erosion and water velocity. The concentration of suspended sediments varies with changes of current velocity. Upstream are typically regions with high velocity flow of water and consequently high erosion so that the composition of river suspended sediment depends mostly of lithology. Downstream in lowland river with the slower flow, composition of suspended sediment are generally less influenced by parent material and more by anthropogenic input.

The definition **floodplain sediment**, like this of the stream sediments, is not given in any ISO standard. The suspended material is deposited onto active, regularly flooded floodplains and levees along rivers with variable water flow. The accumulated floodplain sediments show contamination over time of the drainage basin and therefore floodplain sediments are appropriate for monitoring in longer interval. The field manual for FOREGS atlas suggested sampling of floodplain sediment from the lowermost point of the larger drainage basin (area 1,000 – 6,000 km^2) to which the small catchments are connected (Salminen et al., 2005).

The suitability for monitoring different type of sediment is issue for discussion. The Fraunhofer Institute (2002) implied that suspended sediment is better for monitoring than bottom sediment since they show recent contamination and the bottom sediment show past pollution. Contrarily, Horowitz (1991) suggested that suspended sediments are more physical and chemical variable in comparison with bottom sediment, and the quantity of suspended sediment collected is not always sufficient for the required analysis and consequently bottom sediments are more suitable for monitoring.

2.1. Background value

More recently, as the variability of the natural geochemical background has become better known, it has been recognized that in order to identify and quantify anthropogenic pollution it is necessary to have a map of the geological and/or geochemical background.

The value of geochemical background is necessary to assess the current state of the possible pollution in sediments. Background value could refer to the concentration of HSs in drainage basin and concentrations of HSs should be at or close to background. Background value of anthropogenic substances (organic substances) should be zero.

The background value could be for the area define from earlier geological and geochemical investigations or determine by sampling sediment dating from pre-industrial time. For the floodplain sediment is the value at the deeper, natural level at the sampling site. The surficial floodplain is normally affected by recent anthropogenic activities, and may be contaminated. Deeper samples, which are optional sample media, normally show the natural background variation.

The EuroGeoSurveys Geochemical Atlas of Europe (FOREGS Atlas; Salminen et al., 2005) has provided the needed information about the geochemical background in natural soil, stream water, stream sediments and floodplain sediments. The geochemical background value from FOREGS atlas and/or some other relevant studies (local, regional) could be used as geochemical background for monitoring of the sediments. Additionally, for the floodplain sampling is advisable to determine background value at the sampling site by sampling deeper pre-industrial level of the river bank. The reliable assessment of the drainage basin contamination could perform by comparing pre- and post-industrial floodplain sediments.

3. Selection of compounds to be monitored in sediment

Not all substances should be monitored in sediments. The criterion for the selection of HSs to be monitored from EQS Directive for sediment and biota is their insolubility in water, tendency to accumulate in sediments or they are associated with pore water. Some chemical species become bonded in preference to small mineral particles and organic matter while some are incorporated in residual pore water (ISO 5667-12:2017).

In Guidance Document No. 27 (Updated version 2018) is prescribed: *"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 (Koc) of <500–$1000\ l\cdot kg^{-1}$ are not likely to be sorbed to sediment. Consequently, a log Koc or log Kow 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".*

Member States should arrange monitoring of HSs listed in Part A of Annex I that tend to accumulate in sediment and/or biota, giving particular consideration to the substances numbered (Directive 2013/39/EU, 2013):

- 2 (Anthracene);
- 5 (Brominated diphenylethers);
- 6 (Cadmium and its compounds);
- 7 (C10-13-chloroalkanes);
- 12 (Di(2-ethylhexyl)phthalate (DEHP);
- 15 (Fluoranthene);
- 16 (Hexachlorobenzene);
- 17 (Hexachlorobutadiene);
- 18 (Hexachlorocyclohexane);
- 20 (Lead and its compounds);
- 21 (Mercury and compounds);
- 26 (Pentachlorobenzene);
- 28 (Polyaromatic Hydrocarbons (PAH));
- 30 (Tributyltin compounds (Tributyltin-cation));
- 34 (Dicofol);
- 35 (Perfluorooctane sulfonic acid and its derivatives (PFOS));
- 36 (Quinoxyfen);
- 37 (Dioxins and dioxin-like compounds);
- 43 (Hexabromocyclododecane (HBCDD)) and
- 44 (Heptachlor and heptachlor epoxide).

