Qualitative review report describing the sediment sampling methods' current status and problems in the DTP Countries

Deliverable D 4.1.1

Project title	Sediment-quality Information, Monitoring and Assessment System to support transnational cooperation for joint Danube Basin water management
Acronym	SIMONA
Project duration	1st June 2018 to 1st May 2021, 36 months
Date of preparation	30/04/2019

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

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The WP4 - Activity 4.1 is a qualitative review based on WP3 Questionnaires. Within the review report, current status is described for existing sampling and monitoring legislative framework, practices and experiences, inventory of sampling methodologies, inventory of laboratory methodologies, inventory of evaluation methods and selected references in the DTP countries, including both EU and non-EU members for sediment quality measurements of the water, biota, bottom sediment, suspended sediment and floodplain sediment.

Qualitative review report was made by the following criteria: protocols should be acceptable in all DTP countries, in-line with the ICPDR and the EU requirements, use the latest scientific knowledge and have to be sustainable.

The review of **suspended sediment** sampling procedures includes methodology for suspended sediment sampling: sampling site position in the stream (for example in the middle of the river, closer to river banks), sample volume/mass, tools and procedure including time needed to collect specific volume/mass. The review was made based on articles like Edwards & Glysson (1999) and Lalk et al. (2017), which provide the most detailed descriptions. In the national questionnaires, only Romania describes the method for sampling sediments in suspension with the Rapid collector Nansen bottle (cylinders with flaps for sediments).

The review of **floodplain sediment** sampling procedures which include methodology for floodplain sediment sampling: sampling location (for example how far from the stream), sample volume/mass, tools and procedure. Sampling of floodplain sediment is carried out only in three countries: Austria, Moldova and Croatia. In other countries, sampling of floodplain sediments is not carried out or there are no data or monitoring of sediments is not performed at all. The data for the sampling location were not given. The volume/mass of sample is different, but most partners have no data. The sampling tools are various (stainless steel shovels, PVC or ceramic spoons, scoops) and the procedures are different.

The review of sediment sampling methods is described in the DTP project Danube Sediment Management – Restoration of the Sediment Balance in the Danube River (**DanubeSediment**) on sediment quantity. Sediment transport along the Danube River has an immediate impact on water management activities and flood risk. According to collected data, practices in DTP countries are characterized by: (1) different monitoring methods along the Danube (various instruments, sampling frequencies (from 4/hour to 5/year), sampling methods and laboratory analysis); (2) discrepancies in sediment data; (3) poor sediment data quality at existing monitoring stations and (4) data gaps at relevant locations. Sampling methods are multipoint sampling and isokinetic sampling. Further survey is needed to answer the questions in multipoint sampling: how many verticals (5 - 10 verticals along one transect) and how many points (5 – 10 points along a vertical) should be sampled. In the project were given recommendations for improvements: harmonized protocols in sediment monitoring along the DTP countries, improvement of quality monitoring, continuous monitoring,

validation of the monitoring stations, use of the accredited laboratories, use of surrogate techniques, well trained personnel, automatized sediment monitoring stations, the establishment of sediment balance, river restoration measures, sediment transport models, involvement of researchers in the development of monitoring strategies, monitoring stations, planning and implementation of restoration measures.

The sediment **transport** in Slovenia and Serbia according to standard norms SIST ISO 5667 – 15: 2010 Water quality - Sampling - Part 15: Guidance on the preservation and handling of sludge and sediment samples and EN ISO 5667-15:2013 Water quality - Sampling - Part 15: Guidance on the preservation and handling of sludge and sediment samples, respectively. There is no specific methodology in Austria, Bosnia and Herzegovina (Federation of B&H) and no data for the countries Republic of Srpska (B&H), Bulgaria, Hungary and Montenegro. In Croatia, Moldova, Slovakia, Serbia sediment are transported in refrigerators and in Germany in brown glass bottles. Samples of suspended sediment are put on filters in Romania and after drying and sieving in Ukraine.

Samples in Germany, Moldova, Romania, and Ukraine are **archived**. There are various types of archiving: in Germany samples are stored at -20°C, in Moldova dried and homogenized sediment or soil samples are marked and stored, in Romania in envelopes and filters in a clean, moisture-free room and in Ukraine in a paper bag or polyethylene container with the appropriate markings in a dry, cool room. In Austria, Federation of Bosnia and Herzegovina (B&H) samples are kept until project completion. The Republic of Srpska (B&H), Hungary, Montenegro, and Slovakia gave no data and in Bulgaria, Croatia, Slovenia and Serbia - samples are not archived.

