



# Observations and comments for Transnationally harmonized sediment sampling protocol for HSs in DRB's surface waters proposal

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management

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### Appendix 1 Comments\_IGR\_for\_deliverable\_D431

The observation notes of the D 4.3.1 Observations and comments for Transnationally harmonized sediment sampling protocol for HSs in DRB's surface waters proposal are presented per chapters.

#### 1. Observation of Introduction

**HGI-CGS added:** "Fluvial systems can be strongly influenced by human activity, acting as and/or carrier of pollutants and become a source of pollution if environmental conditions change. The transport of PTEs and POPs depends on topography, oxic-anoxic conditions and kinetics of the sorption/desorption processes. Moreover, pH, salinity, and the presence of organic matter, clay minerals, sulphates, and carbonates also affect metal mobility in the sediments (bottom and stream sediments, suspended matter sediment, floodplain sediment). Sediments provide fine-scale information on the historical record of pollution in a watershed, and if the PTEs and POPs are attached to stored alluvium, it can turn from sink to source of pollutants for sediment interface, bioturbation and resuspension due in dredging or flooding (Audry et al., 2004).

In the introduction we already consider it is necessary to point out that that a sediment quality monitoring in accordance with the WFD requirements of the EU does not include floodplain sediments. The WFD refers to sediment quality in the river channel under non-flood conditions.

The appropriate monitoring of the HSs in sediment should take into account the stream/bottom and suspended sediments in order to investigate comprehensively in sediment-associated contaminants in the Danube river basin. As the WFD requirements do not include floodplain sediment, we recommend to sample this sediment type as an additional option or in a later follow-up project."

**Kata Dudás remarks**: "We should define, what are we talking about. priority substances + priority hazardous substances (WFD annex X list), shortly: PS/PHS. We called them HS in the AF for the DTP monitoring committee. But now we talk to the scientific TG and authorities. So HS is not good."

"Missing: Why is it important to take samples in the harmonized way? Please search some text form AF for introduction, to justify the importance of the protocol." and "Maybe we should mention the IT tool, which will integrate the protocols, and the observation sheet."

JCI comment: "According to chapter INTRODUCTION: TO ALL COLEAGUES SOME GENERAL COMMENTS FIRST

1. We must also clearly define what is ment by sediments in the context of the WFD and this is not all that difficult since it is clear that the WFD refers to sediment quality in the river channel under non

flood conditions. In this context what we call floodplain sediments is not really considered as sediment in the context of the WFD. In the Danube basin, especially in the plains most of the floodplain is under intensive land use (often for agriculture, industry and commerce) and can be viewed as a source of pollution of sediments in the river channel, rather than a place where it is deposited and stored. The effects of this source are cought in samples downstream as the runoff during non flood conditions brings this pollution to the main river. I would therefor like to suggest that we make sure that floodplain sediments are not seen as a sediment component that is to be a part of a sediment monitoring system and process within the context of the WFD. Sampling floodplain sediments has a role to play only in the context of establishing reference (without the antropogenic influence) conditions in the basin but this is to be done as a part of the research survey and must include the dating of these samples so as to place them into a time reference and link to periods when there where no anthropogenic influences and this clearly is beyond the scope of the SIMONA Project. In fact, I suggest that what we call floodplain sediments should really be called alluvial deposits to differentiate it from the sediments in the context of the WFD. This is critical."

Concerning the sentence in the protocol: "This term was used to describe any kind of sediments carried by water or deposited in the river bed. Generally, three types of sediment: stream/bottom, floodplain and suspended sediment, in a river systems and lakes are distinguished in various scientific studies."

JCI comment: "This proves the point. The WFD refers to all kinds of sediment carried by water and deposited in the river bed and not in the floodplain. It is clear that thflood plain sediments (Alluvial deposits) are not seen as sediments by the WFD and we must accept this in our project as a given. This does not mean that we can not suggest that flood plains be considered for defining reference conditions as part of a separate project focused on this and appropriate sampling protocols can be considered within that project. In such a case sediment dating must be obligatory and protocols to ensure that sample representativeness for this is ensured developed."

Concerning the sentence in protocol: "The appropriate monitoring of the HSs in sediment should take into account all these sediment types in order to investigate comprehensively in sediment-associated contaminants."

**JCI comment:** "What benefit do we get from the sampling and analysis of floodplain sediments that we do not get from the sampling of bottom and suspended sediments? What additional information is there to be gained from the sampling of floodplain sediments? Requiring member states to sample more than is required to get the information that we seek will increase the costs of the monitoring program and could lead to its inefficiency."

**JCI comment:** "This sentence is not acceptable to us. Appropriate monitoring of HS to meet WFD requirements shall not include floodplain sediments. See earlier comments for justification of this. Floo plain sediments (alluvial deposits) can be a part of specific surveys and research projects but not part of WFD HS sediment quality monitoring activities and obligations. Appropriate formulation must be found to make this clear."

**HGI-CGS added** description of WP4 Activity 4.2 Developing transnationally harmonized sediment sampling and laboratory protocol for HSs from SIMONA project proposal (page 85):

"This activity will develop the sampling protocol for various fluvial sediments (bottom, suspended and floodplain sediment) which will be an evidence-based sediment quality sampling methodology including – but not limited to ..."

#### 2. Observation of Definition and type of sediments for monitoring

Concerning the sentence: "There are no nationally or internationally prescribed standards for the collection of all types of drainage sediment (stream/bottom, floodplain and suspended sediment) for the monitoring purposes."