In accordance with Article 4 of Directive 2000/60/EC Member States shell take the necessary steps to ensure that such concentrations do not significantly increase in sediment and/or relevant biota.

4. Selection of sediment sampling stations

The ISO standards ISO 5667-12:2017 and ISO 5667-17:2008 prescribed selection of the sampling station for bottom sediments and suspended sediments, respectively.

Depending on the objectives to be achieved the **ISO 5667-12:2017** Water quality — Sampling — Part 12: Guidance on sampling of bottom sediments from rivers, lakes and estuarine areas for choice of sampling stations prescribed the selection of the sampling site and then the identification of the precise point at the sampling site. The same procedures could be applied to the stream and floodplain sediment.

Site conditions for the bottom sediments sampling should meet the following requirements (ISO 5667-12:2017):

- Meteorological and climatic (e.g. temperature, precipitation, solar radiation);
- Hydrological (e.g. discharge, water depth, current, velocity);
- Geological (e.g. characteristics/composition/stratification of sediments, erosion);
- Biological (e.g. with reference to macrophyte accumulation).

Meteorological and climatic condition like low temperature, wind direction, storms, heavy precipitation could cause big waves, frozen water and therefore influence of sampling location. These conditions could impact at the proper work of instruments and the safety factors at the location. In consideration of hydrological situation sampling should provide in of low water level and with low flow rates. Geological background is very important and it is recommended to use prior knowledge or carry out a preliminary investigation using geological maps. Taking account the biological conditions the sampling should be in habitat layer, usually in the top 10 cm.

Guidance for selection of the suspended sediment sampling locations is given in the norm **ISO 5667-17:2008** Water quality — Sampling — Part 17: Guidance on sampling of bulk suspended solids:

- Sampling points should be representative for an extended section of the river;
- Sampling sites should consider the existing network of water-monitoring sites so that could be used related results;
- Location for sampling should be placed taking in account the sources of pollution;
- The sampling site has to have proper access to the water, a satisfactory site for the portable centrifuge, the protection of the sampling equipment from vandals;
- The knowledge of the tributary loadings;
- Collection of suspended sediment samples as far downstream as possible, but above confluence;
- There should be preliminary investigations at potential monitoring sites to determine representativeness of the sampling location;
- Suitable sampling points are often near bridges or gauging stations.

Recommendations for selection of sediment sampling stations for monitoring of sediment are given in Common implementation strategy for the Water Framework Directive (2000/60/EC), **Guidance document No. 25** on chemical monitoring of sediment and biota under the Water Framework Directive (EC, 2010). The sampling site should fulfil following conditions:

- Sampling sediments should perform at sites representative of the water body;
- There is no need for even distribution of sampling sites in a water body;
- Knowledge of hydrological and geo-morphological characteristics;
- Knowing the pollution sources from present or past industries;
- Acquaintance of earlier studies and current monitoring programmes;
- Conduction of a dedicated preliminary survey;
- Understanding hydrogeological conditions like that the tributaries often transport different material because they have different geological background;

- The sampling site should be located downstream of the discharges or the tributary confluence, at a point where complete mixing has been established;
- The sampling sites should not be placed in the mixing zones;
- Determination of sediment homogeneity.

The sediments are more heterogeneous than waters. Expected variance estimates could, perhaps, be extracted from similar ongoing monitoring programmes or, what is more reliable, be assessed from **a pilot project** using the same sampling strategy, sampling matrices etc., as the currently planned monitoring programme. The pilot project should test the homogeneity of a sampling area by setting one or more transects (according to the area extent), where five sampling points for each transect is selected. In each sampling point collect five or more independent surface sediment samples. Pooling of individual samples into one composite sample is not recommended in the pilot phase. The homogeneity check perform for the between-sample (between sampling points in transect) and the within-sample (within sampling points) variance, using an Anova/F-test. The whole transect should be considered as a single sampling site if the within-sample variance is of the same order as, or even exceeds, the between-sample variance. The homogeneity checked areas will serve for the identification of the sampling sites and the number of field duplicates.