The level of surface water at the hydrological stations is monitored for the purpose of flood control measurements in all participating countries in the SIMONA project. In the frame of national and international DTP projects, the hydrochemical composition and concentrations of heavy metals are monitored in surface water and groundwater in most countries. There is no information on the analysis of suspended substances in the water flow.

The maximum **experience in sediment monitoring** is available in Slovakia. Within the project's Monitoring of river sediments within the Partial Monitoring System (1996 - ongoing), at 60 Danube River Quality Monitoring Stations, bottom sediment samples were taken. There is an online database of sediments monitoring which includes: the basic database of the chemical composition of river sediments, basic localization data of monitoring points, results of a mineralogical analysis and granulometric analysis results.

Serbia is monitoring bottom sediment. The sampling design, frequency and sampling locations are determined in accordance with the requirements defined in the Guidance on the design of sampling programs and sampling techniques (ISO 5667-1:2006) and the annual monitoring program defined by the Ministry of agriculture, forestry and water management. The sampling methodology is described in the following standards: SRPS ISO 5667-1:2008, SRPS ISO 5667-3:2007 and SRPS ISO 6107-2:2005.

Bottom sediments in Slovenia are monitored for trends every 3 years, in accordance with Directive 2008/105/EU and the Rules on the monitoring of surface waters. The monitoring in Hungary, Austria,

Romania, Bulgaria are performed through the joint project DanubeSediment and in Croatia were monitored Drava alluvial sediments only during 4 years, (2004-2007).

Bottom sediments in Bulgaria are currently monitored once in every three years (the monitoring started in 2016) in accordance with the Water Framework Directive 2013/39/EC (2000/60/EU, 2008/105/EU) and national legislation.

The review **bottom sediment** sampling procedures includes methodology for bottom sediment sampling like position in the stream (for example riverbed, inner/outer side of meander), sample volume/mass, tools and procedure. The bottom sediment is sampled in Austria, Bulgaria, Croatia, Moldova, Montenegro, Romania, Serbia, Slovakia, Slovenia and Ukraine. No data were provided from Germany, Hungary, Montenegro, Republic of Srpska (B&H), Federation of Bosnia and Herzegovina (B&H). Sampling bottom sediment perform according to norms in Austria (ÖNORM G 1031), in Serbia (ISO 5667-1:2006) and monitoring program of the Ministry of agriculture, forestry and water management), in Slovenia (SIST ISO 5667 – 12:1996 Water quality -- Sampling -- Part 12: Guidance on sampling of bottom sediments), in Ukraine (DSTU ISO 5667-12-2001) and in Bulgaria sampling strategy is defined by the River Basin Management Plan for the Danube Region (2016-2021). Slovakia and Romania gave detailed description in the questionnaires of their sampling strategies.

Measurements ***in situ*** are not performed in most of the countries with exception of Austria and Serbia. Sampling devices for *in situ* measurements are in Austria for - electrical conductivity, water temperature: WTW Type 3320 with sensor Tetra Con 325; - pH: Type 3320 with sensor SenTix 41 (WTW); - oxygen content: Type Multi 3630 IDS with sensor FDO® 925 (WTW); - redox potential: Type pH 330 with sensor SenTix ORP (WTW); - discharge: WTW Type 3320 with sensor Tetra Con 325; MRS-4 Trace (Sommer), Unversal Current Meter F1 (SEBA), Starflow Model 6526 (Unidata) and in Serbia - Van Veen grab sampler/ Graifer/ Core sampler.

Tools for collecting samples in Austria - Stainless steel shovels and sieves (according to DIN 4188), paper bags, in Croatia - PVC or ceramic spoons, in Moldova - scoops or trowels, in Serbia - UWITEC core sampler (in reservoirs and slow flowing waters)/ Van Veen grab sampler/ Graifer/PVC spoons, in Slovakia - UWITEC nuclear excavator, in Slovenia - NLZOH MB and in Ukraine - plastic scoop, a stainless steel blade; the Giller peat drill.

Methodology for collecting samples in Austria includes *in situ* sieving; drying of sample at ambient temperature; crushing; putting sample in polyethylene bottles; in Croatia depends of the parameters intended to analyze; in Moldova the sampling equipment depends of the sampling depth and sampling plan for the study of polluted or non-polluted sites; in Serbia the methodology is in accordance with the standards: SRPS ISO 5667-1:2008, SRPS ISO 5667-3:2007 and SRPS ISO 6107-2:2005.