**JCI comment:** "The ISO standards prescribe the methodology for the collection of bottom sediments as well as suspended sediments for the purpose of the determination of sediment quality. This determination of sediment quality is the essence of the monitoring programme itself as the changes in the quality are what we are aiming to track."

**JCI comment:** "This actually is not true. National and international standards do exist for soil and geological sampling and cover sampling of what we inappropriatelly floodplain sediments instead of alluvial soils or alluvial deposits. ISO 18400-101:2017 specifies the procedural elements to be taken in the preparation and application of a sampling plan. The sampling plan describes among other things what laboratory samples are to be taken, how they are to be taken and from where they are to be taken, in order that the objectives of the investigation programme can be achieved. The principles or basic rules outlined in this document provide a framework that can be used to

- produce standardized sampling plans for use in more regular or routine circumstances,
- incorporate the specific requirements of national legislation, and
- design and develop a sampling plan for use on a case-by-case basis.

ISO 18400-101:2017 is applicable to sampling of soil and soil material, more specifically, e.g.

- soil in the landscape,
- soil stockpiles,
- potentially contaminated sites,
- agricultural soils,
- landfills, and
- forest soils.

Ultimately, the sampling plan provides the sampler with detailed instructions on how sampling should be carried out.

Also as an example see <a href="https://www.alsglobal.com/-/media/als/resources/services-and-products/geochemistry/technical-notes/geochemical-soil-and-sediment-sampling.pdf" https://www.alsglobal.com/-/media/als/resources/services-and-products/geochemistry/technical-notes/geochemical-soil-and-sediment-sampling.pdf"</a>

Regarding the paragraph in the protocol: "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 km2) to which the small catchments are connected (Salminen et al., 2005)."

**JCI comment:** "The bottom sediments also show the accumulation of contaminants over time in the water body. Undisturbed samples have to be taken and different layers analysed."

**JCI comment:** "FOREGS PROJECT CONCLUDED: "Results show that the distribution patterns of both water and solid samples are related to such factors as large-scale tectonic provinces, geochemical variation of large lithological units, extension of the Weichselian glaciation, and contamination reflecting industrialized areas and regions of intensive agriculture."

The bottom sediments also show the accumulation of contaminants over time in the water body. Undisturbed samples have to be taken and different layers analysed. What is meant by appropriate for monitoring over longer time, 20 years, 100 years or more? WFD is all about protection and management of water status and planning with a planning framework of 6 year cycles and looking ahead no more than 20 years (it is already under review). Monitoring within the WFD is to serve the main objectives of the WFD and the Program of measures within each planning period (evaluating effectivness of the program of measures, trends in pollution etc) and what is suggested here is not

within the framework of the WFD. I agree with Markos comments regarding the added value of flood plain sampling as a part of WFD Sediment monitoring."

Relating to the paragraphs: "The suitability for monitoring different types of sediments 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. "

**JCI comment:** "I agree that it is subject for discussion and I agree with both authors. But consider what the purpose and objective of the WFD is and what the monitoring requirements as a function of this are. In summary both are needed, bottom sediments to show us what is coming from upstream and suspended sediment to tell us what is being transported downstream, in other words we can do the balance of what is coming to a water body from upstream, what is being deposited within the water body and what is transported downstream to the next water body while the difference will tell us if there is any generation within the catchment of the water body considered. (water body refers to the section of the river/stream as deliniated by each member state)!"

**HGI-CGS deleted:** "There are no nationally or internationally prescribed standards for the collection of all types of drainage sediment (stream/bottom, floodplain and suspended sediment) for the monitoring purposes."

**GBA rewrote** these chapters: "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~km2) to which the small catchments are connected (Salminen et al., 2005)."

into:

"The fine grained fraction (silt and clay) is transported by rivers as suspended matter, the amount or concentration of which is directly dependent on grain density / size and water velocity. Indirectly, it depends on rock and soil tpye and on erosion rates. The concentration of suspended sediments varies with changes of current profile and velocity. Upstream are typically regions with high velocity flow of water and consequently high erosion so that the natural composition of river suspended sediment directly reflects the lithology in the catchment area. Downstream in lowland river basins with large catchment areas, the natural composition of suspended sediment still reflects the parent material but the influence of individual lithologies can be distinguished less clearly. In both upstream and downstream areas, the concentrations of HSs in the sediment can be overprinted 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 record (historical) contamination within the drainage basin over time. Sampling the entire thickness of a floodplain will give an integral measure of the state of contamination. If individual flood (and depositional) events are sampled, historical time series can be established. Sampling of those deposits which predate industrial activities can reveal natural background values. In terms of monitoring frequency, longer intervals (i.e. only after mayor flooding events) are appropriate for floodplain sediments. 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 km2) to which the small catchments are connected (Salminen et al., 2005)."

GBA added paragraph: "In summary, the analysis of HSs in floodplain sediments will reflect natural background values and historical contamination, while the regular monitoring in bottom sediment will show baseline values and more recent contamination. The analysis of suspended sediment (especially during high flow events), as well as the occasional analysis of floodplain sediments (i.e. the deposits of the last mayor flood event), will reveal the current state of contamination including material from soil erosion."

**HGI-CGS added**: "In summary, both sediment types meet the monitoring requirements of the WFD for the determination of sediment quality. The bottom sediments characterise what is coming to a water body from upstream and the suspended sediments describe the transport of contaminants downstream to the next water body."