The selection of the sampling site for the monitoring of the chemical contamination in suspended sediments in rivers and transitional waters (estuaries) should be in areas where the water flow is lower (in concave stretches of the river, in accumulation areas within estuaries), in natural estuaries and upstream of the tidal limit and in lakes and reservoirs away from the inlet of rivers.

The **Trans National Monitoring Network** (TNMN) in the Danube River Basin aims to contribute to the implementation of the Convention on Cooperation for the Protection and Sustainable Use of the Danube River (DRPC). Enforcement of the EU Water Framework Directive (2000/60/EC) in the TNMN has been completed in 2007. The revised TNMN for surface waters consists of following elements: (1) Surveillance monitoring I (Monitoring of surface water status), (2) Surveillance monitoring II (Monitoring of specific pressures), (3) Operational monitoring and (4) Investigative monitoring. Surveillance monitoring I and the Operational monitoring observe the status of surface water and groundwater bodies once in six years. **Surveillance monitoring II** is joint long-term monitoring of selected quality elements of all ICPDR Contracting Parties in order to control concentrations and loads of selected parameters in the Danube and major tributaries once per year. Surveillance Monitoring II network is based on the national monitoring networks and the activities are harmonized between all partners to achieve a maximum efficiency. Investigative monitoring is carried out if necessary and primarily it is a national task (ICPDR, 2018). 153 sites at 112 TNMN monitoring stations were monitored in the Danube River Basin in 2016 (some monitoring stations contain two or three sampling sites - left, middle and/or right side of the river). The data was collected from 74 sampling sites at 40 stations on the Danube River and from 79 sampling sites at 70 stations at the tributaries.

Selection of TNMN monitoring sites are filled the following criteria (ICPDR, 2018):

- The already monitoring sites which are also suitable long-term trend analysis:
  - Placed just upstream/downstream of an international border;

  - Located upstream of confluences between Danube and main tributaries or main tributaries and larger sub-tributaries;
  - Positioned downstream of the major point sources and
  - Posted to control important water uses.
- Sites relevant for assessing pollutant loads which are transferred across boundaries of Contracting Parties and are transported into the marine environment.

5. Sediment collection

The sediment collection as an important part of the sampling strategy is defined by the types of samples, sampling depth, sampling frequency, sediment fraction to be analysed and sample volume. Sampling procedure should be as much as possible in agreement with the requirements of the Water Framework Directive and in accordance with the relevant ISO norms.

5.1. Composite samples

Sampling composite samples is recommended to get representatives of larger area and to reduce analysis cost. According to the ISO 5667-12:2017 composite samples represent average regional distribution of the concentrations of chemical substances in the sediment and is defined as *"two or more samples or subsamples mixed together in appropriate known proportions, from which the average result of a designed characteristic may be obtained (Note 1 to entry: The individual portions may be derived from the same unit (stratum) or at the same sediment depth below a certain interface. The use of subsamples from the same stratum is limited to situations where a natural mixing of strata is unlikely to have occurred or where the depth of the sediment stratum is sufficient to allow subsampling without artificial mixing during sample operations. Therefore, subsampling from different strata is allowed in relation to the objective of the investigation.)"*

Sampling the composite samples of **bottom sediment** is prescribed in the standard ISO 5667-12:2017. The composite samples should be prepared from equal volumes of homogenised single samples. The subsamples should be taken from the same geological unit. The penetration depth by a grab system sampling is variable and therefore not suitable for making a composite sample in monitoring. The use of grab sampler is not recommended for monitoring purposes since the penetration depth vary with each sample. The core system is more suitable for sampling from the same depth. The composite samples should be prepared in a separate location to avoid risk of contamination. It is advisable to take sample at the location without foreign matter (e.g. pieces of wood, scrap metal, plastic parts) or if it impossible then these matter should be rejected. Sample for the different analyses should be divided on-site into suitable containers. Preparation of composite samples should be preceded with the use of nitrile gloves.

The handling with the **stream sediment** (in the context of the small river and catchment area) and **floodplain sediment** samples should be in accordance with the ISO norms applicable to the sampling bottom sediment. According to the FOREGS, it is recommended to take 5-10 subsamples of the stream sediment in the river length 250 – 500m (Salminen et al., 2005). Composite sample for floodplain sediment should be made from 5 - 10 subsamples.