The review of hazardous substances (**HSs)** measured in sediment was done in every partner countries. Within this review, it should be checked if there are some HSs which are not included in the EU WFD, but are specific for some partner countries due to particular reasons (type of industry, agriculture, legislation).

There is a contradiction between the statement that most countries are sampling sediments - bottom, floodplain, suspended, but no HSs are listed as analyzed. The main problem was missing question in the questionnaires about hazardous substances measured in sediments. The partners provided the list of hazardous substances measured in soils, and additionally several partner countries provided a list of HSs in sediments when requested (Appendix 1). Slovakia and Serbia provided list of HSs in sediments in questionnaires. In Slovakia a list of hazardous substances concentration levels in sediments is implemented in legislation with an overview of legislation limiting the management of sediments on the basis of the limit values for selected elements in sediments (sediment leachates).

The review includes preliminary excel table with a summary of data (HSs recommended in the Directive marked in green) (Appendix 1).

The review of **sampling strategy** (including spatial and temporal sediment sampling design) includes methodologies for selection of sediment sampling locations and setting sediment sampling frequency. It also includes information on number of replicate samples and fraction to be analyzed.

Sampling design should be developed on the legal basis for the monitoring of HSs in sediment in EU, the *state of the art* in particular country and knowledge of a topic of the partners (WP4 Activity 4.1 Review) and knowledge and experience acquired in the projects FOREGS, GEMAS, DanubeSediment.

The most important EU legal documents for developing sampling strategy are Directive 2008/105/EC (Environmental Quality Standards Directive) and Water Framework Directive 2000/60/EC (WFD) with the Common Implementation Strategy for the Water Framework Directive (2000/60/EC) in following guidance's: Guidance Document No. 25 (Guidance on Chemical Monitoring of Sediment and Biota under the Water Framework Directive), Guidance Document No. 19 (Guidance on Surface Water Chemical Monitoring under the Water Framework Directive), Guidance Document No. 27 (Technical Guidance for Deriving Environmental Quality Standards), Guidance document No. 7 (Monitoring under the Water Framework Directive) and some which are not directly connected with the sediment like Guidance document No. 9 (Implementing the Geographical Information System Elements (GIS) of the Water Framework Directive.

The steps for developing a sampling design are prescribed in detail in one part of the Guidance Document No. 25 - Monitoring of chemical substances in sediment: (1) Sampling strategy for chemical monitoring in sediment and (2) Technical aspects of sediment sampling.

(1) Sampling strategy for chemical monitoring in sediment includes:

(a) Selection of sediment sampling stations (sediments are temporally variable; heterogeneous; anthropogenic sources of pollution; in the tributaries there are often different sediment; sites with the sediment fraction <63 µm; alternatively suspended solid matter (SPM) - river channelization; sites should be accessible for years; ...).

(b) Number of replicate samples per station (multiple samples in pilot phase (3 - 5); later composite samples; field duplicates for quality control; ...).

(c) Sediment sampling frequency (once a year for – Directive 2008/105/EC; once every three years for temporal trend analyzes; higher if the sediment changes – it could be several times per year; suspended solids for trend analyses 4 times per year or better monthly; ....).

(d) Sediment sampling depth (thick of the top layer (usually 5 - 10 cm); recommended 1 – 5 cm - depending of the deposition rate; different intervals for sediment core profiles; ...).

(e) Sediment fraction to be analyzed (recommended <63 µm (clay-silt) fraction; widespread in monitoring; reduce influence of grain size distribution; it is SPM or freshly deposited sediment).

(2) Technical aspects of sediment sampling

These should rely on ISO 5667 series of standards important for sediment sampling: Design of sampling programs [ISO, 2006]; Preservation and handling of samples [ISO, 2003]; Sampling of rivers and streams [ISO, 2005]; Sampling from lakes [ISO, 1987]; Sampling of bottom sediments [ISO, 1995]; Guidance on preservation and handling of sludge and sediment samples [ISO, 1999]; Sampling of marine sediments [ISO, 2004].

In the Guidance Document No. 25 there are prescribed other important issues for a sampling design: sample volume, sediment sampler, grab samplers, corers, collecting of SPM and freshly deposited sediments, transport and sieving, preservation and storage.

The qualitative review report based on WP3 Questionnaires was made in the frame of the WP4 - Activity 4.1 This report will serve as one of the factor for WP4 Activity 4.2 – Development of the proposal of harmonized sediment sampling and laboratory analysis protocols for HSs in DTP Countries.