**SK-SGIDS** – remarks for discussion: "We agree with prof. Marjanovic - do not sample floodplain sediment.

*In the Application form, sampling is suggested as follows:* 

- 1x passive sampling
- 1x bottom/stream sediment
- 1x suspended sediment
- 1x surface water
- 1x biota

However, the protocol is focused only on stream sediment and suspended sediment (we propose to cancel floodplain sediment at all)."

GI-BAS added: "Floodplains act as a storage space or sediment sinks for alluvial sediments. While they are being stored the sediments may be reworked by fluvial, aeolian, biological and/or pedogenic agents, often over considerable periods of time. The stored sediments may subsequently be eroded and re-incorporated into the sediment budget of the drainage basin. Because of the protracted residence times of heavy metals within rivers and their floodplains, metal-contaminated sediments may act as major sources of future contamination (Goudie, 2006). These characteristics, the relatively ease of access and straightaway methods for sampling, make floodplain sediments a suitable media for monitoring river's environmental status.

For practical purposes fluvial deposits can be grouped into three major groups (Reineck and Singh, 1980):

- 1. Channel deposits formed mainly from the activity of river channels. They include channel lag deposits, point bar deposits, channel bar deposits, and channel fill deposits.
- 2. Bank deposits deposits formed on the river banks and produced during flood periods. They include levee deposits and crevasse splay deposits.
- 3. Flood basin deposits essentially fine-grained sediment deposits formed during heavy floods when river water flows over the levees into the flood basin. They include flood basin deposits and marsh deposits.

In some rivers, however, differentiation between bank deposits and flood basin deposits do not exist, and thus fluvial deposits can be differentiated into two groups: 1. Channel deposits and 2. Floodplain deposits (Reineck and Singh, 1980).

Generally, floodplain could be considered as the relatively flat area of land that stretches from the banks of the parent stream to the base of the valley walls and over which water from the parent stream flows at times of high discharge (Goudie, 2006). Floodplains are a characteristic trait of the mature and old stages of a river as opposed to the young stage that occurs in the mountainous regions (Reineck and Singh, 1980).

Defining the extent of a floodplain at a locality in terms of the area inundated in floods of particular return periods poses problems, since flooding frequency may be a restricting factor (Goudie, 2006). It has been suggested (Wolman and Leopold, 1957) that the active floodplain is the area subject to the annual flood (i.e. the highest discharge each year). Though this definition could be a subject of discussion, in terms of monitoring the river environmental status defining active and former floodplains (river terraces) is of high importance.

Considering all of the above, when choosing floodplain sediments for a monitoring media, fluvial subenvironments suitable for the purposes should be very carefully determined. For example, the approach of Reineck and Singh (1980) that combines bank and over bank deposits into the "floodplain" environment seems more appropriate for monitoring goals, bearing in mind that the multitude of processes, besides fluvial, that rework these sediments could overall alter the river's chemical print. Thus, the sediments deposited in the natural levees and the crevasse splays could be monitored and would present more realistic results about the quality of the water body, than marsh and flood basin sediments. The latter two sub-environments could be used for monitoring purposes with the precondition of sampling soon after the flooding event. Another reasonable sub-environment for sediment monitoring present the upper portions of the point bars, moreover that often levee deposits and the silty and clayey sediments of the upper sequences of point bars are difficult to be distinguished. As the frequency of flooding is a factor of very high importance for obtaining realistic results, the most suitable sites for monitoring of floodplain sediments are where floods are annual events (or at least occur at a frequency not lower than 2-3 years). Additional recommendations for choosing sampling sites for floodplain sediments are given below in section 4 of this document -Selection of sediment sampling stations.

Thus, bottom sediments seem the more appropriate media when it comes to the needs for long-term monitoring of sediments. Several reasons could be pointed out: 1) Bottom sediments are less chemically and physically variable compared to suspensions, as a result analyses of bottom sediments would give better perspective of the long-term changes in pollution; 2) Bottom sediments analyses, when suitable sampling equipment is usedsampled with suitable equipment, could give time-related changes in the quality of the water body; 3) Sampling of suspended sediments in amounts and manner suitable for analyses is a laborious task, demanding specific equipment and time, which

complicates periodical monitoring, and makes it largehighly impractical; 4) The amount of suspended sediments in small rivers is practically negligible, and the quality of the river sediments in such situations could be very well covered by monitoring stream sediments, i.e. recommendations for suspended sediments monitoring/sampling should be restricted to the lower parts of large rivers.

As a final remark, during the SIMONA project both bottom and suspended (where possible) sediments will be sampled and analyzed. After the testing of the protocols and after having results from the laboratory analyses further comments regarding the need of monitoring of suspended sediments could be given."