5.2. Sampling depth

The sampling depth appropriate for sediment monitoring is the top layer with the recently deposited material and newest status of pollution.

According to CIS Guidance Document No. 25 the top layers are the habitat of benthic organisms and they are sources of food (the protection of ecosystems is the main aim of WFD), they are result of deposition of particulate matter and biological mixing (bioturbation).

The thickness of the top layer is variable; it is usually restricted in most areas to the top 5–10 cm and depends of the deposition rate at the sampling site.

The sampling depth for the **bottom/stream** sediment depends on the deposition rate: in steady sedimentation and undisturbed sediments (lakes) are from 0.5 to 1 cm depth range, in environment where is variable sedimentation it is recommended to sample the top layer of the sediment, from 1 to 5 cm depth range and in highly perturbed sediment or in large fast flowing rivers, more than 5 cm. In accordance with the CIS Guidance Document No. 25 is suggested: *"The sampling depth should be defined for each sampling site."*

The recommended sampling depth for the **floodplain** sediment sampling is 0 – 25cm and this depth range was prescribed in the FOREGS atlas (Salminen et al., 2005).

5.3. Sampling frequency

Sediment sampling frequency should be as much as possible in agreement with the requirements of the Water Framework Directive. In compliance with the prescribed rules of the **ISO 5667-12:2017 ISO 5667-17:2008** the frequency of systematic sediment sampling should take in account seasonal variation, flow extremes like flooding (avoid sampling during or shortly after flooding), result in bed transport and lead to intrusion or washout of inorganic and organic fine material. The changes in sediment are slower than those observed water and for detection any changes in sediment demands longer period. The sampling frequency could be increased in order to detect any variation in sediment.

Directive **2013/39/EU** regulate that monitoring *"should be adapted to the spatial and temporal scale of the expected variation in concentrations"*. In this directive in Article 4 is prescribed spatial monitoring for substances for which is an EQS for sediment and/or biota applied that Member States should monitor at least **once a year**. The sediment is suitable matrix for temporal monitoring and in the directive is given proposal of an interval of **three years** for a long-trend monitoring. Both intervals could be changed if technical knowledge and expert judgement validate another interval. According the WFD reporting cycle is **six years** for temporal trend monitoring, but for the first WFD cycle monitoring is recommended to sample annually to have reliable statistical certainty and then reduce the frequency.

Frequency of the **Surveillance monitoring II** in the Trans National Monitoring Network in the Danube and major tributaries is provided once per year.

The recommendation the frequency of monitoring stream and bottom sediment in SIMONA project is in conclusion with the above WFD and EQS directives, ISO 5667-12:2017 and ISO 5667-17:2008 standards and Surveillance monitoring II in TNMN is **once per year and every three years for trend monitoring**.

The proposal for the frequency of monitoring for floodplain sediment is every **six years**. This interval fits with the six-year cycles suggested by WFD directives.

The monitoring of suspended sediment is recommended **four times per year**.

5.4. Fraction to be analysed

Particle size is one of the most important properties of sediment and the concentrations of metals increased with decreasing sediment particle size (Horowitz, 1991). According to Horowitz (1991) the sediment fraction >63µm should not be ignored in terms of its contribution to the amount of heavy metals concentrations in the sample even though the concentration of trace elements in fraction <63µm is significantly higher.

Usual trend reported in literature presents increasing metal concentrations with decreasing particle size. The clay and silt fraction (<63µm) absorbs and retains higher concentrations of heavy metals compared to the larger fractions and the dissolved concentration retained in the overlying water, however, high concentrations of heavy metals have also been reported in sand fractions (>63µm) (Lin et al., 2003). High concentrations of trace elements associated with large sediment fractions could have various origin: the agglomeration of smaller particles to form coarser, binding of fine fractions to the surface of larger particles, the presence of large grains from pre-existing rock, coarser forms created by binding high organic matter content and Fe/Mn content. Consequently the sediment monitoring using the <63µm particles could omit significant metal contribution from 63µm - 2mm.