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Appendix 1
HSs review

Hazardous substances measured in sediments – priority substances prescribed by the EU WFD and specific substances - review

Country	Austria	Bulgaria	Croatia	Federation Bosnia and Herzegovina (B&H)	Hungary	Moldova	Montenegro	Republic of Srpska (B&H)	Romania	Slovakia	Slovenia	Ukraine	Serbia	
Type of sediment sampled	B, F, S	B, F (?)	B, F	F	No data	B, F, S	No data	No data	B, S, "dragged sediments"	B, stream sediment	No data	-	B	
Hazardous substances measured **in sediments (data provided for soils not included!)**	No data	Anthracene (EU2)	aldrin	lead	No data	No data	Brominated diphenylether (congener numbers 28, 47, 99, 100, 153 and 154)	No data	No data	alachlor		Monitoring of sediments at state level not performed	arsenic	B-bottom; F-floodplain; S - suspended
		Brominated diphenylethers (EU5)	anthracene	cadmium			Cadmium			aniline			cadmium	Part of the priority substances list of the EU WFD
		Cadmium and its compounds (EU6)	endrin	zinc			Chloroalkanes, C10-13			anthracene			chromium	
		C10-13 Chloroalkanes (EU7)	isodrin	nickel			Cyclodiene pesticides: Aldrin, Dieldrin, Endrin, Isodrin			arsenic and its compounds			copper	
		Di(2-ethylhexyl)-Phthalate (DEHP) (EU12)	para-para-DDT	chromium			DDT total (DDT, DDD, DDE)			atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine)			mercury	
		Fluoranthene (EU15)	orto-para-DDT	arsenic			para-para-DDT			benzene			lead	
		Hexachloro-benzene (EU16)	para-para-DDE	mercury			Di(2-ethylhexyl)phthalate (DEHP)			benzenesulfonamide			nickel	
		Hexachloro-butadiene (EU17)	para-para-DDD	copper			Hexachlorobenzene			benzo (a) pyrene			zinc	
		Hexachloro-cyclohexane (EU18)	heptachlor	cobalt			Hexachlorobutadiene			benzo (b) flourantén			Mineral oils	
		Lead and its compounds (EU20)	heptachlor epoxide	acenaphthylene			Hexachlorocyclohexane			benzo (k) fluoranthene			*Polycyclic aromatic hydrocarbons (PAH) total	*Naphthalene+ Anthracene+ Fenantrene+ Fluoranthene+ Benz(a)anthracene+ Krizen+ Benzo(k)fluorantene+ Benzo(a)pyrene+ Benzo(g,h,i)perylene+ Indeno(1,2,3,-c,d)pyrene
		Mercury and its compounds (EU21)	dieldrin	anthracene			Lead			Benzo (g, h, i) pyrelén			Naphthalene	

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		Polyaromatic hydrocarbons (PAH) (EU28)	α-endosulphan	acenaphthene			Mercury			benzothiazole			Anthracene
		Tributyltin compounds (Tributyltin-cation) (EU30)	β-endosulphan	benzo(a)anthracene			Nickel			biphenyl (phenylbenzene)			Phenanthrene
			fluoranthene	benzo(a)pyrene			Pentachlorobenzene			bisphenol A (2,2-bis (4-hydroxyphenyl) propane)			Fluoranthene
			HCB	benzo(b)fluoranthene			Polyaromatic hydrocarbons: Naphtalene, 2-Methylnaphtalene, 1-Methylnaphtalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Indeno (123-cd) pyrene, Dibenzo (a,h) anthracene, Benzo (g,h,i) perylene			Bis (2-ethylhexyl) phthalate (DEHP)			Benz(a)anthracene
			α-HCH	benzo(ghi)perylene			Tributyltin compounds (Tributyltin-cation)			clopyralid			Chrysene
			β- HCH	benzo(k)fluoranthene			Trifluralin			DDT (DDD, DDT, DDE isomers)			Benzo(k)fluoranthene
			γ- HCH	chrysene			Dicofol			desmedipham			Benzo(a)pyrene
			δ- HCH	dibenz(a,h)anthracene			Perfluorooctane sulfonic acid and its derivatives (PFOS)			dibutyl phthalate			Benzo(g,h,i)perylene
			pentachlorobenzene	fluoranthene			Quinoxyfen			1,2-dichloroethane			Indeno(1,2,3,-c,d)pyrene
			benz(a)pyrene	fluorene			Dioxins and dioxin-like compounds			diphenylamine			**Polychlorinated biphenyl (PCB) total

** PCB= PCB 28+PCB 52+PCB 101+PCB 118+PCB 138+PCB 153+PCB 180

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			benzo(b)fluoranthene	ideno(1,2,3-cd)pyrene			Hexabromocyclododecane (HBCDD)			ethofumesate			DDD	
			benzo(k)fluoranthene	naphtalene			Heptachlor and heptachlor epoxide			phenanthrene			DDE	
			benzo(g,h,i)perylene	phenanthrene			PCB congeners (PCB 18, PCB 31 and 28, PCB 52, PCB 44, PCB 101, PCB 149, PCB 118, PCB 153, PCB 138, PCB 180, PCB 194)			flouranthene			DDT	
			indeno(1,2,3-cd)pyrene	pyrene			Arsenic			formaldehyde			***DDT total	*** DDT total= DDT+DDD+DDE
			C10-13 chloroalkanes	PCB			Copper			glyphosate			Aldrin	
			DEHP	TPH			Zinc			hexachlorobenzene			Dieldrin	
			tributyltin	Σ-DDT/DDD/DDE			Cobalt			chlorpyrifos			Endrin	
			PBDE 28	Σ-drins			Molybdenum			Chlorpyrifos-methyl			****Cyclodiene pesticides	****Cyclodiene pesticides= aldrines+dieldrines+endrines
			PBDE 47	HCH						chromium and its compounds			-HCH	
			PBDE 99							indeno (1,2,3-cd) pyrene			-HCH	
			PBDE 100							isoproturon (N, N-dimethyl-N- (4-isopropylphenyl) urea			-HCH (lindane)	
			PBDE 153							cadmium and its compounds			*****HCH total	*****HCH total= alphaHCH+betaHCH+gammaHCH+deltaHCH)
			PBDE 154							cyanides			Alpha-endosulfan	
			PBDE 183							lindane (g-hexachlorocyclohexane)			Heptachlor	
			PCB-28							copper and its compounds			Heptachlor-epoxide	
			PCB-52							2-Methyl-4-chlorophenoxyacetic acid (MCPA)				
			PCB-101							4-methyl-2,6-di-tert-butylphenol				
			PCB-138							naphthalene				
			PCB-153							nickel and its compounds				
			PCB-180							nonylphenols				
			PCB-77							4- (para) -nonylphenol				
			PCB-81							Octylphenols				
			PCB-105							4 (t) -octylphenol				
			PCB-114							lead and its compounds				
			PCB-118							mercury and its compounds				

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Country	Austria	Bulgaria	Croatia	Federation Bosnia and Herzegovina (B&H)	Hungary	Moldova	Montenegro	Republic of Srpska (B&H)	Romania	Slovakia	Slovenia	Ukraine	Serbia
			PCB-123							PCB and its congeners (28, 52, 101, 118, 138, 153,180)			
			PCB-126							pendimethalin			
			PCB-156							simazine (6-chloro-N, N'-diethyl-1,3,5-triazine-2,4-diamine)			
			PCB-157							tetrachloroethene			
			PCB-167							1,2,4-trichlorobenzene			
			PCB-169							1,1,2-trichloroethane			
			PCB-189							trichloroethene			
			dicofol							trichloromethane (chloroform)			
			PFOS							trifluralin			
			quinoxyfen							toluene			
			HBCDD							vinylbenzene (styrene)			
			2,3,7,8-T4CDD							xylenes (isomers of o-xylene, m-xylene, p-xylene)			
			1,2,3,7,8-P5CDD							zinc and its compounds			
			1,2,3,4,7,8-H6CDD										
			1,2,3,6,7,8-H6CDD										
			1,2,3,7,8,9-H6CDD										
			1,2,3,4,6,7,8-H7CDD										
			1,2,3,4,6,7,8,9-O8CDD										
			2,3,7,8-T4CDF										
			1,2,3,7,8-P5CDF										
			2,3,4,7,8-P5CDF										
			1,2,3,4,7,8-H6CDF										
			1,2,3,6,7,8-H6CDF										
			1,2,3,7,8,9-H6CDF										
			2,3,4,6,7,8-H6CDF										
			1,2,3,4,6,7,8-H7CDF										
			1,2,3,4,7,8,9-H7CDF										
			1,2,3,4,6,7,8,9-O8CDF										
			1,2,3,4,6,7,8,9-O8CDF										