#### 2.1. Observation of Background value

**GBA** gave some suggestion for improving the explanation in the text.

HGI-CGS added: "Differentiating between geogenic and anthropogenic contribution to total concentration of PTEs and POPs in stream sediments and/or soils is fundamental in the quantitative assessment of pollution threats to ecosystem and human health (Albanese et al., 2007). Different terms and definitions applied to thresholds sometimes create ambiguity and inconsistency. Reimann and Garret (2005) discuss the terms 'geochemical background', 'threshold' and 'baseline' and their numerous definitions in literature. In Hawkes and Webb (1962) 'background' was defined as the natural concentration of an element in barren earth material. Many studies define background as the natural concentration of an element from parent material and natural processes combined with contributions from diffuse anthropogenic sources. Only Fabian et al. (2017) have found a new method for detecting and quantifying the diffuse contamination at the continental to regional scale based on the analysis of cumulative distribution functions. In the geochemical literature the term 'baseline' mostly defines the natural concentration of an element in stream or bottom sediments and soils with no human influence. The calculation of geochemical baselines is necessary to assess the current state of the environment and to provide guidelines and quality standards in environmental legislation and policy-making, and in environmental risk assessment. Thresholds are utilised to identify breaks in the data population, but they can also be defined as the upper limit of background variation (Reimann et al., 2005, 2017)."

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"One of the problems in determination of the extent and the source of pollution in river channel sediments, by means of trace element and organic compound concentrations, is to estimate natural background concentrations in the sediments, excluding anthropogenic influence. In general, the

overestimation of the anthropogenic contribution of a particular trace element in sediments is possible if the petrography and the origin of sediments are not taken into account."

Concerning the sentence: "Background value of anthropogenic substances (organic substances) should be zero. "

**JCI comment:** "I think it will be very difficult to obtain an absolute zero value of anthropogenic contaminants anywhere in the floodplain from post industrial deposits."

"If this is true one more reason not to do floodplain sediment (Aluvial soil or deposits sampling) since we have reference pre antropogenic conditions. I would use this as a justification for not including floodplain sediments in sediment monitoring protocols. If we want to reconstruct the history of pollution with HS than this is a different case but is this the purpose and scope of SIMONA."

Concerning the paragraph: "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."

**JCI comment:** "I agree but bear in mind that the background value does not change over time and thus should not be a part of the monitoring but of the once off research project. Within SIMONA this should be one of the findings wich should than lead for another and new project for establishing background values and an extensive research project on floodplain sediments as a medium to establish the background values and historical pollution trends."

Concerning the paragraph: "The EuroGeoSurveys Geochemical Atlas of Europe (FOREGS Atlas; Salminen et al., 2005) has provided needed information about 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 be performed by comparing pre- and post-industrial floodplain sediments."

**JCI comment:** "All correct but is this the objective of SIMONA? If we agree that it is, than our protocol must have 2 chapters (one dedicated to river sediments and to be used for WFD monitoring purposes and the other for floodplain sediments to be used for establishing background values for river

sediments). The problem is that you have said that for antrobogenic substances the background values should be set to 0 which is true for man made substances but than we have to decide what to do with those substances which are not man made such as Antracene for example which occurs naturally and is not necesserally connected to industrial activities but can be due to use of coal by ancient preinduustrial communities in the basin. I don't know what to do with this."

HGI-CGS moved text related to the floodplain sediments to Appendix 1 of the 4.1 Output Sediment quality sampling protocol for HSs.

"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 needed information about 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 be performed by comparing pre- and post-industrial floodplain sediments."

## 3. Observation of Selection of compounds to be monitored in sediment

**HGI-CGS added**: Nickel and its compounds, Arsenic and its compounds, Zinc and its compounds, Chromium and its compounds, Copper and its compounds from the List of Priority Substances for the Danube River Basin (ICPDR, 2003).

**Kata Dudás comment:** "This list is can be modify. But we don't want to modify the protocol. So it can be an Annex. Or just leave one note, that list can be modify."

#### 4. Observation of Selection of sediment sampling stations

**Kata Dudás comment** on the sentence: "Site conditions for the bottom sediments sampling should meet the following requirements (ISO 5667-12:2017):"

"these information should be exists? or these should be measure with sediment? requirements for what?"

**GI-BAS added:** "Some further criteria should be applied when choosing a sampling site for floodplain sediments.:

- 1) Distance from the river bed;
- 2) Frequency of flooding sites with frequent flood events are preferable;
- 3) Sites where floodplains are used for agriculture should be avoided;
- 4) Sites where there is a possibility of strong air pollution should be avoided;
- 5) Having in mind the ability of different plant species to extract certain chemical elements from the soils, sites where vegetation is missing or is scarce are preferable then thickly vegetated ones;"

#### 5. Observation of Sediment collection

Concerning the sentence in the protocol: "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."

JCI comment: "The sampling procedure MUST be in accordance with the mentioned documents and norms as I do not believe we have the authority to prescribe a methodology which isn't in accordance with ISO standards and the requirements of the WFD. We can add additional requirements but I do not believe we can remove any of the existing requirements. These samples need to be analysed by accredited laboratories and sampled by accredited samplers. For this to be the case, the samples MUST be collected completely in accordance with the requirements of the ISO standards."

#### 5.1. Observation of Composite samples

No comments.

## 5.2. Observation of Sampling depth

**GBA revised** the text: "In the FOREGS atlas (Salminen et al., 2005), the prescribed sampling depth for the floodplain sediment sampling was 0-25cm. This provides a comprehensive indication of the state

of contamination. However, separate sampling of individual flood events (e.g. the pre-industrial level (once) and the latest flood event (occasionally)) is preferable and results are more meaningful. In this case, sampling depth and thickness depend on the deposition rate. Geological experience is necessary to identify the sediment layer (depth interval) to be sampled."

### **5.3.** Observation of Sampling frequency

Comment on sentence: "Frequency of the Surveillance monitoring II in the Trans National Monitoring Network in the Danube and major tributaries is provided once per year."