A solution might be to carry out a **pre-sampling program** to study the physical characteristics of the sediment in particular river in terms of particle size, and determine the best method of sediment sampling. In rivers where the collection of the <63µm fraction presents is difficult because of gravel beds, the <2mm fraction could be sampled and this fraction used for sediment analysis. Certainly there are significant metal concentrations associated with this size fraction.

The importance of the coarser fraction of sediment is in addition to the biota. Although, the fraction of the <63µm particle size is the fraction that is a major source benthic organisms, the larger fraction is important as habitat for sediment dwelling organisms which are still exposed to contaminants.

Guidance Document No. 19 - Guidance on surface water chemical monitoring under the Water Framework Directive is suggested the use of the <63µm fraction should be analysed for metals and 2mm fraction of the sediment should be analysed for organic contaminants.

Guidance Document No. 25 is described „grain size is one of the most important factors controlling the distribution of natural and anthropogenic components in sediments, along with organic matter content". Therefore, it is recommended for the <63µm fraction (the clay-silt fraction, widespread in monitoring) or an alternative should be the normalisation to the <63µm fraction (to avoid the sieving and risk of contamination).

Considering different viewpoints the **fraction <63µm** is an acceptable compromise for monitoring programmes.

5.5. Sample volume

The collected sample volume should be sufficient to be preserved for all analyses, for quality control analyses and to prepare time-dependent composites (for example, of daily samples of sewage sludge could be produced a composite for monthly analysis) (ISO 5667-15:2009). Additionally sample volume is dependent on the (expected) concentration of the HSs (for organic micro-pollutants the sample volume should be larger than for trace elements), the amount of the fine fractions in which are mostly accumulated pollutants, the sediment porosity and required sample volume for archiving.

The precise calculation of the sample volume is very hard to get. Each chemical analyses requires a specific amount of sediment (considering adequate replicates, archive samples) and before sampling should be calculated the required volume of sediment per sample. The National Oceanic and Atmospheric Administration (NOAA) commonly sample 7-8 litters of sediment at each sampling site for numerous measurement and chemical analyses (Long et al., 1996). According to EPA for the biological, toxicological, and physicochemical analyses performed on sediment samples more than 10 litters of sediment from each site might be required (EPA, 2001).

Recommended sediment sample volume is about **7-8 litters** of sediment per sampling station. During monitoring the sample volume could be reduced or enlarged in accordance with local conditions at the sampling sites.

6. Sampling equipment

Sampling equipment depends on the type of sediment sample. There are common rules and equipment for sediment sampling in general. It should be noted that where the sampling device is made of metal then abrasion and chemical action, for example from sulphides and phosphates, may lead to specific contamination. In cases where sample equipment made from plastics is used, chemical residues may leach from the material into the sample, for example dispersants, or chemicals from the sediment may adsorb into the plastics. Quality control measures should be undertaken in full consultation with the receiving laboratory in order to establish the degree of influence of such effects on the survey results. Some study parameters (e.g. sulphides) may require to be maintained in an oxygen-free atmosphere. In such circumstances, storage and handling under an inert gas atmosphere may be needed. If it is necessary to maintain anaerobic conditions while handling samples, tools such as a glove box should be used. For samples whose measurements can be affected by exposure to oxygen, analysis should be performed as quickly as possible (ISO 5667-12:2017; ISO 5667-17:2008).

Important rules: All hand jewellery must be removed! Smoking is not permitted! All tools and containers must be free of contaminants!

The following sample equipment for all kind of samples (stream, bottom, floodplain and suspended sediments) will be necessary for proper sampling procedure:

- GPS, tablet with the maps or topographical maps for recording geographical coordinates of the sample site;
- Digital camera or tablet for required field photos;
- Permanent drawing ink marker;
- Kraft paper bags;
- Polyethylene bags;
- Strip-locks for the sample bags;
- Spoon, Scoop;
- Sieve set with two preferably wooden or plastic frames containing nylon 2.0 mm mesh and nylon 63µm mesh screens;
- Metal free plastic buckets or containers with lids;
- Plastic or heavy duty cardboard boxes for packing samples;
- Nitrile gloves;
- Printed field observation sheets.

Sampling the **bottom/stream sediment** sample settled in small water depths could perform an operator entering directly on foot into the water and using a scoop to collect sediment. During sampling procedures should be cautious not to mix different layers of sediment (ISO 5667-12:2017).

According to ISO 5667-12:2017, **bottom sediments** could be sampled by corer or grab system. Corer systems are more suitable for monitoring purposes since they do not disturb sediment layer and it is possible to take single samples (subsamples) to prepare one composite sample from the same depth. The detailed description of the corer systems are given in the norm ISO 5667-12:2017.

The sampling of **floodplain sediment** could be performed with the shovel, spade or scoop, dependably of the degree of sediment consolidation and intertwining of plant roots.

Sampling equipment for the **suspended sediments** should be in accordance with the norm ISO 5667-17:2008 for Water quality — Sampling — Part 17: Guidance on sampling of bulk suspended solids:

- The continuous-flow centrifuge types include three types of centrifugal samplers multi-chamber, multi-disc, and single-chamber tubular bowls;
- Sedimentation tank (stationary);
- Sedimentation box (in situ);
- Floating collector (BISAM);
- Plate sediment trap;
- Flask sediment trap.

7. Field observation sheet

The field observation sheet depends on the objectives of sampling (ISO 5667-6:2014; ISO 5667-12:2017). The objective of monitoring is sampling at a specific location over time.

Samples should be labelled at the time of collection and before going on to the next sampling site. The sample numbers (sample unique identifier - ID) will be alphanumerical:

- A three or two digit code identifying the country of origin;
- A two-digit sample number;
- A code identifying the sample type (SS for Stream sediment, BS for bottom sediment, FS for Floodplain sediment FS and SPM for suspended sediment (suspended solid matter)).
- Duplicate samples identified by the same sample number as original with an additional "D" at the end of the number.

Identification of samples should be waterproof. A unique identifier with the date, time and location of sampling should be labelled at the sample container.

In the field observation sheets each sample has to contain minimum following information (ISO 5667-15:2009; ISO 5667-6:2014):

- To register the exact sampling point locations, it is recommended to use Global Positioning System (GPS) technology (ISO 5667-12:2017);
- The name of a river or stream;
- Information on sampling at specific locations (bridge, in stream, from the bank) (ISO 5667-6:2014);
- A description and disposition of sample;
- Details of preservation and sample storage used;
- Any other information as necessary (about storage, ;
- The temperature of the sample should be measured on site and recorded;
- The temperature of cooling device for storage and transport sample should be recorded any deviations from standard protocols;
- Anything noted by the sample collector that can have potentially influenced the sample (e.g. dust in air, fish spawning, nearby traffic);
- The name of the person who provide sampling;
- The date of sampling.

The proposed field observation sheet for SIMONA project is given in **Appendix 1**.

8. Wet – sieving in the field

A wet sieving immediately after sampling at 2mm is necessary to eliminate detritus and benthic organisms and to avoid that organic material degrade and become part of the sediment sample. Performing further wet sieving procedure to separate the fine-grained silt + clay fractions, <63µm. Wet sieving re-suspends fine fraction bond to coarser fraction in the sediment sample. Water from the sampling site should be used for sieving as it reduces the risk of leaching or contamination. The fine fraction remains after sieving deposits in water. Water used for sieving should be reused for sieving subsequent batches (OSPAR, 2018). Sieved fine fraction should be homogenised.

9. Transport

After sampling, all samples are stored in plastics (e.g. PE (polyethylene), PTFE (polytetrafluoroethylene), PVC (poly(vinyl chloride)), PET (poly(ethylene terephthalate))), glass or borosilicate glass (ISO 5667-15:2009).

The temperature of the sample, especially of sludge samples, can influence the properties of the sample. Therefore, the initial temperature of the sludge samples should be measured on site and recorded (ISO 5667-15:2009).

Samples stored in air-sealed transparent polypropylene bags or bottles should be stored in a refrigerator at a temperature between 2 °C and 8 °C. If the temperature of the refrigerator is not appropriate, the laboratory should determine how affects this on the samples and/or the results of the analyses (ISO 5667-15:2009).

According to recommendation of Guidance No. 25, samples are transferred into dark glass bottles for organic analysis or into plastic bags or bottles for trace element analysis. Sampling containers should be filled to the top (minimal headspace) to reduce the likelihood of oxidation and loss of acid volatile sulphide (AVS) during transport. Samples should store in a refrigeration (about 4°C) and transport as soon as possible to the laboratory.