**JUVS comment:** "as far as I know no sampling frequency for sediment has been defined, and concerning water sampling, monthly sampling is recommended in the TNMN manual (12 times a year), except for priority substances that can be done once during a 6 year planning cycle. This refers to water quality testing."

Concerning part of the sentence: "(avoid sampling during or shortly after flooding)",

**JCI comment:** "This is a key point, especially when discussing the sampling of floodplain sediments. It is important to note that the deposition of sediments on floodplains takes place during periods of high water flow, or as the name suggests floods, hence floodplains. The ISO standards clearly prescribe the sampling of sediments during low flow periods. Furthermore, the only sediments deposited on floodplains are sediments which are present during high water levels, the sediments carried during low flow periods do not get deposited on floodplains and therefor these sediments are not a realistic representation of the sediment quality."

**GI-BAS added:** "The recommended frequency for monitoring of suspended sediment is recommended four times per year. We don't see a reason why suspended sediments should be monitored in such high frequency, bearing in mind the inconvenience of sampling. We suggest the same monitoring frequency as bottom sediments – once per year and once every three years for trend monitoring."

#### 5.4. Observation of Fraction to be analysed

**GI-BAS comment**: "Considering the different viewpoints and recommendations of the CIS Guidances No. 19 and 25, the fraction <63  $\mu$ m is an acceptable compromise for monitoring programmes. Isn't it better to test both fractions in order to obtain information on how the geological background associates with the contamination =, especially for heavy metals?"

#### 5.5. Observation of Sample volume

**SGIDS** recommended sediment sample volume is about 7-8 litters of sediment per sampling station..... – based on the analyses, 2-3 litres should be sufficient amount.

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

**HGI-CGS added:** "The quantities of sediments that should be collected will depend on the analyses to be undertaken. Generally, 1 kg of sediment from each sample site should be sufficient for analyses of most contaminats (e.g., 350 g for organics, 50 g for metals and metalloids, 50-200 g for particle size and other physical properties). In addition, 2-3 kg may be required for bioaccumulation or toxicity test, and these sediment samples should be stored cold (not frozen)."

Concerning the sentence in the protocol: "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."

**JCI comment:** "Do we need such a large amount of sediment? As far as I am aware for the purposes of the analysis of the sediment quality in terms of HS's, only a few hundred grams are necessary. This is something which should be checked with the LAB WG. We need to remember that we are developing a sampling protocol only for the purposes of HS monitoring in sediments."

"The volumes given here are recommended for oceanographic work and are inappropriate for river environments. We do not need so much sample for the analysis. Also, for suspended sediments such volumes for are nearly impossible to collect."

Comment on the sentence: "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)."

**Kata Dudás comment** "In oceans the <63um has a bigger part then in rivers. If the <63um fraction is rare, they should take much more litters. In one HU project they take 30 litter / site."

6. Observation of Sampling equipment

**GI-BAS comment**: "Some kind of thermometer? – for measuring temperature of samples and water;

also pH strips, Eh meters? i. e. bottles are excluded as an option? when – in the field or at the

laboratory? we should state it to be clearly understood."

SGIDS comment on Sampling tools and equipment - "how do we get them? How do we harmonize

sampling tools, equipment and consumables in between partners? SK-SGIDS has 1500 EUR for

sampling consumables – in Slovakia it takes at least 3 months to make public procurement and the

result is not guaranteed – it means, if we make a deal on exact material, there is no guarantee we will

get the same.

Central harmonized shopping would be more effective in this case – is there any chance to reallocate

money to other project partners, who have more effective public procurement?

SK-SGIDS doesn't have any experience with passive sampling techniques, suspended sediment

sampling, biota sampling... How will be the sampling organized in the case that any partner is in the

same situation?"

HGI-CGS added: "stainless steel shovels and sieves (according to DIN 4188)"; "Tools for in situ

measurement (pH, temperature, electrical conductivity)"

Kata Dudás added: "SIMONA IT tool tablet/phone"

7. Field observation sheet

Comment on the sentence: "• To register the exact sampling point locations, it is recommended to

use Global Positioning System (GPS) technology (ISO 5667-12:2017);"

Kata Dudás comment: "how to deal with composit samples? We should register each subsampling

point coordinates. (In next year they should go to the same place for trendanalysis.)"

Kata Dudás added: "solid waste in the river"; "or SIMONA IT tool on tablet/phone." and "solid waste

in the river".

Programme co-funded by the European Union funds (ERDF, IPA, ENI)

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### 8. Wet – sieving in the field

Comment on sentence: "Water from the sampling site should be used for sieving as it reduces the risk of leaching or contamination."

**Kata Dudás comment:** "should not use any water for sieving! If necessary use the water part of the sample. And reuse, yes."

## 9. Observation of Transport

No comments.

### 10. Observation of Quality control

No comments.

## 11. Observation of Safety

No comments.

#### 12. Observation of References

References added in the Output 4.1 Sediment quality sampling protocol for HSs from HGI-CGS:

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Albanese, S., De Vivo, B., Lima, A., Cicchella, D. 2007. Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Italy). Journal of Geochemical Exploration 93, 21 –34.

Audry, S., Schäfer, J., Blanc, G., Jouanneau, J-M. 2004. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). Environmental Pollution, Vol. 132 (3), 413-426.

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- Reimann, C., Garrett, R.G (2005): Geochemical background Concept and reality. Science of the Total Environment, 350 (1-3), 12-27.
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Observation of Appendix 1 - the Appendix 1 was written:

Recommendations of the SIMONA project: Monitoring active floodplain sediment

Authors: Sebastian Pfleiderer (AT-GBA), Ajka Šorša (HR-HGI-CGS), Milena Vetseva (BG-GI-BAS)

In various scientific studies of river systems and lakes, there are generally three types of sediments that can be distinguished: stream/bottom, floodplain and suspended. The deposition of floodplain sediments in a fluvial environment takes place outside the river bed during overbank flows. For practical purposes fluvial deposits can be grouped into three major groups (Reineck and Singh, 1980):

• Channel deposits - formed mainly from the activity of river channels. They include channel lag deposits, point bar deposits, channel bar deposits, and channel fill deposits.

Bank deposits - deposits formed on the river banks and produced during flood periods. They
include levee deposits and crevasse splay deposits.

• Flood basin deposits - essentially fine-grained sediment deposits formed during heavy floods when river water flows over the levees into the flood basin. They include flood basin deposits and marsh deposits.

In some rivers, however, differentiation between bank deposits and flood basin deposits does not exist, and thus fluvial deposits can be differentiated into two groups: (1) Channel deposits and (2) Floodplain deposits (Reineck and Singh, 1980).

The fine-grained fraction (silt and clay) is transported by rivers as suspended matter, the amount and concentration of which directly depends on the density and size of the grains and water velocity. Indirectly, it depends on the rock and soil type and erosion rates. The concentration of suspended sediments varies with changes in the current profile and velocity.

Upstream sections are typically regions with high water velocities and consequently high erosion rates so that the natural composition of the suspended sediment in rivers directly reflects the lithology in the catchment area.

Downstream in lowland river basins with large catchment areas, the natural composition of the suspended sediment still reflects the parent material but the influence of individual lithologies can be distinguished less clearly. In both upstream and downstream areas, the concentrations of HSs in the sediment can be overprinted by anthropogenic input.

River floodplains act as sediment sinks for alluvial sediments. While they are being stored the sediments may be reworked by fluvial, aeolian, biological and/or pedogenic agents. The stored sediments may subsequently be eroded and re-incorporated into the sediment budget of the drainage basin. Because of the protracted residence times of heavy metals within rivers and their floodplains, metal-contaminated sediments may act as major sources of future contamination (Goudie, 2006). These characteristics, the relative ease of access and straightaway methods for sampling make floodplain sediments a suitable media for monitoring the river's environmental status.

Generally, floodplain could be considered as the relatively flat area of land that stretches from the banks of the parent stream to the base of the valley walls and over which water from the river channels flows at times of high discharge (Goudie, 2006). Floodplains are a characteristic trait of the mature and old stages of a river as opposed to the young stage that occurs in the mountainous regions (Reineck and Singh, 1980).

Due to the varying frequency of flooding events, defining the extent of a floodplain in a given fluvial system as the area inundated during floods could be problematic. Wolman and Leopold (1957) defined the term "active floodplain" as the area subjected to the annual flood (i.e. the highest discharge each year). Though this definition could be a subject of discussion, in terms of monitoring a river's environmental status, defining the active and former floodplains (river terraces) is of high importance. The floodplain sediments suitable for monitoring are deposits of suspended material onto active, regularly flooded floodplains and levees along rivers with variable water flow.

Furthermore, when choosing floodplain sediments for monitoring media, fluvial sub-environments suitable for the purposes should be very carefully determined. For example, the approach of Reineck and Singh (1980) that combines bank and over bank deposits into the "floodplain" environment seems more appropriate for monitoring goals, bearing in mind that the multitude of processes, besides fluvial, that rework these sediments could overall alter the river's chemical print. Thus, the sediments deposited in the natural levees and the crevasse splays could be monitored and would present more realistic results about the quality of the water body, than marsh and flood basin

sediments. The latter two sub-environments could be used for monitoring purposes with the precondition of sampling soon after the flooding event.

Other reasonable deposits for sediment monitoring are the silty and clayey layers on the top of the point bars. Despite point bars being part of the channel deposits, these top sections are often hard to distinguish from the levee deposits. This and their fine-grained nature make them a suitable sink and subsequently sampling media for HSs in river systems.

The background value for a given area could be defined either from earlier geological and geochemical investigations or by sampling sediments that date from pre-industrial times. For the floodplain sediment, the background value should be considered as the deeper, natural, preindustrial level at the sampling site. The surficial floodplain is normally affected by recent anthropogenic activities and may be contaminated. Deeper samples, which are optional sampling media, normally show the natural background variation.

In summary, the analysis of HSs in floodplain sediments will reflect natural background values and historical contamination, while the regular monitoring in bottom sediment will show baseline values and more recent contamination. The analysis of suspended sediment (especially during high flow events), as well as the occasional analysis of floodplain sediments (i.e. the deposits of the last major flood event), will reveal the current state of contamination including material from soil erosion.

Additionally, for floodplain sampling, it is advisable to determine background values at the sampling site by sampling the deeper pre-industrial level of the river bank. The reliable assessment of the drainage basin contamination could be performed by comparing pre- and post-industrial floodplain sediments.

The selection of the sediment sampling stations should follow the FOREGS Atlas recommendations (Salminen et al., 2005). The field manual for FOREGS Atlas suggests sampling of floodplain sediment from the lowermost point of the larger drainage basin (area  $1,000 - 6,000 \text{ km}^2$ ) to which the small catchments are connected (Salminen et al., 2005). Additionally, some further criteria should be applied when choosing a sampling site for floodplain sediments:

 Distance from the river bed – closer to the river channel should be preferred in order to minimize the effect or chemical overprint of external agents;

Frequency of flooding – sites with frequent flood events (for example annual) are preferable;

- Sites, where floodplains are used for agriculture should be avoided;
- Sites, where there is a possibility of strong air pollution should be avoided;

 Having in mind the ability of different plant species to extract certain chemical elements from the soils, sites, where vegetation is missing or is scarce are preferable then thickly vegetated ones.

Composite samples for floodplain sediment should be comprised of 5 - 10 subsamples.

In the FOREGS Atlas (Salminen et al., 2005), the prescribed **sampling depth** for floodplain sediments is 0 – 25cm. This provides a comprehensive indication of the recent state of contamination. However, the accumulated floodplain sediments record (historical) contamination within the drainage basin over time. The separate sampling of individual flood events (e.g. the pre-industrial level (once) and the latest flood event (occasionally)) is preferable and the results are more meaningful. In this case, **sampling depth and thickness depend on the deposition rate**.

A sampling of floodplain layers deposited in pre-industrial times would reveal the natural background values of contaminants. Geological experience is necessary to identify the sediment layer (depth interval) to be sampled.

In terms of monitoring frequency, longer intervals (i.e. only after major flooding events) are appropriate for floodplain sediments. The proposal for the frequency of monitoring for floodplain sediment is once every six years, which is in compliance with the six-year cycles suggested by the WFD directives. However, because of the susceptibility of floodplain sediments to be reworked by non-fluvial processes, an appropriate approach could be more frequent monitoring at shallower depths (for example, the top 5 cm, or depending on sedimentation rate if such data is available). This will secure the obtaining of more reliable results for the changes in the environmental status. Such higher frequency, however, could be well reasoned after a sufficient amount of data from sediment monitoring has been accumulated.

The analysed size fraction for floodplain sediment samples in FOREGS Atlas is <2 mm, the SIMONA Sediment quality sampling protocol for HSs prescribes the <63  $\mu$ m fraction. Both fractions of floodplain sediment (0 – 63  $\mu$ m and 63  $\mu$ m – 2 mm) are recommended for analysis.

In the **Field observation sheet** in the SIMONA Sediment quality sampling protocol for HSs there is a field "**Others**" where information about the floodplain sediment could be entered.

The sample volume, sample equipment, and other sample preparation procedures should be in accordance with the FOREGS Atlas (Salminen, 2005).

The description of **the field and laboratory Quality control** (QC) is presented in the SIMONA Sediment quality sampling protocol for HSs.

<u>SIMONA recommendation:</u> The appropriate monitoring of PHSs in river sediments should take into account all types of sediment: stream/bottom, floodplain and suspended sediment to comprehensively investigate the sediment-associated HSs.

#### References

Goudie, A. S. 2006. Encyclopedia of Geomorphology Vol. 1. Taylor & Francis e-Library, 1202p.

Reineck, H-E., I. B. Singh. 1980. Depositional Sedimentary Environments: with reference to terrigenous clastics. Springer-Verlag Berlin Heidelberg. 565p.

Salminen, R. (Ed.), Batista, M.J., Bidovec, M. Demetriades, A., De Vivo. B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T. 2005. Geochemical Atlas of Europe. Part 1 – Background Information, Methodology and Maps. Geological Survey of Finland, Espoo, Finland, 526p. <a href="http://www.gtk.fi/publ/foregsatlas/">http://www.gtk.fi/publ/foregsatlas/</a>).

Wolman, M.G., L.B. Leopold. 1957. River floodplains: some observations on their formation. US Geological Survey Professional Paper 282C, 87–107.

# Appendix 2 was written - List of priority substances

# List of priority substances in the field of water policy (Part A, Annex I; Directive 2013/39/EU)

	Number in Part A, Annex I	CAS number <sup>1</sup>	EU number <sup>2</sup>	Name of priority substance
1	2	120-12-7	204-371-1	Anthracene
2	5	not applicable	not applicable	Brominated diphenylethers
3	6	7440-43-9	231-152-8	Cadmium and its compounds
4	7	85535-84-8	287-476-5	C10-13-chloroalkanes
5	12	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)
6	15	206-44-0	205-912-4	Fluoranthene
7	16	118-74-1	204-273-9	Hexachlorobenzene
8	17	87-68-3	201-765-5	Hexachlorobutadiene
9	18	608-73-1	210-168-9	Hexachlorocyclohexane
10	20	7439-92-1	231-100-4	Lead and its compounds
11	21	7439-97-6	231-106-7	Mercury and compounds
12	26	608-93-5	210-172-0	Pentachlorobenzene
13	28	not applicable	not applicable	Polyaromatic Hydrocarbons (PAH)
14	30	not applicable	not applicable	Tributyltin compounds (Tributyltin-cation)
15	34	115-32-2	204-082-0	Dicofol
16	35	1763-23-1	217-179-8	Perfluorooctane sulfonic acid and its derivatives (PFOS)
17	36	124495-18-7	not applicable	Quinoxyfen)
18	37	not applicable	not applicable	Dioxins and dioxin-like compounds
19	43	not applicable	not applicable	Hexabromocyclododecane (HBCDD)
20	44	76-44-8/ 1024-57-3	200-962-3/ 213-831-0	Heptachlor and heptachlor epoxide

# List of Priority Substances for the Danube River Basin (ICPDR, 2003)

	Number in List of PS	CAS number <sup>1</sup>	EU number <sup>2</sup>	Name of priority substance
21	23	7440-02-0	231-111-4	Nickel and its compounds
22	38	7440-38-2	231-148-6	Arsenic and its compounds
23	39	7440-50-8	231-159-6	Copper and its compounds
24	40	7440-66-6	231-175-3	Zinc and its compounds
25	41	7440-47-3	231-157-5	Chromium and its compounds

<sup>&</sup>lt;sup>1</sup>CAS: Chemical Abstracts Service.

<sup>&</sup>lt;sup>2</sup>EU-number: European Inventory of Existing Commercial Substances (EINECS) or European List of Notified Chemical Substances (ELINCS).

# Appendix 3 was written - Field observation sheet

#### **Observation of Field observation sheet from protocol**

Concerning field: "Flow rate – estimated value (m/s)" in the Field observation sheet in Appendix 1

**JCI comment:** "This is possible when collection of suspended sediment and bottom sediments takes place at the same time as water velocity and flow measurements. However, if bottom sediments are collected separately from flow/velocity measurements we believe it will be difficult to estimate the flow rate of the Danube and large rivers at the time of sampling especially if the people collecting the samples are not familiar with average flow rates during different water levels. If it is necessary to know the flow rates, these must be measured prior to sampling."

Concerning field: "Geology and background value:" in the Field observation sheet in Appendix 1.

JCI comment: "Background value of what?"

**HGI-CGS corrections:** "Flow rate – estimated value (m/s), measured prior to sampling

Geology and background value of parent material / lithology in the area"

**Kata Dudás comment:** Field observation sheets - "For field this sheet is ok. But after that for the IT tool we need to use WISE-SoE terms, so maybe it is easier if we can use the WISE fields at the first time." Monitoring Site ID - "WISE use Monitoring site term." and "One is enough, the IT toll will fill the other automaticly."

**Kata Dudás** suggested, as a final version, this field observation sheet:

# Appendix 3 for Sediment sampling

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

Project:				
Sample identifier (ID):				
Sampling matrix: □ bottom sediment; □ suspended particular matter (SPM); □ floodplain sediment; □ other:				
Sampling:   □ accredited;  □ not accredited   U	sed sampling standard number:			
Monitoring Site	e Identification:			
Monitoring Site ID (WISE-SoE):	Monitoring Site ID (national):			
Name of the Monitoring Site:				
Sample location description with specific information road, natural park,) (provide map on opposite side):	(bridge, high power electric lines, railway line, major			
Type of the monitoring site (can be different from repre □ river; □ lake; □ wetland; □ floodplain				
Aim of sampling: □ general status; □ reference site (wit – find contamination source; □ investigation site for oth	thout/small anthropogenic sources);  investigation site			
WGS84	National Coordinate system			
Latitude:	Latitude:			
Longitude:	Longitude:			
Monitoring Site representir	ng the following Waterbody:			
Is it the same waterbody as the Monitoring Site has?   \[ \text{\tinte\text{\tint{\text{\tinit}\text{\text{\text{\text{\text{\text{\text{\text{\text{\texi}\tinity}\\\ \text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\texi}\text{\text{\text{\texi}\text{\text{\text{\text{\texi}\tex{\text{\texi}\text{\texit{\texit{\texit{\texit{\texit{\texi}\tex{\texi{\texi{\texi{\texi}\texi{\texi{\texi{\texi{\texi{\ti	YES or   NO (fill the following fields)			
Waterbody ID (WISE-SoE):	Waterbody ID (national):			
Name of the Waterbody:				
Type of the waterbody: □ river; □ lake; □ wetland				
Monitoring Si	ite conditions:			
River width estimated value [m]				
Depth of water – estimated average depth [m]				
Flow rate – estimated value [m/s]				
Extreme conditions: □ none; □ flooding status; □ ice; □ pollution plume; □ contaminated coast/bank; □ other:				
Geology and background value [mg/kg wet weight]:				
Weather conditions: □ sunny □ cloudy □ changeable □ rainy □ hot □ frosty				
Sediment collection information:				
Water depth above sample [m]:				
Sediment sample depth [cm]:	Little illustration picture here is necessary to make the depths clear			
Collection device: Scoop Corer Other; sampler for SPM				
Sample type: Composite – Number of subsamples:				

How many river meters between the first and last sampling site:					
Sample replicate collected? □ YES or □ NO	Replicate ID/name:				
Sample duplicate collected? □ YES or □ NO					
Sample information:					
Sampling volume estimated, wet weight [litter]:					
Temperature (field observation, right after sampling) [°C]:					
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:					
ollection date: Collection time:					
Sampler/signature:					

## **Conclusion**

- Almost all corrections were accepted, exclude:
  - Comments concerning English language and writing style were accepted only if they improve explanation in the text (the Output 4.1 Sediment quality sampling protocol for HSs will be professionally proofread and corrected);
  - Comments sent too late were not incorporated in the Output (Appendix 1);
- Floodplain sediments were deleted from the sediment sampling protocol and presented as a recommendation in the Output in Appendix 1;
- Appendix 2 was written List of priority substances;
- Background value was more detailed explained;
- The field manual was corrected and adjusted to the SIMONA tools and presented as Appendix 3.