If the monitoring programme requires analysis of the fine sediment fraction, the sample should be split using appropriate sieving techniques (ISO Standard Series 5667, Part 12, 15 and 19; OSPAR, 2018).

10. Quality control

Quality control (QC) appropriate measures assure the quality of results. QC techniques include training, equipment calibration and recording of data (ISO 5667-14). The field QC include sampling of the quality control samples such as field duplicates, field replicates, and field blanks.

Collecting **field duplicates** is part of a comprehensive QC. These samples should be collected at the same time, using the same sampling method and type of equipment. They should be sieved, transported and archived in the manner as original samples. Field duplicates have to be collected at 5-10 % randomly selected sampling points throughout investigated area. These samples are used to measure spatial variability within the sampling area. An assessment of the field variability is particularly important in monitoring programs when the sampling has to be repeated a number of years to detect any changes over longer period (Reimann et al., 2008). The precision of field duplicates can be estimated as those of the analytical duplicates by the formula CV (%) = (SD / X) * 100, where CV is Coefficient of the Variation of the result; SD is Standard Deviation and X is Mean.

Field replicate is a split of the already collected sample. The collected sample should homogenise and after mixing divide into two samples: original and its replicate. The replicate is using for assessing sample handling variability i.e. to determine sediment heterogeneity within a single collected sample, to check sample preparation techniques, laboratory analytical variability and comparison of different laboratory results. It is recommended to sample 5-10 % of the field replicates.

Field blanks are samples of uncontaminated silica sand sampled using the same sampling equipment and procedure as for the sediment sampling. The field blank samples are used to point out that relevant concentration of HSs are not enter into the samples from sampling equipment or during sample handling. Usually 5 % samples are blanks.

11. Safety

Safety should always be a priority. Sampling should be undertaken considering the safety factors influenced by weather conditions, local conditions and experience of local tides and local safety regulations.

General safety precautions are given in ISO 5667-1:2006 Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques. They include precautions to avoid inhalation and ingestion of toxic gases and materials through the nose, mouth and skin. Staff responsible for carrying out sampling should be informed about safety measurements according to the national and/or regional health and safety regulations.

Precautions due to climatic conditions include wearing life jackets and lifelines, before sampling from ice-covered waters, checked the ice, and checked underwater breathing apparatus or other diving equipment. Equipment used for sampling (boats or platforms) should be in a stable condition and appropriate signal should be given to commercial ships and fishing vessels.

Sampling from unsafe sites should be avoided or if this is not possible, the sampling should be conducted by a team not by a single person. Sampling from bridges should be preferred then bank sampling. Safe access to sampling sites in all weather conditions is crucial for monitoring (ISO 5667-12:2017).

12. Reference

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Appendix 1

Field observation sheets in accordance with ISO 5667-6:2014 and ISO 5667-12:2017

Project:
Sample identifier (ID):
Sample location description with specific information (bridge, high power electric lines, railway line, major road, natural park, …) (provide map on opposite side):
The name of river or stream:
River width estimated value (m)
Depth of water – estimated average depth (m)
Flow rate – estimated value (m/s)
Geology and background value:
Latitude:
Longitude:
Weather conditions: □ sunny □ cloudy □ changeable □ rainy □ hot □ frosty
Sediment collection information:
Water depth above sample:
Sediment sample depth:
Collection device: Scoop ______ Corer ______ Other ______
Sample type: Composite – Number of subsamples: ______
Sample replicate collected? YES or NO
Replicate ID/name:
Sample duplicate collected? YES or NO
Sample information:
Temperature
Sediment pH (undisturbed)
Sediment pH (post-homogenization)
Colour (Munsell soil colour chart number):
Texture (particle size description):
Odour: □ none □ light □ strong □ earthy □ mildewed □ putrid □ farm slurry □ fishy □aromatic □ sewage □ fuel/oil
Sample photograph identification
Information on sediment components (seashells, animals, peat, wood, tar, stones, waste, plastics, etc.) ____
Additional comments:
Collection date: Collection time:
Sampler/signature: