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SIMONA

INVENTORY OF DRB's SEDIMENT MONITORING ACTIVITY

Output 3.1

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Compiled by: Veronica Alexe, Anca-Marina Vijdea

Authors (in alphabetical order): Veronica Alexe (IGR), Jasminka Alijagić (GEOZS), Albert Baltres (IGR), Sonja Cerar (GEOZS), Gheorghe Damian (TUCN), Neda Dević (GSM), Katalin Mária Dudás (NAIC), Petyo Filipov (GI-BAS), Edith Haslinger (AIT), Zuzana Hiklová (SWME), Atanas Hikov (GI-BAS), Pavel Hucko (WRI-VUVH), Gheorghe Iepure (TUCN), Danijel Ivanišević (HGI-CGS), Ana Čaić Janković (HGI-CGS), Gyozo Jordan (SZIE), Paul Kinner (AIT), Volodymyr Klos (UGC), Jozef Kordík (SGIDS), Aleksandra Kovacevic (JUVS), Zsófia Kovács (OVF), Tanja Knoll (GBA), Zlatka Milakovska (GI-BAS), Ivan Mišur (HGI-CGS), Tatjana Mitrović (UB-FMG), Daniel Nasui (TUCN), Igor Nicoară (IGS-ASM), Jarmila Nováková (SGIDS), Irena Peytcheva (GI-BAS), Sebastian Pfleiderer (GBA), Vladimír Roško (WRI-VUVH), Robert Šajn (GEOZS), Manfred Sengl (LfU), Ajka Šorša (HGI-CGS), Igor Stríček (SGIDS), Zsolt Szakacs (TUCN), Ľudmila Tokarčíková (SGIDS), Milena Vetseva (GI-BAS), Jelena Vicanovic (JUVS), Anca-Marina Vijdea (IGR), Dragica Vulić (JCI).

Responsible(s) of the deliverable: Anca-Marina Vijdea (IGR)
Co-responsible(s) of the deliverable: Gyozo Jordan (SZIE)

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1. INTRODUCTION

WP3 provides the essential frame for WP4 and WP5 protocol-developing work packages. WP3 has two main objectives: (1) to describe the current status of and common needs for sediment quality monitoring in the DRB countries by compiling an inventory of good practices, national protocols, methods and databases related to sediment quality monitoring; and (2) to verify and demonstrate the integration and added value of surface water sediment quality monitoring by two pilot action for improving transnational water management.

The first objective, the inventory, as a handbook tool, describes existing good practices and the available knowledge in the DRB counties, and presents international examples for sediment quality monitoring. The inventory will ensure that the protocols that will be developed in the other work packages (WP4 and WP5) will be based on the best available knowledge. This tool will contribute to build a "common knowledge on current status of HS sediment monitoring in DRB (SO1)".

In this activity SIMONA partners collected information in the DTP countries: legislative frameworks, experiences, practices, technical procedures, existing sampling, laboratory and evaluation methods, existing water body monitoring and sampling sites, existing methodologies of surface water chemical status assessment (e.g. spatial and temporal aggregation techniques of HSs concentrations, limit values for the national River Basin Specific Pollutants, the natural background levels corrections for metals, in addition to metadata related to sediment quality monitoring, analysis and assessment). This activity was based on a commonly agreed questionnaire in order to ensure transparency and comparability of information among the countries. All this information was included in the deliverable D3.1.1 and its annexes (SIMONA countries questionnaire),including the availability of DTP counties' relevant technological capacities and resources.

The present Output Report "INVENTORY OF DRB's SEDIMENT MONITORING ACTIVITY" was focused on the peculiarities on the river sediments in the Danube River Basin. Only the information related to sediment monitoring activity was extracted from SIMONA countries questionnaires and supplemented with new tables in chapter 2.IV regarding examples in various SIMONA countries for: analyzed elements and their detection limit in digested solid material, XRF-analyzed oxides in sediments, radionuclides measurements in sediments and analytical standards for sediments. This information together with the ones existing at the international level will be the basis for the elaboration of the "Guide for Danube River sediment quality monitoring".

2. SIMONA COUNTRIES' ANALYSIS

The table with contributors from SIMONA partner countries is included in deliverable D3.1.1.
The analysis is presented below in the same order as in the questionnaires of deliverable D3.1.1. and it refers to legislative framework, practices and experinces in partner countries, inventory of sediment sampling methodologies, inventory of sediment laboratory methodologies and inventory of evaluation methods

I. LEGISLATIVE FRAMEWORK

The answers to sediment legislatative framework were structured into tables related to:

- Legislation for river sediments;
- Definitions in partner countries of maximum and normal levels for major and trace elements in river sediments;
- Lists of maximum and normal levels in partner countries for major and trace elements in river sediments;
- Comparison lists of values in national legislations of some partner countries versus other sediment quality guides;

I.1. National or/and European legislation

This chapter implied the enumeration of national or European legislation (laws, governmental orders, and emergency ordinances) that regulates the concentrations of dangerous substances posing a risk to the health of the population or aquatic life in river and marine sediments.

The analysis of the legislation revealed that each country has laws and norms for water (river, drinking, waste), air and soil. In most of the cases, these are specific regulations. In few cases they are included in general environmental laws.
Regarding sediments, only Slovakia and Serbia have specific legislation, while for Romania and Slovenia some previsions regarding sediments are included in the laws referring to water.

Table 1 – List of legislation related to sediments

Country acronym	National, EU or international legislation related to sediments		Link
	Title (national language)	Title(in English)	
AT	-		
BA	-		
BA-SRP			
BG	-		
HR			
DE			
HU			
MD			
ME			
RO	Ord.161/2006	Order no. 161 of 16/02/2006 for the approval of the Normative on the Classification of Surface Water Quality to establish the ecological status of the water bodies (includes quality of sediments)	http://legislatie.just.ro/Public/DetaliiDocument/72574
SK	Smernica MŽP SR č. 4/1999-3 na zostavovanie a vydávanie Geochemickej mapy riečnych sedimentov v mierke 1:50 000	Directive of the Ministry of Environment of the Slovak Republic no. 4 / 1999-3 for the compilation and issue of a geochemical map of river sediments at a scale of 1:50 000	http://www.minzp.sk/oblasti/geologia/pravne-predpisy/
	Metodický pokyn MŽP SR č. 549/98-2 na hodnotenie rizík zo znečistených sedimentov tokov a vodných nádrží	Methodological Instruction of the Ministry of Environment of the Slovak Republic no. 549 / 98-2 for the risk assessment from contaminated sediments of streams and water reservoirs	

Country acronym	National, EU or international legislation related to sediments		Link
	Title (national language)	Title(in English)	
	Vyhláška MZe ČR s MŽP ČR č. 257/2009 Sb. o používání sedimentů na zemědělské půde	Decree of the Ministry of Agriculture with the Ministry of the Environment of the Czech Republic no. 257/2009 Coll. on the use of sediments on agricultural land	https://www.zakonyprolidi.cz/cs/2009-257
	Zákon č. 188/2003 Z.z. z 23. apríla 2003 o aplikácii čistiarenského kalu a dnových sedimentov do pôdy	Act no. 188/2003 Coll. on the application of sludge and bottom sediments to soil	www.slov-lex.sk
		EPA “Consensus-Based Sediment Quality Guidelines”	
		Canadian Standard „Provincial Sediment Quality Guidelines (PSQG)	
		Canadian Standard „Canadian Sediment Quality Guideline for the Protection of Aquatic Life (CSQG)“	
SI			
SR			There are provided details referring to the content of HSs in sediments, but the law title was not listed
UA			

<u>Conclusions</u>

National legislation includes concern for monitoring the environmental quality of groundwater, surface water, air, soils and sediments, for drinking water, waste water (used in industry or by population). Also, European water legislation is implemented in all these countries, annually monitoring the water bodies, in line with EU-WFD (Water Framework Directive).

Regarding the legal norms on sediment pollution, monitoring and establishing quality classes, there is national legislation only in the Republic of Slovakia and Serbia. Some countries (Romania, Slovenia) have some previsions related to sediments in the laws regarding water. For example, in Romania, within the legislation on water quality, there are also mentioned the admissible levels of harmful substances in sediments.

Consequently, the elaboration of SIMONA guide, based on the data in the Danube River Basin, and on the informations in the general guides, is necessary.

I.2. List of hazardous substances in sediments

This chapter refers to the lists of dangerous (hazardous) substances (metals, non-metals, PAHs, PCBs, other parameters) concentration levels, their significance (definition of terms used for thresholds) in sediments, in accordance with the national legislative framework.

Table 2 - Maximum content of trace elements in river sediments

Country acronym	Trace elements[µg/g]- Maximum content - River sediments																	
	Ag	As	B	Be	Cd	Cr	Co	Cu	Hg	Mo	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
AT	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BA-SRP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BG	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HR	-	55	-	-	12	380	-	190	10	200	210	530	-	-	-	-	-	720
DE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HU	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MD	-	2	-	-	3	-	-	-	2.1	-	75	32	-	-	-	-	-	300
ME	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RO	-	29*-	-	-	0.8*-	100*	-	40*	0.3*	-	35*	85*	-	-	-	-	-	150*
RS	-	29	-	-	0.8	100	-	-	36	0.3	35	85	-	-	-	-	-	140
SK	-	55	-	-	12	380	19	190	10	200	210	530	-	-	-	-	-	720
SI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
UA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

*means the for Romania the following valence states: As^{3+}, Cd^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Pb^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+} (Order 161/16.02.2006 pg. 119 "Elements and chemical quality standards for sediments with the granulometric fraction 63Å/m).

Table 3 - Normal content of trace elements in river sediments

Country acronym	Trace elements[μg/g] -Normal Content- River sediments																	
	Ag	As	B	Be	Cd	Cr	Co	Cu	Hg	Mo	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
AT	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BA-SRP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
BG	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HR	-	29	-	1.1	0.8	100	-	36	0.3	3	35	85	3	0.7	-	1	42	140
DE	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HU	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MD	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ME	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
RS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SK	-	29	-	1.1	0.8	100	9	36	0.3	3	35	85	3	0.7	-	1	42	140
SI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
UA	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Knowledge of the contents of the major elements (Na, Ca, Mg, K etc.) characterizes the geological environment, and the traceability of these chemical elements is desirable.

Regarding the maximum content of major elements (Al, Ba, Fe, Mg, Mn, Na, and K) in river sediments, no country indicated these values in the questionnaires, therefore no table was made.

Table 4 - Normal content of major elements in river sediments

Country acronym	Major elements [µg/g]- Normal content - River sediments						
	Al	Ba	Fe	Mg	Mn	Na	K
AT	-	-	-	-	-	-	-
BA	-	-	-	-	-	-	-
BA-SRP	-	-	-	-	-	-	-
BG	-	-	-	-	-	-	-
HR	-	-	-	-	-	-	-
DE	-	-	-	-	-	-	-
HU	-	-	-	-	-	-	-
MD	-	-	-	-	-	-	-
ME	-	-	-	-	-	-	-
RO	-	-	-	-	-	-	-
RS	-	-	-	-	-	-	-
SK	-	160	-	-	-	-	-
SI	-	-	-	-	-	-	-
UA	-	-	-	-	-	-	-

Table 5 - Comparative list of dangerous (hazardous) substances concentration levels in sediments used in Slovakia and Serbia versus sediment quality international guides

Indicator	Dutch General Environmental Quality Standards (mg.kg^{-1})			Canadian CSQG (mg.kg^{-1})		Canadian PSQG (mg.kg^{-1})		Slovakia Methodological instruction of the MoE No. 549/98-2 (mg.kg^{-1})				Slovakia Methodological instruction of the MoE No. 549/98-2 – water solution (mg.l^{-1})		Slovakia Decision No. 531/94-540 (mg.kg^{-1})			Serbia Sediment quality (mg./kg^{-1})		
	M	L	V	ISQG	PEL	LEL	SEL	TV	MPC	TVd	IV	TV	MPC	A	B	C	TV	MAV	RV
Metals																			
As	85	85	150	5.9	17	6	33	29	55	55	55	0.8	25	29	30	50	29	42	55
Ba	-	-	-	-	-	-	-	160	300	-	-	73	220	500	1000	2000	-	-	-
Be	-	-	-	-	-	-	-	1.1	1.2	-	-	0.02	0.2	3	20	30	-	-	-
Cd	2	7.5	30	0.6	3	0.6	10	0.8	12	7.5	12	0.08	0.4	0.8	5	20	0.8	6.4	12
Co								9	19	-	-	0.2	2.8	20	50	300	-	-	-
Cr	480	480	103	37.3	90	26	110	100	380	380	380	0.2	8.7	130	250	800	100	240	380
Cu	35	90	400	35.7	197	16	110	36	73	90	190	0.4	1.5	36	100	500	36	110	190
Hg	0.5	1.6	15	0.17	0.486	0.2	2	0.3	10	1.6	10	0.01	0.2	0.3	2	10	0.3	1.6	10
CH3Hg	-	-	-	-	-	-	-	0.3	1.4	-	-	0.01	0.02	-	-	-	-	-	-
Mn	-	-	-	-	-	460	1100	-	-	-	-	-	-	-	-	-	-	-	-
Mo	-	-	-	-	-	-	-	3	200	-	-	2.9	290	1	40	200	-	-	-
Ni	35	45	200			16	75	35	44	45	210	3.3	5.1	35	100	500	35	44	210
Pb	530	530	103	35	91.3	31	250	85	530	530	530	0.2	11	85	150	600	-	-	-
Sb	-	-	-	-	-	-	-	3	15	-	-	0.3	6.5	-	-	-	-	-	-
Se	-	-	-	-	-	-	-	0.7	2.9	-	-	0.05	5.3	0.8	5	20	-	-	-
Sn	-	-	-	-	-	-	-	-	-	-	-	0.2	18	20	50	300	-	-	-

Indicator	Dutch General Environmental Quality Standards (mg.kg^{-1})			Canadian CSQG (mg.kg^{-1})		Canadian PSQG (mg.kg^{-1})		Slovakia Methodological instruction of the MoE No. 549/98-2 (mg.kg^{-1})				Slovakia Methodological instruction of the MoE No. 549/98-2 – water solution (mg.l^{-1})		Slovakia Decision No. 531/94-540 (mg.kg^{-1})			Serbia Sediment quality (mg./kg^{-1})		
	M	L	V	ISQG	PEL	LEL	SEL	TV	MPC	TVd	IV	TV	MPC	A	B	C	TV	MAV	RV
Tl	-	-	-	-	-	-	-	1	2.6	-	-	0.04	1.6				-	-	-
V	-	-	-	-	-	-	-	42	56	-	-	0.8	4.3	120	200	500	-	-	-
Zn	480	103	2500	123	315	120	820	140	620	720	720	2.8	9.4	140	500	3000	140	430	720
Inorganic compounds																			
P total	-	-	-	-	-	600	2000	-	-	-	-	-	-	-	-	-	-	-	-
F total	-	-	-	-	-	-	-	-	-	-	-	-	-	500	1000	2000	-	-	-
S sulphide	-	-	-	-	-	-	-	-	-	-	-	-	-	2	20	200	-	-	-
Br total	-	-	-	-	-	-	-	-	-	-	-	-	-	20	50	300	-	-	-

Explanations:

TV – target value – negligible risk, undisturbed natural environment, uncontaminated sediment and 100% survival of aquatic organisms, represents 1/100 MPC);
MPC – maximum permissible concentration – represents the maximum permissible risk, the level ensuring the survival of 95% of all species of organisms in the given ecosystem;
TVd – tested value – the environmental risk is not expressed, the value lies in the interval between MPC and IV can be used for deciding on sediment management;
IV – intervention value – represents a serious risk; the concentration of a substance in which only 50% of all species of the ecosystem are protected;
A – reference value,

B – indication value (if value exceeded, site monitoring is required),
C – intervention value (if value exceeded, remediation measures are required);
MAV-maximum allowed value;
RV-remediation value (intervention value)

Canadian CSQG means Canadian Environmental Quality Guidelines.
Canadian PSQG means Provincial Sediment Quality Guideline.
Lowest Effect Level (LEL): indicates a level of contamination that can be tolerated by the majority of sediment dwelling organisms. Sediments meeting the LEL are considered clean to marginally polluted.
Severe Effect Level (SEL): indicates a level of contamination that is expected to be detrimental to the majority of sediment dwelling organisms. Sediments exceeding the SEL are considered heavily contaminated.
ISQG = interim sediment quality guideline.

For many categories of soil use, sediments, surface and underground waters, a long list of organic substances is included in national legislations. A list of these substances, including the maximum acceptable and normal values is difficult to achieve because of the dissimilar national legislations.

A short list found in most of the questionnaires of deliverable D 3.1.1.includes:
-**16 PAHs** - mononuclear and polynuclear aromatic compounds (Benzen, Etil-benzen, Toluen, Xilen, Stiren, Fenol, Benz(a)piren, Naftalina, Antracen, Fenantren, Fluoranten, Benzo(a)antracen, Crisen, Benz(ghi)perilen, Indeno(1,2,3-cd)piren, Benz(k)fluoranten).
-**7 PCBs** Bifenilipoliclorurat (PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180)
-**11 pesticides** gamma-HCH (lindan); HCH (suma alfa-, beta-, delta-HCH); DDT/DDD/DDE (suma); Aldrin; Dieldrin; Endrin; Drinuri (as sum) Atrazin; Endosulfan; Heptaclor; organo-stanic coumpounds.

For this abridged list, it is necessary to compare the maximum and normal values as set out in the national legislations, in the EU-WFD and in the Sediment Quality Guides.

It is worth mentioning that in the aquatic environment the danger of chemical elements resulting from biochemical activity must be analyzed for establishing the list of hazardous substances.

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I.3. List of national and international guides of techniques

This chapter regarded the lists of national, and international guides of techniques on the design of sampling, transport, storage, samples preparation (sieving, fraction extraction, separation, etc.) recommended in documents.

Most of the countries do not specify whether the standards (sampling, handling, preservation, screening, laboratory analysis for sediment samples) are mandatory in national legislation.
Based on the data provided in the questionnaires listed as annexes to deliverable D3.1.1, these standards are listed in Table 8 of Chapter III.
In chapter 2.IV there are specified the analytical standards corresponding to all methods of analysis (IV.2.2 – IV.2.8).
The sampling strategies listed in table 9 for water, sediments and biota were mentioned by the majority of country partners.

The data used in assessing the ecological and chemical status should come from composite samples, in accordance with the minimum recommendations regarding the collection of composite samples, their transport and storage contained in the series SR ISO 5667/2002. In case of using other standards of collection, transport and storage, these should reach at least the same precision and accuracy performances as the recommended standard.

The values of the foreseen indicators will be settled by means of analyses and measurements, performed in laboratories certified for the environmental field, using the national or European standards recommended for the respective indicator.

I.4. Recommended remedy measures

National legislations do not foresee remedial measures. There are indicated only the criteria to establish the poor quality of the analyzed environmental element, as well as its classification into the "intervention class" (name generally used by all partner countries).
The information available in the literature may be a support for the recommendation (in line with the Danube basin characteristics) of measures in the preparation of the guide.

II. PRACTICES, EXPERIENCES

II.1. Significant projects

Even before 2000, projects related to sediment monitoring have been carried out in the Danube River Basin (Table 6).

Table 6 – Joint projects carried out in the Danube Basin

Project Title	Period	Participant Countries
WATER	2007 - 2013	Bulgaria, Romania
Joint Danube Survey 1, 2, 3	2001, 2007, 2013	ICPDR
Romanian-Bulgarian cross-border joint natural and technological hazards assessment in the Danube Floodplain – ROBUHAZ-DUN	2007 - 2013	Romania, Bulgaria
Danube Floodplain	2018 - 2020	Romania, Austria, Bulgaria, Croatia, Czech Republic, Germany, Hungary, Slovakia, Slovenia, Serbia
Sustainable management of sediment resources (SedNet)	2002 - 2004	EUROPE(SedNetwork (https://sednet.org/)
FOREGS Geochemical mapping of Europe	1998 - 2005	Europe European Geological Surveys (EGS)
Geochemical Mapping of Agriculture and Grazing Land Soil in Europe (GEMAS)	2008 - 2014	Europe European Geological Surveys (EGS)
Trans-boundary contamination risk assessment and modelling for sustainable soil management, food safety and natural riverine habitat protection in the Drava River floodplain	2017 - 2018	Slovenia, Hungary
Reinforcing S&T Capacities of Two Emerging Research Centers for Natural and Industrial Pollutant Materials in Serbia and Slovenia (RESTCA-TERCE-NIPMSS	2008 - 2011	Slovenia, Serbia
HydroMorphological assessment and management at basin scale for the	2016 - 2019	Croatia,Italia

Project Title	Period	Participant Countries
Conservation of Alpine Rivers and related Ecosystem Services (HyMoCARES) https://www.alpine-space.eu/projects/hymocares/en/home		
Sava River Basin: Sustainable Use, Management and Protection of Resources	2004 - 2007	Slovenia, Croatia, B&H, Serbia
DanubeSediment „Danube Sediment Management - Restoration of the Sediment Balance in the Danube River“	2017 - 2019	Hungary, Austria, Romania, Germany, Bulgaria;, Croatia; Slovenia, Slovakia; Germany, Serbia
FramWat „Framework for improving water balance and nutrient mitigation by applying small water retention measures“	2017 - 2020	Poland, Slovakia,Hungary, Slovenia, Croatia, Austria

II.2. Significant papers

Table 7 lists guides and books published on the topic of monitoring carried out in the Danube Basin, some of them produced within the framework of common projects in this region.

Table 7 – Selected representative guides and books for the monitoring of the Danube Basin

Title	Publication Year	Covered Territory	Authors
FOREGS Geochemical Mapping Field manual	1998	Europe	Salminen, R. et al.
Geochemical Atlas of Europe-Part 1	2005	Europe	Salminen, R. et al
Geochemical Atlas of Europe-Part 2	2006	Europe	De Vos, W. et al.
EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) - Field manual	2007	Europe	EuroGeoSurveys Geochemistry Working Group

Title	Publication Year	Covered Territory	Authors
Sediment quality and impact assessment of pollutants	2008	Europe	Barcelo, D, & Petrovic, M.
Chemistry of Europe's Agricultural Soils-Part A	2014	Europe	Reimann, C. et al.
Chemistry of Europe's Agricultural Soils-Part B	2014	Europe	Reimann, C. et al.
EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) - Field manual	2008	Europe	EuroGeoSurveys Geochemistry Working Group
Geokemijski atlas Hrvatske (Geochemical Atlas of Croatia)	2009	Croatia	Halamić, j. & Miko, S. (eds)
Geokemijski atlas Siska (Geochemical Atlas of Siska)	2014	Croatia	Šorša, A. & Halamić, J
Assessment of the natural and anthropogenic sources of chemical elements in alluvial soils from the Drava River using multivariate statistical methods	2011	Slovenia, Croatia	Šajn, R., Halamić, J., Peh, Z. Galović, L., Alijagić, J.
Handbook for Sediment Qulity Assessment	2005		Simpson et al.
Monitoring Pesticide Residues in Surface and Ground Water in Hungary: Surveys in 1990–2015	2015	Hungary	Székács, A., Mörtl, M. & Darvas, B
2nd Sava River Basin Analysis Report	2016	Croatia	International Sava River Basin Commission

II.3. Monitoring sites

This chapter refers to existent waterbodies and sampling sites (Ramsar, Natura2000 etc.) and current quality monitoring stations of the Danube River.

Current quality monitoring stations of the Danube River, together with existent waterbodies and sampling sites were provided by every country. All countries provided tables with monitoring sites, their coordinates (in geographical system WGS84 or in national system), accompanied by the river or site name. Austria provided the requested monitoring stations on the Danube River already as ESRI shapefiles.

Some countries, as Croatia, Slovenia, Federation of Bosnia and Herzegovina in BiH, Serbia, Bulgaria and Ukraine provide also some attributes, distinguishing for example between monitoring stations for sediments, for river water, for the Trans National Monitoring Network (TNMN), or between monitoring HSs stations in sediments and in biota. All the atributes are listed in the annexes of the respective countries in deliverable D 3.1.1.

For some countries, (Austria, Germany), only surface water monitoring stations along the Danube were provided, while for others (Slovenia, Bosnia and Herzegovina, Montenegro, Ukraine), the stations referred only to the tributaries. There is also the third categories of countries which have Danube crossing or as a border of their territory (Bulgaria, Croatia, Hungary, Romania, Serbia, Slovakia and the Republic of Moldavia), which provided also monitoring stations for some tributaries. For example, In Romania there are listed and represented, besides the monitoring stations on the Danube, also those in the Somes – Tisa basin, which is a test zone of SIMONA project.

Of course, Austria and Germany have also numerous monitoring stations along the tributaries. For example, the Austria monitoring stations can be viewed at:

https://wasser.umweltbundesamt.at/h2odb/fivestep/abfrageQdPublic.xhtml

In Austria, for monitoring bottom sediments, the same Danube river surface water stations are used, but only at one station (Hainburg), chemical analyses have been performed recently (concentration of organic compounds in 2014). For suspended sediment there are 47 stations, which were provided by the Geological Survey of Austria as ESRI shapefiles.

For making up the maps, the Catchment Characterisation and Modeling database CCM version 2.1 of the Joint Research Centre of the European Commission was used. The respective dataset for the Danube Catchment had been produced in 2005 in the Lambert Equal Area projection (ETRS 1989 LAEA). The detailed description of the whole European dataset can be found in (Vogt et al., 2007).

The countries borders were downloaded from the EUROSTAT EC site at:

https://ec.europa.eu/eurostat/web/gisco/geodata/reference-data/administrative-units-statistical-units/countries

For the map physical background OpenStreets data were used. For each contry a map was computed based on the provided monitoring stations. Per total, there were provided 1293 monitoring stations in SIMONA countries questionnaires.

II.4. Polluters data availability

This chapter refers to the Data and metadata availability (including information on ambient or natural concentrations of HSs for establishing intervention measures) and to the list of past or current economic polluters referring to the direct effect on the quality of sediment in the Danube (the HSs whose possible concentrations are likely to be exceeded), information on the HSs biological effects, evidence of impact of anthropogenic activities.

Hungary: the polluters are known, but not listed. There is a lack of information about the contamination of overland flow and about the illegal sources.

Some other countries gave a link to the pollutants.

Austria: database of chemical analysis for water quality at:

https://wasser.umweltbundesamt.at/h2odb/fivestep/abfrageQdPublic.xhtml

Croatia: - register of major accidents at: http://iszz.azo.hr/rpot/nes.htm

Now this resource is not working and all needed information and raw data is located in Institute of Geology and Seismology.

It is supposed that increased concentrations of arsenic, lead, zinc, cadmium and ammonium are possible in the Croatian part of the Danube River Basin, due to their geogenic origin. In addition, anthropogenic contamination is possible due to big cities (Zagreb, Varaždin, Osijek, Slavonski brod) and industrial regions (NW Croatia, Slavonski brod, Sisak), as well as intense agriculture.

Republic of Moldavia: annual reports for the environmental status on the territory of Republic of Moldova are available from the site of State Hydrometeorological Service http://www.meteo.md/index.php/calitatea-mediului/c/

The River Basin Management Plan for the Danube-Prut and Black Sea pilot river basin district is available at:

https://www.euneighbours.eu/en/east/stay-informed/news/moldova-eu-supported-management-plan-danube-prut-and-black-sea-river-basin

The database of POPs polluted sites at: http://pops.mediu.gov.md.

Romania listed the main economic polluters, indicating also the polluting activities and the associated HSs.

In the Somes – Tisa basin, these polluters are listed for river, lakes, groundwater and air at:

https://www.eea.europa.eu/data-and-maps/data/waterbase-water-quality-1

https://www.eea.europa.eu/data-and-maps/data/waterbase-emissions-6

Serbia: http://www.sepa.gov.rs/index.php?menu=320&id=2015&akcija=showExternal

Slovakia: Within the monitoring of stream sediments in the programme of SGIDS, there are tables with data and metadata availability: basic localization of monitoring points, chemical composition, granulometric analysis and mineralogical analysis. In addition, there is a list of current economic polluters with direct effect on the Danube sediments.

Slovenia: Results of chemical analyses of sediments (besides water and biota) can be downloaded from the Slovenian water quality database via: http://www.arso.gov.si/vode/podatki/.

Sediment in the Drava river contains exceeded values of metals (values from 2016).

On the basis of these data (and of the list of big cities, legislation and literature data), which will be completed with relevant data by partner countries, the list of HSs for SIMONA project will be made.

II.5. Monitoring problems

Austria: monitoring is carried out in accordance with the WFD.

Croatia: did not implement sediment monitoring procedures, while water and biota monitoring are ongoing according to the guidelines of the WFD.

Procedures of monitoring in the past included the analysis of a smaller number of parameters and the sampling was done for more locations.

Hungary: Monitoring is carried out in accordance with the WFD.

Republic of Moldavia: The national monitoring program in Republic of Moldova is not working now on regular basis due to government reforming and lack of funding. There are several regional projects that can be a scientific support for the environmental monitoring in Republic of Moldavia.

Montenegro: The information on the state of environment with the Proposal of Measures is one of the basic documents in the field of environment and it is issued annually. The monitoring program is implemented by the institutions selected in the tender procedure, according to State laws.

Serbia: The implementation of the WFD requests a bigger number of parameters, which leads to additional costs. The country faces budget problems related to the analysis of so many parameters, therefore the sampling locations suffered a decline since 2011.

Therefore, it is proposed in SIMONA that a special attention to be paid to a realistic approach in the selection of relevant HSs, which will be analyzed in order to establish sediment quality.

Slovenia: Monitoring is carried out in accordance with the WFD.

Ukraine: The monitoring of the current status of the Danube water basin in Ukraine along the Tisza River is carried out by the Basin Department of the water resources of the Tisza River.

http://buvrtysa.gov.ua/newsite/?page_id=107

In the framework of the former agreement between the Ministry of Water Management of the Ukrainian SSR and the General Water Directorate of Hungary on the topic "Information and measurement system for flood forecasting and water resources management in the river basins" (Budapest, 16.12.1986), in 2000, the creation of an automated information and measurement system for forecasting floods and water resources management in the Tisza River Basin (AIVS-Tisza) was launched.

With assistance from the Government of Hungary, eight hydrological stations in the Tisza basin were built and put into operation in the Transcarpathian region.

III. INVENTORY OF SAMPLING METHODOLOGIES

This chapter describes the characteristic aspects regarding sampling methodologies for sediments.

III.1. Sediments

III.1.1. Type of sampled/measured sediment

All countries have experience with sediment sampling in the framework of scientific research projects according to chapter 2.II.1. In some countries the authorities monitor sediments. Tables 2, 3, 4 and 5 show this information.

III.1.2. Design of sampling strategy

For all partner countries, the sampling design, frequency and sampling locations are determined in accordance with the requirements defined in the "Guidance on the design of sampling programmes and sampling techniques" (ISO 5667-1:2006), as well as in the periodical (annual) monitoring programmes defined by competent ministries (Ministries of agriculture, forestry and water management, Environmental Protection Agencies etc.).
The sediments are monitored every 3 years (according to the Directive 2008/105/UE).
For the countries where sediment monitoring is not performed, the selection of the sample locations is made according to the objectives of the research projects and the design of the sampling strategy according to ISO 5667.

In Slovakia, the *Geochemical Mapping Programme* (in SGIDS), notably at large regional scales, requires the selection of an optimum geological material to be sampled. The sampled material should not only have suitable geochemical properties, but should be also available more or less throughout the mapped area. Another very important fact that should be borne in mind is that the same sampling procedures must be used throughout the sampling campaign, and all over the sampled area. Each collected sample is stored in a separate polyethylene bag. Where it is possible, 1.2 kg of the finest clay material were collected from at least three points over a distance of about 20 m along the stream.
The Water Research Institute in Slovakia uses for bottom sediments sampling the UWITEC Core tube sampler (and its components) working on the gravity principle, with a telescopic rod and the possibility of driving straight into the sediment.

In Ukraine, in order to assess anthropic pollution during ecological and geochemical studies of bottom sediments, water flow sites with oozy sediments are selected, which in most cases (if there are man-made sources of water flow contamination) correspond to the so-called "man-made" sediments (oozy fraction <0.1 mm, fully concentrating the chemical pollution elements). For sampling of bottom sediments in the watercourse, the selected locations are those in which sludge is accumulated (entrance to bays, places behind the banks with backflow, etc.). Sampling takes place once a year, in the summer time, during the period of lowest water.

III.1.3. Parameters of sediment quality/quantity measured in situ

Only Austria answered this question, the in situ measured parameters being: electrical conductivity, pH, redox potential (in water-saturated sediments).
In Romania the quantity of collected sediment depends on the texture, but no parameters are measured in situ.

III.1.4. Sampling devices for in situ measurements

In some questionnaires there are listed: shovel (made of wood or stainless steel), drills for manual drilling or Scissor grab (of stainless steel), such as Van Veen grab sampler/Graifer/ Core sampler, PVC spoons. The sediment is stored in a glass (650 mL).
A detailed description of the sampling technique is made in the Romanian questionnaire:

- for sediments in suspension, it is used the rapid collector Nansen bottle (cylinders with flaps for sediments).
- for dragged sediments the frequently used devices consist in: trap Nansen bottle (ISCH type) and sieve Nansen bottle.
- for river bed sediments, the under water sampling is done with GRAIFER, CAROTIER, and from the floodplain (dry sampling) with an ordinary shovel.

More explanations regarding the collecting procedure are found in the deliverable D3.1.1.

III.1.5. Methodology for in situ measurements

In Austria in situ measurements are done with multi-parameter portable devices. The instruments are calibrated prior to the measurement campaign (and for pH every morning).

III.1.6. Tools for collecting samples for laboratory measurements

At this question, answers were received from several countries. Austria, for example, uses stainless steel shovels and sieves, according to DIN 4188.
Various devices are used in the Republic of Moldavia: Ekman dredge for soft sediments on deeper water sites, simple cylinders for soft and thin sediments (10 – 30 cm), Auger sampler for thicker sediments.
In Ukraine a plastic scoop, or a stainless steel blade is used for 0.2 - 0.3 m thick silt and sandy sediments. For 0.3 - 3.0 m thick mud, the Giller peat drill is used.

III.1.7. Methodology of sample collecting for laboratory measurements

To this question, there are detailed answers for many countries. Information refer to similar procedures according to ISO standards.
Generally, as the questionnaire of Slovenia shows: "the sediment sample is wet sieved through sieves (made of inert plastics) with a size of 200 μm and then of 63 μm. The fraction with a grain size below 63 μm is used for chemical analysis. Water from the same surface water was used for sieving."
In the case of preparation of the sample for further analysis, as Croatia shows: "sampling is conducted according to the parameters intended to be analyzed later":
a) sampling for polar parameters (pesticides, pharmaceuticals, hormones, personal care products etc.) is conducted only after the water has drained, and as close as possible to the point where the sample was collected. The sediment sample is grabbed with the clean plastic spatula/spoon (inert plastics), to the depth of maximum 2 cm. The sample is stored in a dark glass bottle.
b) sampling for all other parameters is conducted from the watercourse, using polyethylene spoon. The sample is taken from the sediment surface or up to 1 cm deep. The samples should be composite, taken from three different points within a perimeter of 2 m. The sample is stored in a glass or plastic bottle, overflown with water from the sampling location before sealing the bottle.
Sample homogenization is conducted by mixing and, for some samples, by sieving.
In Ukraine an average sample of not less than 0.5 kg is put in a white cloth bag marked with a label. The sample will be dried in a well ventilated room (under a canopy) at ambient temperature and swept through during drying. After drying, the sample is sieved through a nylon sieve with a diameter of 1 mm, divided in four parts (for laboratory samples and a duplicate). For sample identification in the laboratory, the neccesary data are written on the paper bags. The duplicate samples are stored in a kraft paper bag or polyethylene container (with the appropriate markings, too), placed in a dry, cool room.

Figure 1 below shows the sample preparation scheme used by IGR for various analyses of the Danube and Danube Delta sediments.

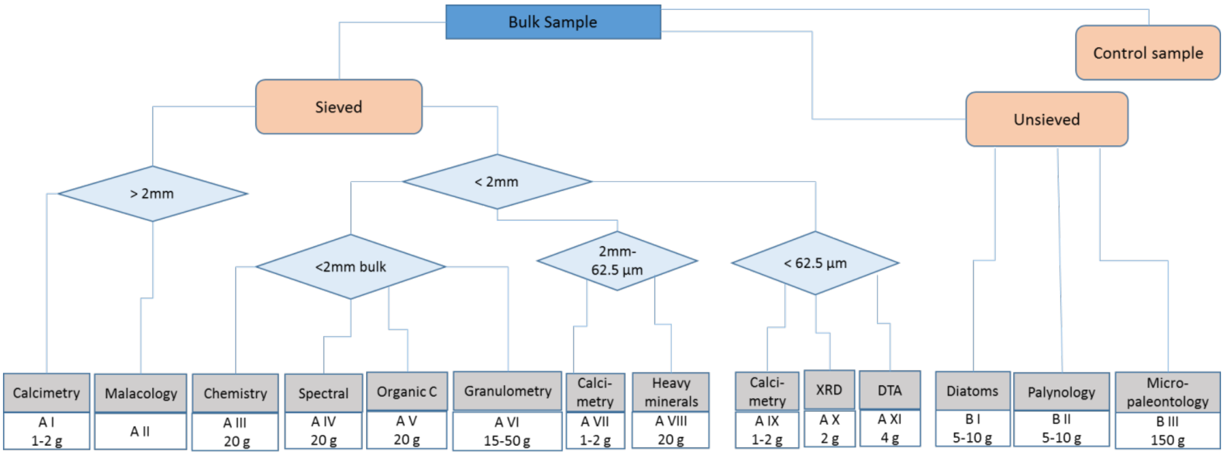


Fig 1. Sample preparation scheme for various analyses of the Danube and Danube Delta sediments

According to the Romanian partner (TUCN), for the tributaries in the Somes – Tisa catchment, sampling is done as follows: the collected sample (with the probe or shovel) is poured on a tray; the water is drained from the tray and the sample is spread on a piece of cloth to drain all the water; the sample is very well mixed, then it is spread in a layer of the same thickness; one part (one quarter, one half etc.) is taken from the global sample, depending on the size of the sample and texture. The weight of the global sample depends on the maximum diameter of the sediments, as follows:

- when the maximum diameter is greater than 7 cm (cobble), the weight of the aggregate sample should be about 10 kg;
- if the maximum sediment diameter is between 3 and 7 cm (pebble), the weight of the aggregate sample will be 3 - 5 kg;
- if the maximum diameter is between 1 and 3 cm (coarse gravel), the weight of the bulk sample will be about 1 kg;
- for a maximum diameter of less than 1 cm (fine gravel), the average sample will be several hundred grams.

The average sample is placed in a strong cloth bag.

The following data shall be filled in on a sheet of paper: the river, hydrometric station, the collecting date, the weight and the diameter of each cobble larger than 8 - 10 cm that was part of the average sample, but no longer inserted into the bag.

III.1.8. Transport methodology of samples for laboratory measurements

Transport of the samples is done with cooling at 2˚C - 8˚C. If it is intended to store the samples for longer periods (more than a month), it is recommended to freeze the samples at -20˚C.

A very detailed description is offered by Slovakia questionnaire, according to Geochemical Mapping Field Manual (Stream sediments) and Reservoir Sampling (Water Research Institute WRI – VÚVH). Sediment sampling, sample transport and sample conservation are standardized by EN ISO 5667- Part 15*: Guidance on the preservation and handling of sludge and sediment samples*.

III.1.9. Sample archiving

At this question, the answers are centralized in Table 8.
A rich experience exists in all countries. A national monitoring according to a procedure guide exists only in few countries.

III.2. General conclusions

For water, soil, sediments and biota samples the protocols for sampling, transport and storage are conform to the following ISO documents:

Table 8 - Protocols for sampling, transport and storage used for sediments, soil, water and biota.

Procedure	Sediment	Soil	Water	Biota
SAMPLING - procedures to locate points from which samples may be taken for examination - recomandated instruments that may be installed for in situ measurement including statistical implications - methods of collecting samples - procedures for determining quantities, number of samples -freqvency of sampling - what laboratory samples are to be taken, how they are to be taken and from	ISO 5667-1:2008. Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques for all aspects of sampling of water (including waste waters, sludges, effluents and bottom deposits). ISO 5667-17:2012. Water quality. Sampling. Part 17: Guidance on sampling banks and suspended material ISO 5667 Part 12: Bottom sediments. Water quality -- Sampling -- Part 13:2011 Guidance on sampling of sludges	ISO 10381-1:2002. Soil quality -- Sampling -- Part 1: Guidance on the design of sampling programmes Part2:Guidance on sampling techniques) (has been revised by ISO18400-101:2017; ISO 18400-104:2018; ISO18400-107:2017) ISO 18400-100:2017. Soil quality -- Sampling -- Part 100: Guidance on the selection of sampling standards https://www.iso.org/standard/67788.html ISO 18400-101:2017Soil quality -- Sampling -- Part	ISO 5667-1:2018. Guidance on the design of sampling programmes and sampling techniques ISO5667-6:2014. Guidance on sampling of rivers and streams ISO 5667-11:2009. Water quality — Sampling — Part 11: Guidance on sampling of groundwaters. https://www.iso.org/standard/42990.html Part4: Lakes and water reservoirs Part5: Drinking water Part8: Rainfall Part10: Waste Part 15: Natural waters	ISO 5667-16:2017. Water quality. Sampling. Part 16: Guidance for biological analysis Water Framework Directive (2000/60/EC) Guidance document No.32 on biota monitoring HRN EN 13946:2015 (Guidance standard for the routine sampling and pretreatment of benthic diatoms from rivers and lakes) HRN EN 15708:2010 (Advisory norm for testing, sampling and laboratory

Procedure	Sediment	Soil	Water	Biota
where they are to be taken, in order that the objectives of the investigation programme can be achieved		101: Framework for the preparation and application of a sampling plan https://www.iso.org/standard/62842.html ISO 18400-102:2017. Soil quality -- Sampling -- Part 102: Selection and application of sampling techniques. https://www.iso.org/standard/62843.html ISO 18400-103:2017. Soil quality -- Sampling -- Part 103: Safety https://www.iso.org/standard/62363.html ISO 18400-104:2018. Soil quality -- Sampling -- Part 104: Strategies https://www.iso.org/standard/65223.html ISO 18400-202:2018 Soil quality -- Sampling -- Part 202: Preliminary investigations	ISO 5667-23:2011. Water quality -- Sampling -- Part 23: Guidance on passive sampling in surface waters https://www.iso.org/standard/50679.html	analysis of phytobenthos in shallow streams

Procedure	Sediment	Soil	Water	Biota
		https://www.iso.org/standard/65225.html ISO 18400-203:2018. Soil quality -- Sampling -- Part 203: Investigation of potentially contaminated sites https://www.iso.org/standard/65226.html EPA/625/12-91/002 EPA/600/R-92/128 -Alaska Department of Environmental Conservation, 2009, Draft Guidance on MULTI INCREMENT Soil Sampling, Division of Spill Preventions and Response, Contaminated Sites Program, www.itrcweb.org/ism-1/references/multi_increment.pdf		
SAMPLING Recording and reporting, correlating, decision making		ISO 18400-107:2017.Soil quality -- Sampling -- Part 107: Recording and reporting	Water quality -- Sampling -- Part 14::2014 Guidance on quality assurance and quality control of	SRPS EN 27828:2009Water quality - Methods of biological sampling - Guidance on handnet

Procedure	Sediment	Soil	Water	Biota
		https://www.iso.org/standard/62365.html ISO 28258:2013 Soil quality -- Digital exchange of soil-related data https://www.iso.org/standard/44595.html Now under development ISO 28258:2013/DAmd 1 https://www.iso.org/standard/72743.html ISO 15903:2002 Soil quality -- Format for recording soil and site information https://www.iso.org/standard/29028.html	environmental water sampling and handling	sampling of aquatic benthic macro-invertebrates
TRANSPORT AND STORAGE (methods for containing, storing and transporting samples to prevent deterioration or contamination)	ISO 5667-15:2013. Water quality - Sampling - Part 15: Guidance on the preservation and handling of sludge and sediment samples		Part 5667-15: Natural waters ISO5667-2018Water quality -- Sampling -- Part 3: Preservation and handling of water samples https://www.iso.org/standard/72370.htm	

Regarding the design of the sampling strategy for water, sediments and biota samples, Table 9 contains the information provided by all partners.

Table 9 – Sampling strategies for water, sediment and biota

Country	SAMPLES			Observations
	WATER	SEDIMENT	BIOTA	
AT	Federal Environment Agency Austria (UBA)	-**bottom and floodplain** (Geological Survey of Austria) -**bottom, floodplain and suspended** (UBA) Sampling of stream sediments is standardized by the Austrian norm ÖNORM G 1031	The Environment Agency of Austria collects biota samples according to the GZÜV-monitoring network.	For water sampling, UBA follows a fixed design of location and number of sampling sites. Sampling frequency of water at risk is 4 times per year. Surface water sampling frequency is 1 time per month, additional sampling is carried out sporadically depending on governmental contract or running project. -Biota sampling according to the GZÜV-monitoring network
BA	Water sampling is executed by the ExEA	Sediment sampling is executed by the ExEA	Phytoplancton, phytobenthic, macrophytic, benthic invertebrate and ichtyofauna.	Water and sediment sampling strategy is defined by the River Basin Management Plan for the Danube Region (2016-2021)
BA-SRP	Sampling locations for trend analysis: upstream/downstream of the country border, near the confluence points of	There are no data on sediment.	Phytoplankton, phytobenthic, macrophytic, benthic invertebrate and ichtyofauna	Sampling locations for ecological and chemical status of certain water bodies and sampling locations for background concentrations are situated at specific

Country	SAMPLES			Observations
	WATER	SEDIMENT	BIOTA	
	bigger streams, downstream of larger contamination sources.			locations, different from those for trend monitoring. Priority substances are monitored in rivers and lakes every month. Other physico-chemical parameters are monitored every 3 months; Hydrology – continuously (respectively monthly), other hydromorphological features – every 6 years; fish, macroinvertebrates and flora - every 3 years; phytoplankton – every 6 months.
BG	Sampling strategy is defined by the River Basin Management Plan for the Danube Region (2016-2021) and is executed by the ExEA.	Sampling strategy is defined by the River Basin Management Plan for the Danube Region (2016-2021) and is executed by the ExEA.	БДС EN ISO 5667-16:2017 Water quality. Sampling. Part 16: Guidance for biological analysis	
HR	According to the methodology requested by Water Framework Directive (WFD).	Croatia does not monitor yet the sediments, but it monitors water and biota. Water and biota are investigated according to the methodology requested by WFD.	fish tissue, shellfish, gammaridae	Sampling biota (2017-2019) design is done in order to fulfill WFD requirements (2000/60/EC) (Guidance document No.32 on biota monitoring). During next three years, from 2019 onward, this methodology will be tested on 41 surveillance monitoring stations for all required parameters (chemical status). Frequency will be 1 per year. The same parameters are planned to be analyzed in

Country	SAMPLES			Observations
	WATER	SEDIMENT	BIOTA	
				the sediment on all those stations, as well. Poly-aromatic hydrocarbons are a specific test in the shellfish and gammaridae tissue, but sampling is difficult since they live in clean water and sandy bottom. Radionuclide monitoring in water, sediment and biota, at country level, is performed by Institute for Medical Research and Occupational Health, Zagreb.
HU	According to the methodology requested by Water Framework Directive (WFD).	Hungary does not accredited monitor yet the sediment. Hungary samples bottom sediments.	fish (mainly chub)	investigating monitoring program to find the best sampling sites for long-term biota and sediment monitoring
MD	Centre of Environmental Quality Monitoring (CEQM) of Hydro-meteorological Service of Republic of Moldova performs hydro-biological monitoring in Danube – Prut river basin by 6 groups of hydro-biologic indicators	All types of sediments	CEQM monitoring: bacterioplankton, phytohytoplankton, zooplankton, phitobentos,macrophytes.	Biota monitoring(Institute of Zoology) for scientific projects on territory of Republic of Moldova including Danube – Prut river basin. Institute of Geology and Seismology takes samples of plants, agriculture crops, fish, milk, eggs, and meat for the risk assessment of the pollution in scientific projects.
ME	Systematic testing of the quality of surface and groundwater in the territory of Montenegro is	Montenegro is not monitoring yet the sediments.	Agency for the Protection of Nature and Environment implements	There is a lot of experience across within projects. The locations of the biota monitoring program are different each year.

Country	SAMPLES			Observations
	WATER	SEDIMENT	BIOTA	
	carried out in accordance with the Program on Systematic Testing of Quantities and Water Quality in Montenegro, which is adopted by the competent Ministry of Water Management, Forestry and Agriculture. The program defines a network of stations for water quality, as well as the scope, type and frequency of water quality tests. In situ measured parameters: temperature, pH value, electrolytic conductivity, turbidity and alcalinity.	Montenegro samples bottom sediments.	a biodiversity monitoring program since 2013. *Turbellaria, Hirudinae, Oligochaeta, crabs (Cladocera, Copepoda, Decapoda) and insects (Odonata, Placoptera, Trichoptera, Ephemeroptera, Diptera).*	Selecting the biota sampling location: sites of national importance, protected areas and NATURA 2000 habitats.
RO	National Organization of Romanian Waters (According to the methodology requested by Water Framework Directive)	Sediments in suspension, dragged sediments, river bed sediments (experience within projects)	National Organization of Romanian Waters (plankton, bacteria, periphyton, protozoa, algae, fungi, macrophytes, macro invertebrates, bivalves and fish)	The design of biota sampling is done in order to fulfill WFD requirements (2000/60/EC) and to establish water quality. Biota is selected in agreement with the dangerous substances that might be accumulated in the living organisms.

Country	SAMPLES			Observations
	WATER	SEDIMENT	BIOTA	
			The biological elements which form the basis of the assessment of the ecological status of the Danube and major rivers will be taken into consideration according to the following ranking: 1. phytoplankton; 2. phytobenthos; 3. macrozoobenthos; 4. macrophytes / angiosperms; 5. fish	The ecological status of continental aquatic ecosystems must be established on the basis of biological quality elements, taking into account the hydromorphological, chemical, physico-chemical, and specific pollutants indicators that influence biological indicators. The assessment of these elements may indicate the presence of natural conditions, their minor alterations or the magnitude of the anthropic impact and, respectively, the state of water body quality over a certain period of time. For artificial or irreversible modified aquatic ecosystems, the ecological potential is established as: very good (E), good (B), or moderate (M).
SK	Methodology developed within the project „Geochemical Atlas of Europe. Part 1 - Background Information, Methodology and Maps“. In situ measured parameters: temperature (water, air), pH, Eh, Ec, O2	There is the Geochemical Mapping Programme (SGIDS) for Stream sediments. The Water Research Institute WRI – VÚVH)Tperforms the Reservoir SEDIMENT SAMPLING.		A precised and detailed sampling strategy for water and sediments was established in FOREGS GEOCHEMICAL MAPPING FIELD MANUAL. http://weppi.gtk.fi/publ/foregsatlas/index.php

Country	SAMPLES			Observations
	WATER	SEDIMENT	BIOTA	
SI	The program for monitoring the status of waters for the period 2016 - 2021 (Water Management Plan) has been prepared in accordance with national and European legislation. Slovenia is involved in the Transnational Monitoring Network (TNMN) on the Danube tributaries, on the Sava and the Drava Rivers.	Bottom sediments. For the general chemical status in Slovenia, sediments are monitored at most surveillance measuring points; In addition, they are also monitored at sites where pollution loads are detected (eg PCBs in Krupa, Lahinja, Kolpa). No parameters are measured in situ.	Fish (priority species *Salmo marmoratus* and *Brown Trout.*) crustaceans and mollusc s In inland waters. The TNMN biological monitoring program is adapted to the requirements of the Water Framework Directive (Directive 2000/60 / EC).	Sediments are monitored for trends every 3 years, in accordance with Directive 2008/105/EU, Decree on the status of surface waters and the Rules on the monitoring of surface waters.
SR	Sampling is done in accordance with the Annual monitoring program, as well as the Regulation on limit values of polluting substances in surface and groundwaters and deadlines for their achievement. In situ measured parameters include: water trasnparency, alkalinity, pH, Ec, turbidity, and	Bottom sediment (The Serbian Environmental protection Agency)	Biota is not monitored by the Serbian Environmental Protection Agency within it's Danube river monitoring program.	The design of sampling, frequency and sampling locations are determined in accordance with the requirements defined in the Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1:2008), as well as the annual monitoring program defined by the Ministry of agriculture, forestry and water management. Responsible institution for radionuclide monitoring in the environment, is the National Directorate for Radiation and Nuclear Safety and Security. http://monradrs.srbatom.gov.rs/

Country	SAMPLES			Observations
	WATER	SEDIMENT	BIOTA	
	presence of certain compounds.			The Annual Monitoring program does not include the monitoring of specific radionucleides but rather total beta radioactivity is monitored. However, radionucleide concentrations are monitored through projects and specific requests.
UA	Sampling planning is carried out according to DSTU ISO 5667-1: 2003, DSTU ISO 5667-2: 2003, DSTU ISO 5667-3: 2001, DSTU ISO 5667-4: 2003, DSTU ISO 5667-6: 2001. No in situ parameters are measured.	Bottom sediments. Sampling locations are selected according to DSTU ISO 5667-12-2001.	No biota sampling.	For sampling of bottom sediments in the watercourse, places are selected in which sludge deposits are accumulated (entrance to bays, places behind the banks with backflow, etc.). Sampling takes place during the summer low water period once a year.

IV. INVENTORY OF LABORATORY METHODOLOGIES

According to “Guidance document No. 25 on chemical monitoring of sediment and biota under the Water Framework Directive”, and other ISO standards and countries experiece for analysing water, sediment and biota, new laboratory methods have been standardized, in accordance with ISO/IEC 17025 “General requirements for the competence of testing and calibration laboratories”.

IV.1. Mechanical preparation of samples

Inventory techniques and procedures for sediment samples are similar in partner countries and consist of: drying, sieving, grinding, homogenization (e.g. in Slovakia - Fig. 2)

Generally sediment sample preparation is done according to standard methods involving crushing, grinding, wet sieving (disk mill - grain size <60 μm) for metal analysis; chemical drying with sodium sulphate (water-free) and grinding for organic substances.

- in-situ sieving to <180μm and <40μm grain size (two samples per site);
- drying of sample at ambient temperature (<30˚C) until water content <2 wt%;
- crushing of components which agglomerated during drying using porcelain mortar;
- storage of sample in polyethylene bottles (2 bottles per sample, one for analysis, one retention sample).

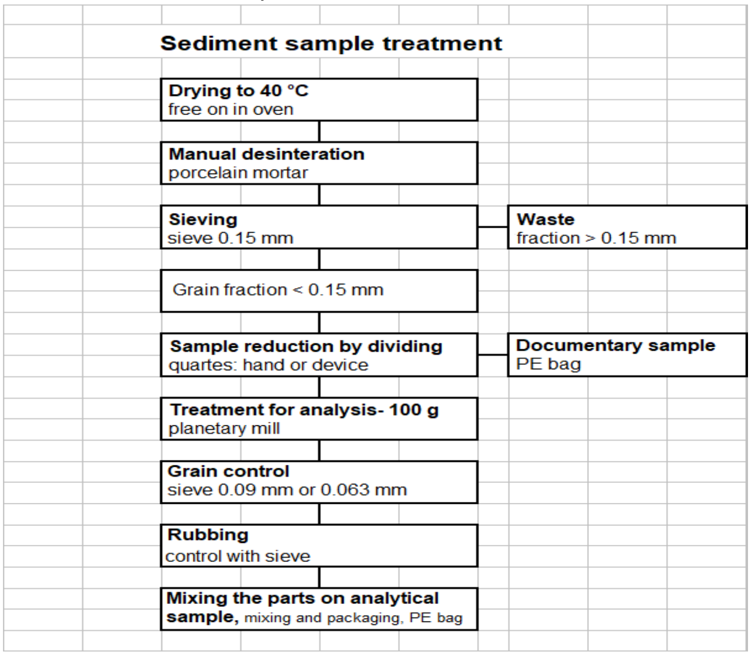


Fig. 2 Procedure for sediment samples preparation in Slovakia

IV.2. Chemicals

The chemical preparation of the samples is done in accordance with the method, the analysis technique and depends on the sample type (water, sediment, biota) Sample preparation, usually as part of analytical method (e.g. acid digestion, etc.) for the hazardous substance analyzed is in agreement with the matrix in which this is being analyzed (water, sediment, sludge). The most relevant parameters of the extraction methods (the nature of the reagent according to type of sample, power for wave digestion, extraction time or temperature) are sets in analitycal quides. Generally all partners mention the same documents:

- For example, related to soil: Guidance Document No: 25 (Guidance on chemical monitoring of sediment and biota under the WF Directive 2000/60/EC) or ISO 11466:2004 (Soil quality -- Extraction of trace elements soluble in aqua regia, Pretreatment of samples for physicochemical analyses) and according to ISO 5667-15:2009 (Water quality - Sampling - Part 15: Guidance on the preservation and handling of sludge and sediment samples) mechanical preparation are made.
- For metal analysis in solids by ICP-AES technique, or ICP-MS, or AAS the following procedure is used: 100 mg of the sample is transferred to a Pt-dish, mixed with 2.5 ml HNO_3 (65%), 2.5 ml $HClO_4$ (60%) and 5 ml HF (40%). This solution is concentrated to near dryness. Then 5 ml HNO_3 (65%) is added to the residue and the solution is heated two times until all fumes evaporate. Finally, the residue is mixed with 0.5 ml HNO_3 (65%) and diluted with 50 ml H_2O. The following elements are measured: Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Nb, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Hf, Ta, W, Pb, Bi, U. According to ISO 17294 (Application of inductively coupled plasma mass spectrometry (ICP-MS)) using microwave acid digestion ICP-MS,ICP-OES or AAS, instruments are used with appropriate ISO analitical standard for sediment analysis. For example, a river sediment microwave and acid digestion procedure recomandated from MILESTONE laboratoratory uses a progam suitable for digestion of 6 samples simultaneously. A two-steps procedure is required: "after weighing the samples, 4ml of H_2SO_4 96%, and 3ml of H_3PO_4 85% are added and then the electric program began (5 minutes for each of the following four steps power (250W, 400W, 650W, 350W). After cooling down, the vessels are opened with care (the reaction is exothermal), and 6ml of HNO_3 65% and 12ml of HBF_4 40% are added. The vessels are left open for few minutes, then are capped and closed with the torque wrench or with the capping tool.This digestion procedure is suitable for metals determination".

- Preparation of the sample and procedure for **XRD** measurements: Whole rock and clay mineralogy (< 2µm fraction) is determined by XRD at the Department of Mineral Resources of the Austrian Geological Survey. Samples for bulk mineral analysis are dried, ground and loaded into a sample holder as a randomly oriented powder. The semi-quantitative mineralogical composition is obtained by the SEIFERT AutoQuan software using the Rietveld method. Samples for clay mineral analysis are treated with 15% H_2O_2 for 24h in order to remove organic matter and subjected to ultrasound for further disaggregation. The <2 µm fractions are separated by centrifugation. The clay fractions are saturated with 1N KCl and MgCl solutions by shaking for 24h, and thereafter washed in distilled water. Oriented mounts of the <2µm fractions were made through the suction of 25 mg of suspended clay placed on a porous ceramic plate and left to dry at room temperature. Such oriented XRD mounts are subsequently analysed in air-dried, ethylene glycol, dimethylesulfoxide and glycerol treated states. The clay samples are run from 2 – 50 °2Θ using the same measurement setup, as in the case of bulk-rock samples. Identification of clay minerals was carried out according to Moore and Reynolds (1997). The clay minerals were identified by their basal (00l) diffraction lines on glycolated specimens of the Mg-treated samples. The relative percentages of the clay minerals in the fraction < 2 µm are determined after Schultz (1964).
- Preparation of the sample and procedure for **XRF** measurements: Sample preparation follows a standardized method involving crushing, grinding, sieving (disk mill - grain size <60 µm) and preparation of pressed pellets.
  1) Pellet analysis (5 g of a powder is homogenized and mixed well with 1 g of binder – wax, and then pressed with 20 tons to a 40 mm pellet).
  2) Fused bead analysis (0.5 g of a powder is homogenized with 7 g of Lithiumtetraborate and then fused at ~ 1100 °C to a 32 mm bead. For some materials a pre-oxidation may be necessary).
  3) Powder analysis (4 g of a powder is poured into a sample cup with an inner diameter of 32 mm. The bottom of a sample cup is covered with a 4 µm polypropylene film).

Accuracy and precision are ensured by the application of analytical standards. Major applied methods are certified according to ISO/IEC 17025 and other documents that provide analytical performance:
-ISO11929:2010 Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation – Fundamentals and application;
-JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement;

-Measurement uncertainty. IAEA-TECDOC-1585, IAEA, Vienna 2008;
-Guide to expression of Uncertainty in Measurement. (GUM), 1995.ISO;
-“The Fitness for Purpose of Analytical Methods; A Laboratory Guide to Method Validation and Related Topics (ISBN 978-91-87461-59-0. Available from www.eurachem.org.).

Analytical results are verified by the use of certified substances or materials (CRMs) or by interlaboratory comparisons. The list of equipment (combined systems) for analysis (IV.2.2-IV.2.8 in the questionnaires) is presented in table 15.

IV.2.1. Procedure for organic matter

The content of organic matter (humus) in the soil is established by calcining to constant weight.
The GC-MS procedure for organic compounds content determination in sediment (PAH, inorganic compounds, PCB, dioxins, PBDE, DEHP, nonylphenol, octylphenol, triclosan, triclosan-methyl, AHTN, HHCB and others) is listed in in most of the questionnaires.
For example, in Bulgaria:

- total organic carbon; dissolved organic carbon; soil/ sediment (BSS ISO 14235:2002);
- soil quality; organic carbon determination by sulfo-chrome oxidation.

IV.2.2. ICP-MS, ICP-AES systems

By ICM-MS method, according to ISO 17294, the following elements are measured: Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Nb, Mo, Ag, Cd, In, Sn, Sb, Cs, Ba, Hf, Ta, W, Pb, Bi, U. By EPA 6020 the following elements are measured: As, Al, B,Co,Cr, Cu, Fe, Ni, Pb, Zn, Sb. The detection limit depends on each element, ranging in the interval 0.1µg/l - 1 µg/l for trace elements and 1 - 50 µg/l for alcalynes.The countries list of ICP-MS instrument systems is shown in Table 15.

ISO 17294-1:2004 Water quality -- Application of inductively coupled plasma mass spectrometry (ICP-MS) specifies the principles of ICP-MS and provides general directions for the use of this technique for determining elements in water. Generally, the measurement is carried out in water, but gases, vapours or fine particulate matter are described in the separate parts of ISO 17294.
ISO 17294-2:2016 specifies a method for the determination of the elements aluminium, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, caesium, calcium, cerium, chromium, cobalt, copper, dysprosium, erbium, gadolinium, gallium, germanium, gold, hafnium, holmium, indium, iridium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese, mercury, molybdenum, neodymium, nickel, palladium, phosphorus, platinum, potassium, praseodymium, rubidium, rhenium, rhodium, ruthenium, samarium, scandium, selenium, silver, sodium, strontium, terbium, tellurium, thorium, thallium, thulium, tin, tungsten, uranium and its isotopes, vanadium, yttrium, ytterbium, zinc and zirconium in water (for example, drinking water, surface water, ground water, waste water and eluates). Taking into account the specific and additionally occurring interferences, these

elements can also be determined in digests of water, sludges and sediments (for example, digests of water as described in ISO 15587 1 or ISO 15587 2).

The working range depends on the matrix and the interferences encountered. In drinking water and relatively unpolluted waters, the limit of quantification (xLQ) lies between 0.002 µg/l and 1.0 µg/l for most elements. The working range typically covers concentrations between several pg/l and mg/l depending on the element and pre-defined requirements.

A list of analyzed elements and their detection limits in digested solid material and water are taken from the Austrian questionnaire (Table 10) and are similar to those reported in most parteners countries owning these type of equipment (ICP-MS).

The following standards are also used:

- EN 1617l 2016 - Processed sediment and soils. Element determination with (lCP-MS).
- EN ISO 11885 (75 7466) - Determination of Ag, Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Sr, Ti, V, Zn in water and aqueous extracts (ICP-OES).

In Serbia EPA Method 8270 D:2014 is used for semi-volatile organic compounds by GasChromatography/Mass Spectrometry. The limits of quantification are listed in deliverable D3.1.1.

Table 10 - Analyzed elements and their detection limits in digested solid material and water in Austria

ELEMENT	DETECTION LIMIT	ELEMENT	DETECTION LIMIT	ELEMENT	DETECTION LIMIT
Calcium (Ca^{2+}) – mg/l	0,01	Copper (Cu) – mg/l	0,0001	Manganese (Mn^{2+}) – mg/l	0,0001
Magnesium (Mg^{2+}) – mg/l	0,001	Mercury (Hg) – mg/l	0,0001	Aluminium (Al) – mg/l	0,0001
Sodium (Na^{+}) – mg/l	0,01	Molybdenum (Mo) – mg/l	0,0001	Arsenic (As) – mg/l	0,001
Potassium (K^{+}) – mg/l	0,05	Nickel (Ni) – mg/l	0,0001	Cadmium (Cd) – mg/l	0,0001
Strontium (Sr^{2+}) – mg/l	0,001	Lead (Pb) – mg/l	0,0001	Cobalt (Co) – mg/l	0,0001
Barium (Ba^{2+}) mg/l	0,0001	Antimony (Sb) – mg/l	0,0001	Chromium (Cr) – mg/l	0,0001
Lithium (Li^{+}) – mg/l	0,0001	Silicon (Si) - mg/l	0,0001	Zinc (Zn) – mg/l	0,001
Rubidium (Rb^{+}) – mg/l	0,0001	Uranium (U) – mg/l	0,0001	Iron (Fe^{2+}) – mg/l	0,001
Caesium (Cs^{+}) – mg/l	0,0001	Vanadium (V) – mg/l	0,0001		

IV.2.3. AAS systems

By AAS method, according to ISO 12020 the trace elements (Ni, Cd, Pb, Cr, As, Cu) are measured in water. The detection limit depends on each element, being between 0.05 μg/l and 0.5 μg/l, and for all elements there is an analitycal standard.

According to ISO 11047/1998 - Soil quality -- Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc are performed by flame and electrothermal atomic absorption spectrometric methods.

AAS-systems equipped by Flame, (flame atomic absorption spectrometry), THGA and Hydride Generation System (FIAS400), GFAAS (Graphite furnace atomic absorption spectrophotometry) for Pb and CVAAS analyzer for Hg (according to EPA 245.7) are listed in Table 15.

It is also used EPA Method 245.7 - Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry.

IV.2.4. XRF

The elements and/or compounds (HSs) measured by XRF are: Al_2O_3, As, Ba, CaO, Cr, FeO, K_2O, MgO, MnO, Na_2O, Ni, P_2O_5, Pb, Rb, SiO_2, Sr, V, Y, Zn and Zr. The detection limit for metals is 1ppm and for oxydes 0.01%-1%. A list of analyzed oxides and their detection limits in solid materials are taken from the Austrian questionnaire and are similar to those reported in most partner countries owning these type of equipment (ED-XRF or WD-XRF).

Table 11 – XRF-analyzed oxides and their detection limits in solid materials in Austria

ELEMENT	DETECTION LIMIT	ELEMENT	DETECTION LIMIT
SiO_2	1 %	Na_2O	0.1 %
TiO_2	0.01 %	K_2O	0.01 %
Al_2O_3	0.01 %	P_2O_5	0.01 %
FeO	0.01 %	MgO	0.1 %
MnO	0.01 %	CaO	0.05 %

As, Ba, Cd, Ce, Co, Cr, Cs, Cu, La, Nb, Nd, Ni, Pb, Pr, Sr, V, Y, Zn, Zr are analyzed in solid geological samples to about 1ppm detection limits.

ISO 18227:2014 (Soil quality - Determination of elemental composition by XRF) specifies the procedure for a quantitative determination of major and trace element concentrations in homogeneous solid waste, soil, and soil-like material by energy dispersive X-ray fluorescence (EDXRF) spectrometry or wavelength dispersive X-ray fluorescence (WDXRF) spectrometry using a calibration with matrix-matched standards.

ISO 18227:2014 is applicable for the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, Ta, W, Hg, Tl, Pb, Bi, Th, and U. Concentration levels between approximately 0,0001% and 100% can be determined, depending on the element and the instrument used.

ISO 12677 - Determination of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, MnO, K_2O, Na_2O, P_2O_5 in geological material, soils, sediments, sludge by XRF.

ISO 17225 (1-7) - Determination of As, Ag, Ba, Bi, Br, Cd, Ce, Cl, Cr, Cs, Cu, Ga, La, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Te, Th, U, V, W, Y, Zn, Zr in geological material, soils, sediments, sludge by XRF.

IV.2.5. DC-arc - AES

No answers in the questionnaires.

IV.2.6. Radionuclides

In Bulgaria, the situation is summarized in Table 12.

Table 12 – Radionuclides measurement in soils/sediments in Bulgaria

PARAMETER IN SOILS/SEDIMENTS	STANDARD.	METHOD
Specific activity of gamma-emitting radionuclides (238U, 226Ra, 232Th, 230Th, 210Pb, 40K, 137Cs, 134Cs, 60Co et al.), exposition up to 24 h.	ISO 18589-3	gamma-ray spectrometry
		radiochemical

In Croatia radionuclide monitoring in water, sediment and biota, at country level, is performed by the Institute for Medical Research and Occupational Health, Zagreb.

- Gamma-ray spectrometry measurements were carried out using an ORTEC High-Purity Germanium Coaxial Photon Detector System comprising a GMX type detector (relative efficiency of 74.2% and peak full width at half maximum of 2.24 keV, all at 1.33 MeV 60 Co). The detector system measures gamma rays in the energy range between 40 and 2000 keV, which covers the gamma ray emissions of the studied radionuclides. Energy and efficiency calibrations were performed using certified calibration sources obtained from the Czech Metrology Institute.

- Canberra HPGe "P"-TYPE detector measures **radionuclides** ^{40}K, ^{137}Cs, ^{134}Cs, ^{232}Th, ^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{235}U, with detection limits depending on the time of analysis, media type, radionuclide itself and used instrument.
- Accuracy and precision are ensured by the application of analytical standards. The majority of the applied methods are certified according to ISO and other documents that provide analytical performances.
- The standards of the Czech metrology institute were used to adjust the measurement system, while quality control was performed through regular participation in inter-laboratory comparisons organized by the International Atomic Energy Agency, the World Health Organization and the EU Joint Research Center.

In Ukraine:

- Radionuclides in water are measured with QUANTULUS-1200 spectrometer DSTU ISO 9696-2001 (H3, Rn222, Ra226, Ra228, U, β, α);
- Radiometer of alpha-active gases РГА 03 (Альфа -1М). ISO 13165-1: 2013 (Ra226, U). "Instruction and methodological guidelines for the assessment of the radiation situation in the contaminated area" Goscomgidromet of the USSR, August 17, 1989 (Sr90).
- For bottom sediments, soils and biota: gamma-spectrometric complex based on the multichannel analyzer NOKIALP 490 with a semiconductor detector of the type DGDK-220 (226Ra, 232Th, 40K, 137Cs, 134Cs and others).

In Serbia, the radionuclides are measured in sediments, according to the standards presented in Table 13.

Table 13 - Radionuclides measurement in sediments in Serbia

Sediments	Standard
Analysis of radionucleide content (Gamaspectrometric analysis)	ISO 18589-3:2011
Measuring of total alfa and beta radioactivity	MARLAP:2004
Determination of Sr-90 activity by β radiation measurements	ВДМ 02:1972

Total β radioactivity is measured (Bq/l).No data about detection limits is available.

IV.2.7. Organic compounds (HSs)

The GC-MS procedure for organic compounds content determination in sediments (PAH, tinorganic compounds, PCB, dioxins, PBDE, DEHP, nonylphenol, octylphenol, triclosan, triclosan-methyl, AHTN, HHCB and others) is listed in in most of the questionnaires.
Organic compounds in biota: GC-MS; HRGC/HRMS for PBDE and dioxins; LC-MS/MS for PFOS and HBCDD.
Organic compounds in water and sediments: GC-MS, GC-MS/MS and LC-MS/MS.

The Priority Substances relevant according to the Water Framework Directive are:
-**Pesticides** (herbicides, insecticides): Aclonifen, Bifenox, Cypermethrin, Dicofol, Heptachlor, Heplataclorepoxide, Quinoxyfen, Cybutrine, Dichlorvos, Tetrabutryn;
-**Industrial chemicals**: Perflourooctane sulfonic acid (PFOS), Hexabromocyclo-dodecane (HBCDD);
-**Combustion by-products**: Dioxins and dioxin-like PCB-s;
-**Pharmaceutical substances** (steroids-hormons): 17-alpha-ethinylestradiol, 17-beta-estradiol, Diclofenac;

The associates standardized Analytical Methods for measuring pesticides and for **organic industrial pollution** are indicated in all countries questionares (and the PSs are listed in the national legislation) for water and digested soil and sediments. Usually, these standards are:
- **EPA 8270** for **16 Pesticides (herbicides, insecticides)**: Aclonifen, Aldrin, Bifenox, Cypermethrin, Chlorpyrifos (-ethyl, -methyl), DDT (including DDE, DDD), Dicofol, Dieldrin, Endrin, Heptachlor, Heplataclorepoxide, Quinoxyfen, Cybutrine, Dichlorvos, Tetrabutryn, Trifluralin + Hexachlorobenzene, Hexachlorocyclohexane.
- **EPA 8280B** for **combustion by-products**: **Dioxins and dioxin-like PCB-s**
- **EPA 1698** for **steroids** 17-alpha-ethinylestradiol, 17-beta-estradiol
- **EPA 542** for **some pharmaceutical substances** (Hormon, Diclofenac)
-**EN 16181:2018** for **Polyaromatic Hydrocarbons**: Anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)-pyrene, Fluoranthene.

A very detailed list of organic compounds and associated ISO standards, including LOD, LOQ measurement uncertainty for water, sediment, biota, is available in the Croatian questionnaire (deliverable D3.1.1).

Usualy compounds with a log Kow>5 (octanol-water) should preferably be measured in sediments, or in suspended particulate matter (SPM), while compounds with a log Kow<3 should preferably be measured in water. Information about log Kow can be

linked to informations about BCF or BAF. Sediment and water information can be linked to biota.
It has been determined that substances with a molecular weight (MW) > 1100 are too large to cross membranes into the organism and the equivalence (generally accepted) is the relationship between BCF 5000 criterion and log Kow:

$$5.0 < \log Kow < 7.5 \text{ and } MW < 1100$$

where:
BCF - bioconcentration factor
BAF - bioaccumulation factor
log Kow - logarithm to base 10 of the octanol / water partition coefficient.

A complete list of the dangerous substances (organic coumpounds and Hg, Cd, Pb) measured in sediments, together with details of the analytical precision and analytical standard is taken from Slovenia questionnaire. The techniques are similar to those reported in all countries owning these equipments (ICP-MS, GC-MS, etc.).

Table 14 – Analytical standards for HSs in sediments in Slovenia

Parameter in sediments	Measure principle	Reference	Unit	LOD	LOQ	Measure-ment uncer-tainty
Dicofol	GC/MS	IM/GC-MS/SOP 092: ver 8	µg/kg	30	70	25%
PFOS*	LC-MS-MS	Internal method, GLS OC 400:2013-12	µg/kg	0,0923 - 1,04	1,43 - 3,11	20%
Quinoxyfen	GC/MS	IM/GC-MS/SOP 092: ver 8	µg/kg	5	30	25%
2,3,7,8-T4CDD	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,7,8-P5CDD	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,4,7,8-H6CDD	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,6,7,8-H6CDD	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,7,8,9-H6CDD	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,4,6,7,8-H7CDD	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,4,6,7,8,9-O8CDD	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3,7,8-T4CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,7,8-P5CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%

Parameter in sediments	Measure principle	Reference	Unit	LOD	LOQ	Measure-ment uncer-tainty
2,3,4,7,8-P5CDF-	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,4,7,8-H6CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,6,7,8-H6CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,7,8,9-H6CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3,4,6,7,8-H6CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,4,6,7,8-H7CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,4,7,8,9-H7CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
1,2,3,4,6,7,8,9-O8CDF	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
3,3´,4,4´-T4CB (PCB 77)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
3,3´,4´,5-T4CB (PCB 81)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3,3´,4,4´-P5CB (PCB 105)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3,4,4´,5-P5CB (PCB 114)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3´,4,4´,5-P5CB (PCB 118)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3´,4,4´,5´-P5CB (PCB 123)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
3,3´,4,4´,5-P5CB (PCB 126)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3,3´,4,4´,5-H6CB (PCB 156)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%

Parameter in sediments	Measure principle	Reference	Unit	LOD	LOQ	Measure-ment uncer-tainty
2,3,3´,4,4´,5´-H6CB (PCB 157)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3´,4,4´,5,5´-H6CB (PCB 167)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
3,3´,4,4´,5,5´-H6CB (PCB 169)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
2,3,3´,4,4´,5,5´-H7CB (PCB 189)	HRGC/HRMS	EPA 1613B, EPA 1668C:2010	µg/kg	0,0002	0,0005	20%
alfa - HBCDD*	LC-MS-MS	Internal method, GLS OC 210:2013-10	µg/kg	0,011 - 0,202	0,0322 - 0,0725	15%
beta - HBCDD*	LC-MS-MS	Internal method, GLS OC 210:2013-10	µg/kg	0,011 - 0,202	0,0322 - 0,0654	50%
gama - HBCDD*	LC-MS-MS	Internal method, GLS OC 210:2013-10	µg/kg	0,011 - 0,202	0,0322 - 0,071	30%
Heptachlor	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
cis-heptachlorine oxide	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
trans-heptachlorine oxide	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
2,2',4,4',5,5'-HexaBDE	HRGC/HRMS	EPA 1614:2010	µg/kg	0,05	0,1	20%
2,2',4,4',5,6'-HexaBDE	HRGC/HRMS	EPA 1614:2010	µg/kg	0,05	0,1	20%
2,2',4,4',5-PentaBDE-	HRGC/HRMS	EPA 1614:2010	µg/kg	0,05	0,1	20%
2,2',4,4',6-PentaBDE	HRGC/HRMS	EPA 1614:2010	µg/kg	0,05	0,1	20%
2,2',4,4'-TetraBDE	HRGC/HRMS	EPA 1614:2010	µg/kg	0,05	0,1	20%
2,4,4'-TriBDE	HRGC/HRMS	EPA 1614:2010	µg/kg	0,05	0,1	20%
alfa - HCH	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
Anthracene	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,005	0,01	21%

Parameter in sediments	Measure principle	Reference	Unit	LOD	LOQ	Measure-ment uncer-tainty
Benzo (a) pyrene	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,005	0,01	26%
Benzo (b) fluorantene	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,005	0,01	18%
Benzo (ghi) perilene	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,005	0,01	17%
Benzo (k) fluorantene	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,005	0,01	16%
beta - HCH	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
C10-13 chloroalkanes	GC/MS/NCI	IM/GC MSD:ver 1	µg/kg	0,2	0,5	30%
Di (2-ethylhexyl) phthalate (DEHP)	GC/MS	ISO 13913:2014	µg/kg	20	50	25%
Dibutyl tin compounds	GC/MS/MS	ISO 17353:2004	µg DBT/kg	0,5	1	20%
Fluorantene	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,005	0,01	15%
gama - HCH (Lindan)	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
Hexachlorobenzene	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,003	0,005	20%
Hexachlorobutadiene	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,01	0,02	20%
Heptachlor	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
Indeno (1,2,3-cd) pyrene	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,005	0,01	19%
Cadmium	ICP/MS	ISO 17294-2, modif.:2016	mg/kg	0,01	0,1	19%
Naftalen	GC/MS	IM/GC MSD/SOP 055: ver 5	mg/kg	0,01	0,05	42%
Pentachlorobenzene	GC/ECD	ISO 10382 modif.:2002	mg/kg	0,005	0,01	20%
Lead	ICP/MS	ISO 17294-2, modif.:2016	mg/kg	2	5	16%
Tributyl tin compounds	GC/MS/MS	ISO 17353:2004	µg TBT/kg	0,5	1	20%
Mercury	CV-AAS	EPA 7473:2007	mg/kg	0,01	0,05	21%

IV.2.8. XRD

For the semi-quantitative mineralogical composition for pre-treated samples see chapter IV.1. Whole rock and clay mineralogy (< 2 µm fraction) is obtained by the SEIFERT AutoQuan software using the Rietveld method. The relative percentages of the clay minerals in the fraction < 2 µm are determined after Schultz (1964) at the Department of Mineral Resources of the Austrian Geological Survey.

For all methods and elements the analytical standards are listed in the country questionaires (deliverable D3.1.1). The detection limits are also listed and in many cases the accuracy too.
The complete list of available laboratory equipments (IV.2.2-IV.2.7.) is presented in a synthetic way (in combination with the analytical method) in Table 15.

IV.3. Inventory of national laboratories

Accredited laboratories in Austria: MAPAG, PorrUmwelttechnik, Wruss, Seibersdorf, NUA, CEWE.
The list of Moldavian accredited laboratories, where HSs are analyzed, is presented in national language on http://www.acreditare.md/public/files/registre/1-Registru-LI-28.12.2018.pdf

IV.4. Good practices

In Germany it is mentioned a national guidance "Länderarbeitsgemeinschaft Wasser, RaKon Arbeitspapier IV.4", where a procedure for calculating water concentrations from SPM-concentrations is described for highly accumulative substances. AA-EQS for water for PCB and triphenyltin-cation will only be used when the analysis of sediment/SPM is not possible
Many national guides provide also the concentration of an atomic element and the concentrations of its compounds in order to identify traceability, bioaccumulation, and determine the actual toxicity produced by the presence of a metal in the aquatic environment.

IV.5. Protocols

Moldova lists 12 protocols developed within various projects for inter-laboratory comparison related to:

- determination of metals (cadmium, copper, nickel, iron, lead, manganese, chromium, zinc) and determination of organo-chlorinated pesticides and polychlorobiphenyls in soil, rocks and plants;
- determination of calcium, magnesium, chromium, strontium, sodium and potassium in water;
- determination of organochlorinated pesticides and polychlorobiphenyls in water and raw materials.

For the parameters for which the laboratory has accreditation, the laboratory also participates in inter-laboratory comparative schemes (Aquacheck, Aglae, QualcoDanube, Quasimeme, etc).

The chemical laboratory of the Geological Survey of Austria takes part periodically in ring trials for soil and water analyses testing the ICP-MS, ICS, photometer and titrator. Methods are described in section IV.2. Intercomparison follows the standard DIN 38402 (esp. Part 42: Interlaboratory trials for method validation, evaluation; Part 45: Interlaboratory comparisons for proficiency testing of laboratories; Part 51 Calibration of analytical methods; Part 60 Quality assurance). Up to 25 laboratories for soil, 46 laboratories for water from Austria, Slovenia, Italy and Germany take part in these trials.

During the NATIONAL PROGRAMME for monitoring of sediments in water bodies in Bulgaria, an intercomparison and intercalibration protocol between laboratories was developed.

IV.6. CONCLUSIONS

The list of laboratory equipment includes analytical instrumentation systems dedicated to analyzing trace elements using ICP-MS, ICP-AES, F-AAS, GF-AAS, AAS-with hydride generators, XRF-spectrometry, mercury analyzers using CV-AAS or C-ASA.

All chemical trace or major elements mentioned in the legislative guidelines for environmental quality assessment (water, soil, sediment, biota) in the atomic state can be analyzed with existing equipment. For all analyzes there are analytical guides, especially ISO and EPA.

More detailed identification of minerals in sediments is realized, for example, using electron microscopy (SEM, TEM) and electron microanalysis or X-ray powder diffraction analysis.

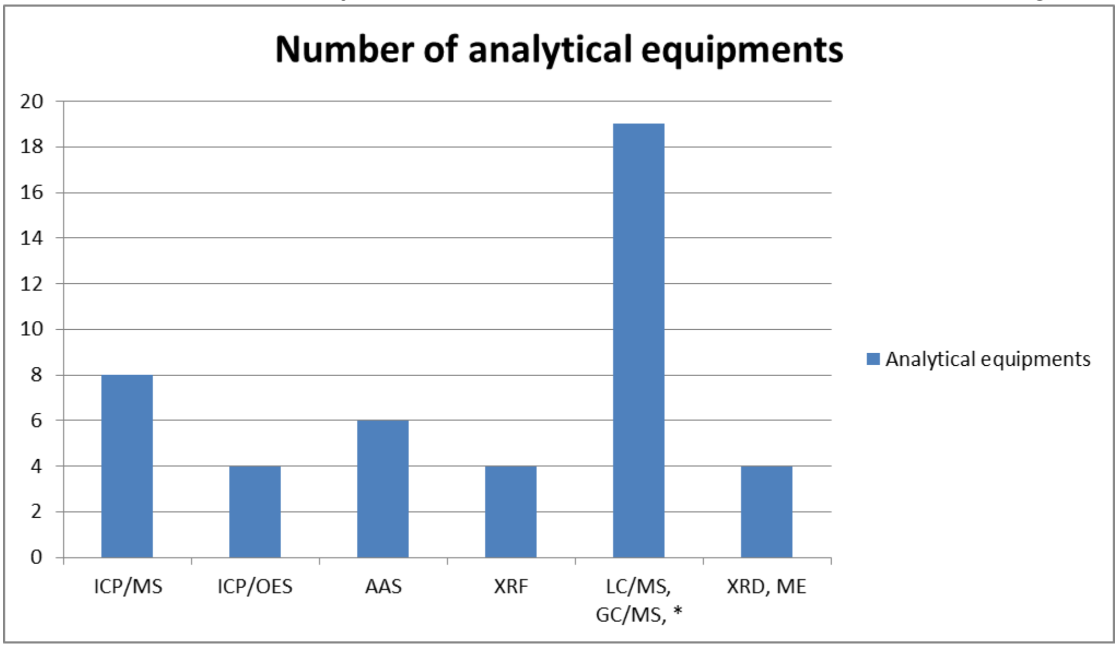
As is known from literature, each technique is associated with certain elements and matrices, so that, having several types of equipment offers the possibility to perform high quality analyzes.

There is the possibility of intercomparison and intercalibration between laboratories, and the experience of developing the protocols for these comparisons is reported.

The list of laboratories equipment includes also hyphenated instrumental systems such as high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), gas chromatography mass spectrometry (GC-MS), liquid chromatography mass spectrometry (LC-MS), dedicated to methods of analysis of organic compounds that are listed in the legislation for environmental quality assessment (water, soil, sediments, biota).

For these parameters all analyzes are also standardized (ISO or EPA). The number of these compounds is large and variable, depending on the country, and a selection of the parameters of interest is required, correlated with the reports on the sources of pollution (especially the wastewater discharges) when the criteria list is drawn up for SIMONA.

The complete list of available laboratory equipments is synthetically presented (in combination with the analytical method) in Table 15 and as numbers in Fig. 3.



** - other equipments that analyze organic compounds*

Fig. 3 Number and types of analytical equipments in SIMONA countries

Table 15 - List of analytical methods and equipments

Country	ICP-MS	ICP-AES	AAS	XRF	XRD/SEM,TEM	Instrument for organic compounds (HSs)
AT	ICP-MS 7500 Agilent	-	-	Epsilon 5 PANAnalytical	X-Ray diffraction: PANalytical X'Pert Pro Powder	
BA	-	-	-	-	-	-
BA-SRP	-	-	AAS, flame and graphite technique, Shimadzu FAAS AA6300 and Hg analyser AMA 254.	-	-	-
BG	ICP-MS	-	Flame AAS	-	-	GC-MS
HR	ICP-MS, Perkin Elmer ELAN 9000 and ICP QQQ 8900 Agilent Technologies	-	-(CV-AAS for mercury).	-	-	Biota: GC-MS; HRGC/HRMS for PBDE and dioxins; LC-MS/MS for PFOS and HBCDD Water and sediment: GC-MS, GC-MS/MS and LC-MS/MS.
DE	ICP-MS	-	-	-	-	GC-MS
HU	-	-	-	-	-	-
MD	-	-	-	Equipment AAnalyst800, Perkin Elmer Inc, by Plame, THGA and Hydride	-	-

Country	ICP-MS	ICP-AES	AAS	XRF	XRD/SEM,TEM	Instrument for organic compounds (HSs)
				Generation System (FIAS400)		
ME	-	-	-	-	Olympus SZX10 binocular brand and the Olympus CX23 microscope for biota samples optic analysis	-
RO	-	ICP-AES Baird 2070	Hg analyzer Hydra –II And CC (Teledyn)	-EDXRF-Minipal4-PANalytical -Portable XRF Olympus DELTA DPO-6000	- Shimadzu 6000 X-ray diffractometers - INEL Equinox 3000 X-ray diffractometer - microscope JEOL JSM 5600 LV -ME Gemini II-Carl Zeiss	-
SR	ICP-MS, Perkin Elme	Perkin ElmeICP-OES, Perkin Elmer	FAAS, AAS-ETA Perkin Elmer Flow Injection Mercury/Hydride Analyses Using Perkin Elmer FIAS-100	-	-	Water and sediment: GC-MS, GC/MSD
SK	- ICP-MS Aurora M90 Bruker - ICP-MS Agilent 7900	- ICP-OES 5100 Agilent - ICP-OES 5110 Agilent	- AAS AMA- 254, Altec Prague (Hg in water) - AAS AMA- 254, Altec Prague (Hg in soils) - Agilent AA Dou 240FS/ 240Z (Au, Ag in geological materials)	-Energy dispersive XRF (X-ray fluorescence) spectrometers – SPECTRO XEPOS	-	-Agilent 7890B GC-FID -Varian 3900 GC-FID -Varian 450-GC GC-ECD -Agilent 7890B GC-MSD -Agilent 597B GC-MS -Agilent 7010B GC-MS Triple Quad

Countr y	ICP-MS	ICP-AES	AAS	XRF	XRD/SEM,TEM	Instrument for organic compounds (HSs)
						-Agilent Infinity 1260 HPLC-DAD/FLD -Agilent 6470 LC/MS Triple Quad
SI						
UA			TERMOSIENIFICSOLAAR 6M (England) AASsystems (AAS-ETA; F- AAS)			

Gas chromatography with Flame-ionization detector (GC-FID),
Gas chromatography with Electron Capture Detector (GC-ECD),
Gas chromatography Mass Spectrometry (GC-MS),
Gas chromatography Tandem Mass Spectrometry (GC-MS/MS),
High Performance Liquid Chromatography with Diode Array Detector and Fluorescence Detector (HPLC-DAD/FLD);
Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS)

V. INVENTORY OF EVALUATION METHODS

V.1. Establishing threshold values for HSs

This question refers to how threshold values for HSs are set in sediment (e.g. average of the last measured values, average with the treatment of outliers, average of the values measured in areas without anthropogenic influence, enrichment factor, conservative elements for normalization, etc.).

BULGARIA: Quality standards for priority substances and other specific pollutants are defined by the Regulation of the Ministry of the Environment and Water, Bulgaria. They refer to surface water and partly to biota, whereas for sediments there are no such standards. An average annual value is used, which means that for each representative monitoring site for a water body, the arithmetic mean value of the concentrations measured at different times of the year does not exceed the value set in the standard. A maximum permissible concentration is also used, which means that the measured concentration at any point of monitoring within the water body does not exceed the standard.

REPUBLIC OF MOLDAVIA: The threshold values for soil were set for the territory of the country after analyzing the publications about the analysis of trace elements in different objects. This work was made in Soviet time for all regions of former USSR including Republic of Moldavia. Other source for evaluating trace elements threshold values is represented by the reference sources as Klark values.
The organic HSs should to be on zero level, because they are artificial substances.

BOSNIA AND HERZEGOVINA (REPUBLIC OF SRPSKA): Threshold values are harmonised with WFD, which means that there were no investigations which would set specific threshold values.
Threshold values for HSs are set only for water samples, which is stated in the Regulation on water classification and categorization of water courses (Official Gazette of Republika Srpska 41/01), and available at http://www.voders.org/propisi-i-obrasci/pravna-regulativa

HUNGARY: Environmental Quality Standards (EQSs) are delivered for the surface waters and biota according to EU-WFD, but not for sediments.

ROMANIA: For soils there are 4 sets of values correlated with the soil type, without taking into account the soil composition.
For waters there is only one set of values (the geological particularities and water hardness are not specified).
For sediments (with 10% organic matter and specified granulometric class according to Order 161/2006), the contents of few toxic metals are set. There is no reference to the geological background.

SLOVAKIA: Quality standards for priority substances and other specific pollutants are defined by the Regulation of the Ministry of the Environment in Slovakia. They refer to surface water and groundwater, soils, whereas for sediments there are no such standards.
For sediments there are four sets of values which refer to hazardous substances:
TV – target value – negligible risk, undisturbed natural environment, uncontaminated sediment and 100% survival of aquatic organisms, represents 1/100 MPC);
MPC – maximum permissible concentration – represents the maximum permissible risk, the level ensuring the survival of 95% of all species of organisms in the given ecosystem;
TVd – tested value – the environmental risk is not expressed, the value lies in the interval between MPC and IV can be used for deciding on sediment management;
IV – intervention value – represents a serious risk; the concentration of a substance in which only 50% of all species of the ecosystem are protected.
An overview of legislation for management of sediments on the basis of the limit values of selected elements in sediments (sediment leachates) is presented in Table 16.

Table 16 – Example of thresholds for sediments in Slovakia

Indicator	Act no. 188/2003 Coll.	Decree of the MoA and MoE no. 257/2009	Decree of the MoE no. 372/2015		EPA "RCRA"
	Total content [mg.kg-1]	extraction with the HNO_3 (Hg total content) [mg.kg-1]	Aqueous extract [mg.l-1]		TCLP extract [mg.l-1]
			non-hazardous waste landfill; leachability class II.	hazardous waste landfill; leachability class III.	
As	20	30	0,2	2,5	5
Sb	-	-	0,07	0,5	-
Cr	1000	200	1	7	5
Hg	10	0,8	0,02	0,2	0,2
Ni	300	80	1	4	-
Pb	750	100	1	5	5
Cd	10	1	0,1	0,5	1
Cu	1000	100	5	10	-
Zn	2500	300	5	20	-

SLOVENIA: The environmental quality standards (EQS) are defined as the maximum permissible concentration that protects against acute poisoning and as an average annual value that protects against chronic influenza according to WFD.

GERMANY: Environmental Quality Standards are derived according to EU rules (WFD implementation).

V.2. Fixed or variable threshold values for HSs

This question refers to the type of threshold (fixed or variable) and if the threshold values depend on on the sample form, drainage basin lithology, time of the year or some other parameter.

BULGARIA: The quality standard values are fixed, but when assessing the results of the monitoring for different quality standard, Basin Directorates can take into account the natural background concentrations of metals and their compounds, water hardness, pH, dissolved organic carbon and other water quality parameters.

CROATIA: Threshold values for inorganic compounds are set according to WFD, but due to specific geology, there is the possibility that some of these values should be revised.

HUNGARY: The EQS values are fixed, but when criteria of "Good status" are not met; then (if it is possible) to use EQS-corrections.

SERBIA: Threshold values for inorganic compounds are set according to WFD, some of these values should be revised.

REPUBLIC OF MOLDAVIA: The threshold value were evaluated for different soil types, depending on the granulometric and organic content.

SLOVAKIA: The quality standard values are fixed for specific water management plan. After new data collection the values can be revised. There are taken into account the natural background concentrations of metals and their compounds, water hardness, pH, dissolved organic carbon and other water quality parameters, that are linked to drainage basin lithology.

SLOVENIA: The environmental quality standards are generally fixed. For some metals (Cd, B, Hg, Cu, Zn, Co, Sb) the natural background and bioaccumulation (Ni and Pb) are taken into account.

BOSNIA AND HERZEGOVINA (REPUBLIC OF SRPSKA): Threshold values are fixed, although some of them cover specific range

ROMANIA: The quality standard values are fixed, but they may depend on lithology if there are very large differences in the substrate.

V.3. Corrections for threshold values

The question refers to the corrections that may be applied to threshold values (amount of quartz, organic matter etc.).

SERBIA: Corrections are applied in the case of sediments where organic matter content and particle size fractions are taken into account during the determination of threshold values.

MOLDOVA: Corrections are applied by additional analyses that are made: granulometry, organic content.

SLOVAKIA: No correction for water. In case of results interpretation for sediments (but in Slovakia there are no threshold values) we use corrections (granulometry, organic matter content).

V.4. Basis of the environment quality objectives

This question aims to find out if the environmental quality objectives are based on measuring the total metal concentration and / or some dangerous compounds of that metal in different valence states.

BULGARIA: For most metals, the total metal concentration is measured. For chromium the 3- and 6-valence form is measured. For some elements such as Cd, Cu, Zn, quality standards vary depending on the water hardness.

CROATIA: Total metal concentration.

SERBIA: Total metal concentration.

MOLDOVA: The total content and different mobility forms of inorganic HSs were analysed for different type of soils for the country area in the past.

BOSNIA AND HERZEGOVINA (REPUBLIC OF SRPSKA): Only total metal concentrations are measured. It seems that there are no differentiation between concentrations of geogenic and anthropogenic origin. For example, strongly bounded metals vs weakly bounded metals.

HUNGARY: For most metals, the dissolved (<0,45 μm) total metal concentration is measured. For chromium the 3- and 6-valence form is of interest. For Cd the quality standards vary depending on the water hardness. And for some elements such as Cu, Zn, Pb, Ni usually bioavalilable EQS-corrections are used. For As and Hg usually the ABC (ambient background) EQS-corrections are used.

SLOVAKIA: The mobility of the elements (mainly potentially toxic trace elements) is experimentally evaluated by several approaches. These are, in particular, extraction experiments in laboratory conditions that imitate the changing conditions in the environment and help predict the risk of element mobilization from solid sediment phases. The most relevant parameters of the extraction methods are the nature of the reagent (type of substance, power), extraction time (from several hours to the days), or temperature. In Slovakia several one-step extraction methods and sequential extraction methods were tested.
For most metals, the total metal concentration is measured. For chromium the 3- and 6-valent form is measured. For some elements such as Cd, Cu, Zn, quality standards vary depending on the water hardness.

SLOVENIA: For most metals, the total metal concentration is measured. For some elements such as Cd, Cu, Zn, environmental quality standards vary depending on the water hardness.

UKRAINE: To estimate the level of contamination, the gross concentrations of elements in the bottom sediments are mainly used; sometimes for Cr the estimation based on the valence value is used. This is done in the case when Cr is the leading contamination element.

V.5. Algorithm for defining the environment quality categories

The question refers to the algorithm (e.g. weight coefficients) used for determining the environment quality categories.

UKRAINE: In the practice of ecological and geochemical research in the past of the USSR and today among the geochemists in Ukraine for assessing the pollution of rivers a methodology based on the intensity of the accumulation of chemical elements in bottom sediments and water is used (Yanin E.P., Technogenic geochemical associations in the bottom sediments of small rivers, M., IMGRE, 2002. 52c.).

In connection with the polyelemental nature of technogenic contamination of bottom sediments, to determine their total contamination by heavy metals, a method is used which involves the calculation of the total indicator (the sum of the coefficients of the concentration of anomalous chemical elements) of the accumulation of chemical elements (Zc) with a subsequent comparison of this indicator with the scale of contamination levels (Table 17).
In turn, the overall indicator of the accumulation of chemical elements, or the total pollution factor (Zc), was calculated by the formula:

$$Zc=\sum Ci/Cb-(n-1),$$

where:
Ci – the content of the chemical element in the sample;
Cb – background content of the chemical element;
n- number of chemical elements in the sample with abnormal content (Ci/Cb>2).

Table 17 - Tentative scale of estimation of river pollution by the intensity of accumulation of chemical elements in bottom sediments in Ukraine

Zc	Level of technogenic pollution	Level of sanitary-toxicological danger	Toxic elements concentration in river water
< 10	Weak	Allowable	Most elements within the background
10-30	Medium	Moderate	Most elements exceed the background, and some reach the level of MPC
30-100	High	Dangerous	Some elements exceed the MPC level
100-300	Very high	Very dangerous	Most items exceed the MPC level
>300	Extremely high	Extremely dangerous	Most elements consistently exceed the MPC level

V.6. Relations between specific HSs and the contamination and pollution sources

This questions regards the way in which specific HSs relate with sources of contamination and pollution.

UKRAINE: The geochemical association of pollution elements and their concentration in environmental objects (mainly in soils and bottom sediments) identifies the source of emissions (there are certain geochemical associations for emissions of major types of industrial enterprises in Ukraine and Russia). Such a technique is also not formally adopted at the State level.

V.7. Representations of results, targeted audience and availability

The questions refers to the way the results are presented in the reports (e.g. using complex representation for scientific community or simple representation for target groups), if the reports include methodology, full results, QA/QC, models and if the results are public or can be obtained by request.

CROATIA: Results are presented in regular publications, which can be found on https://www.voda.hr7 and https://www.mzoip.hr/

SERBIA: Data is published in annual reports released by Environmental agency which contained the data in tabular form along with the analytical methodology. The reports are available to the public:
http://www.sepa.gov.rs/index.php?menu=5000&id=13&akcija=showExternal

HUNGARY: All public information is available via http://www.vizugy.hu/; inclouding last RBMPs: http://www.vizugy.hu/index.php?module=vizstrat&programelemid=149.

MOLDOVA: The mode of the presentation are different:

- Form of the approved test report for beneficiary of analysis;
- Scientific presentation;
- Simple presentation for population and civil society

Reports by specific projects financed from public sources are available free from internet. Test report of the private beneficiary is available only with the permission of the beneficiary. Scientific publication are available depending of publishing rules.

BOSNIA AND HERZEGOVINA (REPUBLIC OF SRSPKA): The results are presented as a simple representation and the final report includes methodology, full results, QA/QC and models. The results can be obtained by request.

SLOVAKIA: Data (groundwater and surface water) is published in annual reports released by the Slovak Hydrometeorological Institute which contained the result

interpretation (data comparison with standards). The reports are available to the public: www.shmu.sk.
Presentation of the results of the stream sediment monitoring is difficult to interpret because of the complexity of the conditions of their chemical composition (weathering, sedimentation, migration of substances). The composition of the stream sediment represents the natural features of the river basin area as well as the anthropogenic effect. Interpretation of results (in SGIDS) takes into account the following approaches:

- application of statistical analysis (descriptive statistics, temporal variability);
- legislative approach (comparing the measured contents of the elements with specific limit concentrations);
- combined legislative and geostatistical approach (legislative assessment of the pollution parameters and the subsequent geostatistical treatment of the results in the map of the distribution of the contamination index).

SLOVENIA: The results of monitoring are available on the web site of the Slovenian Environment Agency (MOP-ARSO). http://www.arso.gov.si/en/
The original data (concentrations) are available in MS Excel files also on the web site: http://www.arso.gov.si/vode/podatki/arhiv/kakovost_arhiv2018.html

UKRAINE: Results of ecological-geochemical studies in reports are provided for target groups. The report includes a methodology and full results. These results are open to everyone.

V.8. Space-time risk assessment methods

This question refers to the existence of a method for space-time risk assessment after determination of contamination and/or pollution.

BULGARIA: The assessment method for the change in concentrations of pollutants (HS) is the same for biota and sediment.
When obtaining at least 4 consecutive results as a trend assessment approach, the nonparametric method of Mann Kendall (Hirsch and Slack, 1984) is used. The method is suitable because it allows working with less than 6 results. There is no claim for a normal distribution of the results, which in any case cannot be assessed with such scarce data.
The nonparametric method of Mann Kendall is applicable when the pollutant values (x_i) are considered to follow the model:

$$x_i = f(t_i) + \varepsilon_i$$

where:
$f(t_i)$ - a continuous decreasing or increasing function of time and the residues
ε_i - are assumed to belong to the same distribution with an average value of zero.
Other scientific assessment methods are also applied.

CROATIA: The legislation incorporates the following directives:
https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31996L0082&from=HR
https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32003L0105&from=EN

MOLDOVA: The specific procedure of Environmental Risk Assessment is elaborated by scientific groups for polluted sites study on the base of the compilation of recommendations from different guides.

SLOVAKIA: Methodological Instruction of the Ministry of Environment of the Slovak Republic no. 549 / 98-2 for the risk assessment from contaminated sediments of streams and water reservoirs (A, B, C values). Directive of the Ministry of Environment of the Slovak Republic no. 1 / 2015-7 to develop a risk analysis of the contaminated area (groundwater, rock environment, soils) (ID, IT values).

UKRAINE: Methods of space-time risk assessment after the detection of pollution are used in the practice of ecological and geochemical research. Mainly, these are modelling and forecasting methods, but they are not perfect.

CONCLUSIONS

The quality standard values are fixed set in legislative acts.
Some legislations take into account the natural background concentrations of metals and their compounds, water hardness, pH, dissolved organic carbon for water, soil type (clayey, sandy, silty), the geological specifities of underground or surface waters.
Some legislations take into account the fact that sometimes, a metal is more toxic in some of its molecular compounds (especially in the aquatic environment) and besides “Total Metal Analysis“, analyzes of metal compounds are also made.
Generally there is no difference in the national legislations between pollution and contamination.
In every country generally it is known that specific HSs are generated by specific industries.
The results of monitoring are generally open to public in all countries.

The legislation does not specify exact methods for remedying pollution because laws have a general character, but when developing an ecosystem guide, these details must be reflected. There are differences regarding the establishment of the ecological quality classes, although the classification criteria are the same.
All these criteria are much more developed for water and soil than for sediments. Therefore, SIMONA guides could contribute to all the above mentioned issues related to sediment monitoring.

3. CONCLUSIONS AND COUNTRY LEVEL EXECUTIVE SUMMARIES

AUSTRIA

I.LEGISLATIVE FRAMEWORK

Regarding river sediments, the Quality Ordinance for the Ecology of Surface Water specifies monitoring parameters (list of substances, sampling frequency) and permissible levels in sediments.

II PRACTICES, EXPERIENCES

Nation-wide studies have established chemical base line values for stream bed sediments (Geochemical Atlas of Austria, 2015), groundwater (GeoHint, 2018) and soil (2004). Monitoring sites and data are available online.

- Water Information System Austria (WISA) for surface and groundwater as well as suspended river sediments
- Interactive Resources Information System (IRIS) for stream bed sediments
- The institutions include
- Austrian Environment Agency (groundwater and surface water, stream bed and suspended sediments, biota) for regular national monitoring and on a project basis for specific studies
- Geological Survey of Austria (stream bed sediments, floodplain sediments, groundwater) on a project basis
- Austrian Institute of Technology (thermal/mineral water) on a project basis
- University of Natural Resources and Life Sciences, ViaDonau and Verbund Hydro Power AG (suspended sediments) on a project basis

III.INVENTORY OF SAMPLING METHODOLOGIES

Stream bed sediment sampling is standardized by an Austrian norm and consists of one sampling site per 10 km^2 or at least on site per catchment (up to highest order). Mayor rivers are not sampled except downstream of emitters (settlements, industrial sites, treatment plants etc.). Only sites with active sediment are sampled, duplicate sampling is carried out for quality control for every 50th sample. In-situ measurements include temperature, electrical conductivity, pH and redox potential. Two grain size fractions (< 180 µm and < 40 µm) are sampled. Chemical analysis includes 40 elements excluding organic substances.

Suspended sediment sampling is carried out according to Austrian legislation implementing the EU Water Framework Directive. Most sampling is carried out at river banks using bottles mounted on telescope poles, some samples are collected automatically at fixed stations by means of pumps. At one station, the multi-point method is used. Sampling frequency ranges between three days up to 6 hours (during floods). Samples are analyzed for sediment concentration, transport and load, as well as for grain size distribution. Chemical analyses are not performed.

IV.INVENTORY OF LABORATORY METHODOLOGIES

Hydrochemical analyses are standardized by Austrian/international norms. Laboratory requirements are prescribed by the Ordinance for the Qualification of Chemical Laboratories.

Sediment sample analyses are performed by the Geological Survey of Austria using ICP-MS, ICS, XRF and XRD. 37 inorganic parameters are determined.

V .INVENTORY OF EVALUATION METHODS

Several units within the Austrian Environment Agency are responsible for, and involved in, the characterization of evaluation methods.

BOSNIA and HERZEGOVINA (Republic of Srpska)

I.LEGISLATIVE FRAMEWORK

The legislative framework of Republika Srpska (laws, governmental orders, and emergency ordinances) which regulates the concentrations of dangerous substances posing a risk to the health of the population or aquatic life in surface and drinking waters was presented. Unfortunately, legislative framework on concentrations of dangerous substances in soil, river sediments, marine sediments, sewage, therapeutic sludge, air and biota, have not been established yet.

II PRACTICES, EXPERIENCES

The paper, titled „Considerations on reservoir sedimentation and heavy metals content within the Drenova reservoir“ and written by Radislav Tošić, Slavoljub Dragićević, Snežana Belanović, Ilija Brčeski and Novica Lovrić, was found to be appropriate.

III.INVENTORY OF SAMPLING METHODOLOGIES

The sampling design strategy, along with a list of parameters of water quality which are measured in-situ, and a methodology for collecting samples were described. It was emphasized one more time that there are no biota and sediment monitoring (bottom, suspended or floodplain) in Republika Srpska.

IV.INVENTORY OF LABORATORY METHODOLOGIES

Analytical methods and equipment used for the hazardous substance analyzed in agreement with the corresponding matrix were described.

Laboratories that are in charge of analyzing HS are requested to perform quality controls according to EN ISO/IEC 17025, and participate in proficiecy testing performed by the laboratory certified according to EN ISO/IEC 17043.

V .INVENTORY OF EVALUATION METHODS

The existing system for setting HSs threshold values in water was addressed. Fixed threshold values for HSs are set only for water samples in Regulation on water classification and categorization of water courses (Official Gazette of Republika Srpska 41/01) which is available at http://www.voders.org/propisi-i-obrasci/pravna-regulativa/.

The environmental quality objectives are based on measuring the total metal concentration.

Final annual reports include methodology, full results, QA/QC, models. Results can be obtained on request.

Several faults can be found within the current monitoring procedures:

- the lack of financial resources, inadequate laboratory capacities and lack of appropriate laboratory equipment and devices;
- the lack of regulations or criteria for including/excluding parameters from the monitoring programme for priority substances, which would allow more efficient use of budget resources;
- there are no systematic investigations on the concentration of priority substances in samples of biota and sediment.

BULGARIA

1. Responsible Institutions

- Ministry of Environment and Water (MOEW) through Water Management Directorate (https://www.moew.government.bg/en/)
- Executive Environment Agency (ExEA) (http://eea.government.bg/en)
- Basin Directorate Danube Region (BDDR) (http://www.bd-dunav.org/)

2. Legislative framework

Main European and National documents, applied in the development of the national program for the monitoring of sediment in surface waters:

- Water Framework Directive 2013/39/EC (2000/60/EO ,82/176/ЕИО, 83/513/ЕИО, 84/156/ЕИО, 84/491/ЕИО, 86/280/ЕИО, 2008/105/ЕО)
- Guidance document 19 – on surface water chemical monitoring under the WFD;

- Guidance document 25 – on chemical monitoring of sediment and biota under the WFD;
- National Regulation for quality standards for priority substances and other hazardous substances in the environment.

3.Monitoring of Hazardous Substances in Surface Waters Sediments in Bulgaria

In Bulgaria surface waters sediments are monitored in accordance to the respective River Basin Management Plan (currently for the period 2016-2021). Only bottom river sediments are sampled – from the shallower part of the river bed, during low water level. The frequency of sampling is once per 3 years. There are currently 35 monitoring station for surface waters sediments. Three of the stations are part of the Transnational Monitoring Network. Twenty Hazardous Substances are currently monitored – all part of the Priority Substance List of the European Water Framework Directive (Substances numbers - 2, 5, 6, 7, 12, 15, 16, 17, 18, 20, 21, 26, 28, 30, 34, 35, 36, 37, 43 and 44 from the List). Samples are also analyzed for TOC content and <0,063 mm grain fraction content.

For sampling, laboratory analysis, and evaluation the WFD recommendations along with its respective guidance documents are used. The following documents are used for the design of sampling, transport, storage, and sample preparation:

- БДС ISO 5667-12:2017 – Water quality. Sampling – bottom sediments from rivers, lakes, and estuary zones
- БДС EN 16171:2016 – Sediments, processed bio-wastes, and soils. ICP-MS elements determinations.
- ILM 4006/2010 – Organochlorine pesticides and polychlorinated biphenyls determination in soils, sediments, and sludge.

4. Positive practices and problems in the current state of the HSs monitoring in surface water sediments in Bulgaria

The lack of experience in surface waters sediment sampling and monitoring, the lack of participation of national responsible or academic institutions in previous European projects with similar objectives, and some technical and laboratory constraints are the major difficulties in the monitoring process in Bulgaria.

On the positive side, national institutions such as MOEW and ExEA are willing to collaborate and interested in the SIMONA Project and its results. There is generally well-developed and continuously updating national monitoring regulation and the WFD is transposed in the National legislation which is a big step to standardizing the monitoring. Standardized documents (ISOs) are used for the sampling, transport, storage, and laboratory analysis. And national experts with long term experince in einvironmental monitoring are willing to participate in the trainings and workshops of the SIMONA project.

CROATIA

I.LEGISLATIVE FRAMEWORK

Croatia is in the process of setting up methodology for sediment sampling and analysis. There are no laws or any other official directives for sample media, except the obligation of implementation of EU Water Framework Directive in the next years.

In the national legislation threshold limit values are prescribed only for agricultural soil for metals: Cd, Cr, Cu, Hg, Ni, Pb and Zn; organic compounds: PAHs, PCB, insecticides based on chlorinated hydrocarbon and herbicides. The threshold limit values are not prescribed for sediment. There are prescribed threshold limit values for water: groundwater, surface water, nearshore water, lakes, rivers, drinking water and bathing water. Mostly are in use ISO standards for sampling sediment, soil, water and biota, as well as for transport and storage. Recommended remedy measures associated with the concentration of the hazardous substances (HSs) are defined in Croatian legislative according to the situation. Croatia is also part of the International Commission for the Protection of the Danube River (ICPDR). Commission has a manual for accident warning system which also applies in Croatia.

II PRACTICES, EXPERIENCES

Croatia has experience in the national and international projects like: Basic Geochemical Map of Croatia (1998 – 2009), FOREGS Geochemical mapping of Europe (1998-2005), Monitoring of Drava alluvial sediments (2004 - 2008), Origin, fate and Transport modelling of Nitrate in the Varaždin Alluvial aquifer – TRANITAL (2017 - 2021), Geochemical Mapping of Agriculture and Grazing Land Soil in Europe (GEMAS) (2008 - 2014). We participated in significant scientific papers like: FOREGS Geochemical Mapping Field manual (1998), Geochemical Atlas of Europe-Part 1 (2005), Geochemical Atlas of Europe-Part 2 (2008), Chemistry of Europe's Agricultural Soils-Part A (2014), Chemistry of Europe's Agricultural Soils-Part B (2014), Geochemical Atlas of Croatia (2009).

Croatia did not implement sediment monitoring procedures, while water and biota monitoring are ongoing according to the guidelines of the Water Framework Directive 2000/60/EC.

III.INVENTORY OF SAMPLING METHODOLOGIES

Water and sediment sampling design strategy is according to the methodology requested by Water Framework Directive. Type(s) of sediment sampled are bottom and floodplain. No parameters of sediment quality/quantity are measured in situ. The methodology for collecting samples for laboratory measurements is conducted according to the parameters intended to analyze later on. Transport of the samples is done in refrigerators. Samples are not archived.

IV.INVENTORY OF LABORATORY METHODOLOGIES

The samples are prepared first mechanically; water – filtration; sediment – drying, sieving, homogenization and biota – homogenization, cryogen grinding. Organic matter content in water and sediment is not being determined. Radionuclide monitoring in water, sediment and biota, at country level, is performed by Institute for Medical Research and Occupational Health, Zagreb. The measured radionuclides are: 40K, 137Cs, 134Cs 232Th, 238U, 226Ra, 228Ra 210Pb, 235U. Detection limits depend on the time of analysis, media type and used instrument. The accuracy and precision of the analytical procedures are calculated using certified reference material, sample duplicate, repeatability of measurements.

V. INVENTORY OF EVALUATION METHODS

Threshold values for inorganic compounds are set according to WFD, but due to specific geology, there is possibility that some of these values should be revised. Corrections for threshold values are not used (amount of quartz, organic matter etc.). The environmental quality objectives are based on measuring the total metal concentration. Croatian legislative framework does not define difference between contamination and pollution. There is only contamination. Actions in case of contamination are defined according to the situation. All information regarding actions are prescribed in Croatian legislative acts. The space-time risk assessment after determination of contamination is incorporated in the Croatian legislation from following directives: 96/82/EC and 2003/105/EC.

HUNGARY

I.LEGISLATIVE FRAMEWORK

Hungary is implementated the EU Water Framework Directive, and adapted the CIS guidance documents to the national strategies. Hungary is part of the International Commission for the Protection of the Danube River (ICPDR), therefore the ICPDR guidances are also adapted to the national legislative framework and to the daily rutine. Mostly are in use ISO standards for sampling, for transport and storage, as well as for laboratory analisys too.

HU has investigative monitoring programs for find the best monitoring sites for long-term biota and sediment monitoring. The surface water threshold limit values (EQSs) are not yet prescribed for sediment, just for water and biota.

III. INVENTORY OF SAMPLING METHODOLOGIES

Sampling design strategy is done according to the methodology requested by Water Framework Directive. HU has 3 type of monitoring programs with different monitoring sites and different sampling frequencies (Surveillance monitoring program; Operative monitoring program; and Investigate monitoring program).

The methodology for collecting samples for laboratory measurements is conducted according to the parameters intended to analyze later on. Transport of the samples is done in refrigerators. Samples are partly archived.

V. INVENTORY OF EVALUATION METHODS

HU has different EQSs for different spatial scales:

- EU level – EQSgeneric (2013/39/EU): protect min. 90% of EU waterbodies
- National/regional level – EQSregional: protect min. 90% of the WBs in the region
- Local level – EQSlocal: protect one waterbody or one group of waterbodies

MOLDAVIA

I.LEGISLATIVE FRAMEWORK

National legislation defines the threshold concentration for metal and nonmetal trace elements in soil, river water and drinking water, as well as PAHs in soil and water, persistent organic pollutants and microbial parameters in water. Also maximum admissible level of organic substances and pesticides in soil were defined by national legislation.

Analytical standards for water and soil sample analyses are National analytical standards and some international standards. ISO and ASTM standards are used as guides and techniques for sampling, transport, storage, preparation for analyses of sediment, soil and water.

II PRACTICES, EXPERIENCES

In Moldova it was implemented the National System of Environmental Quality Monitoring (2013-2015). In the Lower Prut region the monitoring stations are watching both the river and adjacent lake water bodies, by water and sediment sampling for HSs, POPs, PAHs and heavy metal analyses. The State Hydrogeological Service offers annual on-line reports for the environmental status of the state territory. A River Basin Management Plan is available.

III.INVENTORY OF SAMPLING METHODOLOGIES

The study of surface water bodies is made both for water and sediment samples. VOCs were collected first, followed by Semi VOCs (PCBs, pesticide), oil and grease, and total petroleum hydrocarbons (TPHs), then other parameters: total metals, dissolved metals, microbiological samples, and inorganic nonmetals. Sample size varies in the range of 5 mL for total petroleum hydrocarbons in liquid wastes, 100 mL for total metals, and 1 L for trace organics such as pesticides.

Sediments taken in consideration are of all types. Monitoring of sediments in important water bodies (wetlands, lakes, polluted sites etc.) are performed every year, and by particular projects or, after contamination events, according to planned remediation actions. Ekman dredge is used for soft sediments on deeper water sites. Soil sampling kit Burkle 5350-1005 are used to take deeper sediment or soil samples.

IV.INVENTORY OF LABORATORY METHODOLOGIES

Water, sediment and biological samples are treated according to the specific recommendations for analytical methods. SOPs were elaborated according to ISO 17025 in accredited laboratory "GEOLAB" in Moldavian Accreditation System. Soil and sediments are analyzed for organic matter by GOST 23740-2016 Methods. For AAS analysis Equipment AAnalyst800, Perkin Elmer Inc, equipped by Plame, THGA and Hydride Generation System (FIAS400). The analytical procedures for various elements are described in SOP elaborated in TL "GEOLAB". For organic compounds (HSs) in water and sediments EPA reference methods are utilized in accredited laboratories.

V .INVENTORY OF EVALUATION METHODS

Threshold values for HSs were evaluated for different type of soil depending of granulometric and organic content. For corrections additional analyses are required, such as granulometry and organic content. The legislation determines classes (categories) of environment quality. The specific procedure of Environmental Risk Assessment is elaborated by scientific teams studying polluted sites, by compilation of recommendations from different guides.

MONTENEGRO

The information on the state of environment of Montenegro with the Proposal of Measures is one of the basic documents in the field of environment and it is issued annually by the Agency for Nature and Environment Protection of Montenegro.

https://epa.org.me/informacije-o-stanju-zivotne-sredine/

https://epa.org.me/izvjestaj-o-stanju-zivotne-sredine-na-bazi-indikatora/

The monitoring program is implemented by the institutions selected in the tender procedure, except for the monitoring of the quality of air implemented by D.O.O. "Center for Ecotoxicological Testing of Montenegro.

In Montenegro there is not a regulation for the maximum allowable concentration of pollutants in sediments. Also, there are no laws, regulations or any other official directives for sampling the sediments, except the obligation to implement EU WFD in the next years.

Harmonized monitoring of surface waters, in line with the EU Water Framework Directive, includes: monitoring of **hydromorphological elements** following biological monitoring - the quantity and dynamics of water flow, groundwater connection, river continuity, variation of river width and depth, ***structure and sediment of the bottom of the river***, structure of the coastal belt, etc.

The Montenegro doesn't has monitoring of river sediment, but the "**Geological Survey of Montenegro**" has a lot of experience (especially for sampling sediments in streams) across Projects ("Geochemical reconnaissance stream sediment survey and other geochemical investigations in northeastern Montenegro" in 1975 for the United Nations, "Research of mineral resources in Montenegro" and "Basic geochemical map of Montenegro", which was completed in 2019).

ROMANIA

I.LEGISLATIVE FRAMEWORK

I.1.The legislative framework includes national laws (some transposing European directives) on environmental quality and environment elements (natural and artificial surface waters, groundwater, waste water, air, soil and sediments)

According to Order 161/2006, there is only one set of admissible values for river waters and one for sediments. This law provides also for biota regulations.

I.2.The biological, physico-chemical parameters (nutrients and specific non-synthetic and synthetic pollutants) provided in the legislative documents are comparable to those stipulated in the European legislation and in Romania's questionnaire (deliverable D 3.1.1.), the threshold values for the chemical parameters called "non-synthetic polluants" (metals) and "synthetic pollutants "(organic compounds) are listed for river waters, soils, drinking water and sediments.

I.3. Quality assurance and classifications are in line with European legislation for surface and groundwater monitoring. Monitoring is carried out by "Apele Romane" (Romanian Waters), which publishes an annual report available to the public.

I.4. Generally, legislative documents do not require the use of some sampling, transport or in-situ or laboratory sampling guides, but contain recommendations (e.g. metal analysis using ICP-MS or AAS for water in authorized laboratories in accordance with Order 161/2006). Another example of recommendation is the need for mechanical preparation of sediments for which the granulation under 63 micrometers is provided for the listing of the allowed threshold of pollutants in Order 161/2006 (granulometric method or preparation is not mandatory in the mentioned law).

In the questionnaire of Romania (deliverable D 3.1.1) there are listed the ISO guidelines used in the research projects or in the monitoring carried out by the authorities regarding the sampling, transportation, manipulation, preparation and analysis in situ and in the laboratory of waters, soils, sediments and biota.

II PRACTICES, EXPERIENCES

The Romanian questionnaire lists the national and international projects concerning the Danube Basin water survey, as well as the monitoring stations. From 5000 existing titles related to the Danube river and Delta (since 1960 to present), 137 are listed. There are public data on the current economic pollutants agents, type of activity and polluting chemicals.

III.INVENTORY OF SAMPLING METHODOLOGIES

The sampling (location, number of sampling stations,sampling frequency), transport and preservation of the sample in accordance with the analysis to be carried out, takes place according to the ISO guidelines listed in the questionnaire for water, soils, sediment and biota.

The Romanian Waters Administration (Apele Române) takes samples of waters (additional sediments and biota). All these samples determine the water quality. No biota and sediments are monitored for determining their quality. Except for some information regarding the thresholds of some polluting chemical substances (non synthetic and synthetic) specified in Order 161/2006, there is no guide on the quality of sediments. The research projects use information from the literature.

IV.INVENTORY OF LABORATORY METHODOLOGIES

Non-synthetic chemical substances are analyzed by ICP-OES, ICP-MS, AAS (flame, graphite furnace, hydride generator, etc., as well as associated technologies) or by XRF when the detection limits are relevant.

ISO or EPA analytical standards are used and these contain information on preparation procedures in accordance with the matrix, sample type, and analyzed element (microwave acid digestion or other technologies). For sample preparation procedures, analytical standards are used. Verification of the quality of the analysis is done by using CRM substances, interlaboratory comparisons and calibration programs or by monitoring the accredited laboratories by the appropriate institutions.

V .INVENTORY OF EVALUATION METHODS

The parameters for water, soil and sediment quality determination are set by legislation. For waters, biological and physico-chemical parameters (nutrients, non-synthetic and synthetic hazardous substances) have threshold values established according to the water body typology. The typology includes the geological background, and there can be several types of lithologies on a river course. So, especially for the chemical parameters of the non-synthetic pollutants, the geological background is taken into account. In particular, for groundwater, the aquifer includes the influence of the geological factor. The legislation includes also the analysis of non-synthetic hazardous substances both in atomic state, and in more dangerous forms (in ionic complexes). Especially in the case of sediments, the chemical element in valence states known to be harmful to aquatic life is analyzed.

SERBIA

I.LEGISLATIVE FRAMEWORK

Numerous regulations and rulebooks deals with the allowable values of polluting substances in surface and groundwaters and set limits for their achievement, also with the parameters of ecological and chemical status of surface waters and the parameters of chemical and quantitative status of groundwater. For soils, the regulations apply for maximum permissible values of polluting with harmful and dangerous substances and on systematic monitoring of soil quality, indicators for land degradation risk assessment and methodology for the development of remediation programs.

Threshold limit values are given for the assessment of sediment quality and for pollutants in soil. Quality objectives of HSs in sediments are also reglemented.

Numerous international analytical standards were addopted, concerning biological parameters, physico-chemical parameters, microbiological parameters, priority substances, polluting substances.

The guides of techniques on the design of sampling, transport, storage, sample preparation of sediment, soil, and water are: SRPS ISO 5667-1:2008; SRPS ISO 5667-12:2005; EN ISO 5667-15:2013 ; ISO 11466 (for sediment); ISO 10381-1:2002; ISO 18400-101; ISO 10381-1; JUS ISO 11464:2004 (for soil); SRPS EN ISO 5667-1:1999; SRPS EN ISO 5667-3:2012; SRPS EN ISO 5667-6; SRPS EN 13946:2015; SRPS EN 27828:2009; SRPS EN ISO 5667-6 (for water).

Serbia is part of the International Commission for the Protection of the Danube River (ICPDR).

II PRACTICES, EXPERIENCES

Along the Danube River are in operation a number of ten water quality, supervisory and operational monitoring stations, and many quality monitoring stations along rivers in the Republic of Serbia.

Surface water quality monitoring is institutionally assigned to the Environmental Protection Agency (SEPA). Introducing the requirements of the EU Water Framework Directive into the monitoring program has not been completed yet.

National and European projects referring to geochemistry of waters, soil and sediments in the Republic of Serbia are: FOREGS Geochemical mapping of Europe (1998-2005); Sustainable management of sediment resources (SedNet) (2002-2004); Sava River Basin: Sustainable Use, Management and Protection of Resources (2004-2007); Geochemical Mapping of Agriculture and Grazing Land Soil in Europe (GEMAS) (2008-2014); Reinforcing S&T Capacities of Two Emerging Research Centers for Natural and Industrial Pollutant Materials in Serbia and Slovenia (RESTCA-TERCE-NIPMSS) (2008-2011); Operational monitoring of surface and groundwaters in the Republic of Serbia (2017-2019).

Among significant scientific papers, signed by Serbian scientists, are FOREGS Geochemical mapping of Europe (1998-2005); Sava River Basin: Sustainable Use, Management and Protection of Resources (2004-2007); Sediment quality and impact assessment of pollutants (2007); EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) - Field manual (2008); Sediment regime of the Danube River in Serbia (2013).

III.INVENTORY OF SAMPLING METHODOLOGIES

Serbia is involved in transposing the EU WFD Directive and its accompanying Guidance Documents which define some of the methodology which should be used for sampling purposes.

Sediment sampling are in accordance with the requirements defined in the Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1:2006).

Sampling devices utilized are VanVeen grab sampler/ Graifer/ Core sampler. Sampling methodology follow SRPS ISO 5667-1:2008, SRPS ISO 5667-3:2007, SRPS ISO 6107-2:2005.

IV.INVENTORY OF LABORATORY METHODOLOGIES

For chemical analyses the equipment include ICP-MS, Perkin Elmer and FAAS, AAS-ETA, ICP-OES, GC/MSD Perkin Elmer.

A long list of HSs priority substances are taken in consideration. The values for the limits of detection are not available, so only the limits of quantification are listed.

Responsible institution for radionuclide monitoring in the environment, is the National Directorate for Radiation and Nuclear Safety and Security. Total β radioactivity is measured (Bq/l) following TRS 295:19891, ISO 9696:1992, ISO

9697:1992, ВДМ 02:19723 (for water), and ISO 18589-3:2011, MARLAP:2004, ВДМ 02:1972 (for sediment).

V .INVENTORY OF EVALUATION METHODS

Threshold values for inorganic compounds are set according to WFD, some of these values should be revised.

In Serbia a clear difference between contamination and pollution cannot be drawn from the definitions given within the legislative framework. In case of contamination and pollution the steps which are undertaken are defined in the specific plans created by organizations in accordance with the requirements of national legislation. These plans include remediation programs and specific measures tailored to the industry in question.

SLOVAKIA

I. LEGISLATIVE FRAMEWORK

The most significant legislation used in Slovakia that regulates the concentrations of dangerous substances posing a risk to environment in sediments, is as follows (use of legislation depends on the different project objectives):

- Directive of the Ministry of Environment of the Slovak Republic no. 4 / 1999-3 for the compilation and issue of a geochemical map of river sediments at a scale of 1:50 000
- Methodological Instruction of the Ministry of Environment of the Slovak Republic no. 549 / 98-2 for the risk assessment from contaminated sediments of streams and water reservoirs
- Directive of the Ministry of Environment of the Slovak Republic no. 1 / 2015-7 to develop a risk analysis of the contaminated area
- Act no. 188/2003 Coll. on the application of sludge and bottom sediments to soil
- Decree of the Ministry of Environment of the Slovak Republic no. 283/2001 on the implementation of certain provisions of the Act on Waste
- Act no. 255/2011 Coll., Amending Act no. 514/2008 Col. management of waste from the mining industry.

In Slovakia, the choice of the analytical method is primarily conditioned by the required output quality, the quantification limit and the financial point of view. From the most accessible methods, it is possible to mention the following:

- Atomic Absorption Spectrometry (AAS),
- Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP - AES),
- Inductively Coupled Plasma – Mass Spectrometry (ICP - MS),

- X-ray Fluorescence Spectrometry (XRF).

More detailed identification of minerals in sediments is realized, for example, using electron microscopy (SEM, TEM) and electron microanalysis or X-ray powder diffraction analysis.

The mobility of the elements (mainly potentially toxic trace elements) is experimentally evaluated by several approaches. These are, in particular, extraction experiments in laboratory conditions that imitate the changing conditions in the environment and help predict the risk of element mobilization from solid sediment phases. In addition to extraction methods, colony or batch experiments are also used to evaluate element mobility.

The most relevant parameters of the extraction methods are the nature of the reagent (type of substance, power), extraction time (from several hours to the days), or temperature. In Slovakia we tested several one-step extraction methods and sequential extraction methods.

An important prerequisite for obtaining representative results is correct sampling, which is guided by professional procedures, methodologies, standards. The most important ones in Slovakia (specifically for sediments) can be found at:(www.sutn.sk , www.iso.org):

- STN ISO 5667-12: 2001 Water quality. Sampling. Part 12: Guidance on sampling of bottom sediments.
- STN ISO 5667-15: 2002 Water quality. Sampling. Part 15: Guidance on preservation and handling of sludge and sediment samples.

II. PRACTICES, EXPERIENCES

List of significant ongoing projects in Slovakia focused on surface water and sediments is as follows:

- Monitoring of river sediments within the Partial Monitoring System of geological factors (SGIDS)
- Monitoring the impact of the Gabčíkovo water works on the quality of surface waters and sediments (WaterWork Company, state enterprise, Bratislava)
- DanubeSediment „Danube Sediment Management - Restoration of the Sediment Balance in the Danube River“ (international)
- FramWat „Framework for improving water balance and nutrient mitigation by applying small water retention measures“ (international)

Significant scientific papers related to mainly sediments are as follows:

- Geochemical atlas of the Slovak republic, part VI. Stream sediments (Bodiš et al., 1999)

- Evaluation of the Waste Water Tanks in the Slovak Republic in relation to the changes in the retention volume and the possibilities of improvement of their ecological status I, part Evaluation of Environmental Properties of Sediments (VS Palcmanská Maša) (Čuban, 2018)
- Evaluation of environmental impacts of sedimentation of small water reservoirs and possibilities of their solution (Hucko, 2011)
- Influence of erosion processes in river basins on water quality in streams. Final report (Hucko, 2009)
- Analyzes of bottom sediments as required by the Ministry of Environment of the Slovak Republic no. 549 / 98-2. VÚVH Bratislava (Hucko, 2007)
- Assessment of the impact of sediment extraction on VD Hričov (Hucko, 2007)
- Influence of the quality of surface waters and river sediments with organic substances from point sources of pollution in selected areas (Hucko et al., 2004)
- Verification of the sediment management system from water reservoirs (Hucko et al., 2003)
- Monitoring of the quality of surface waters and sediments of streams, canals and dams influenced by the Gabčíkovo water work. Final report for the period until 31 December 2004 (Valúchová et al., 2005)
- Mobilization of selected potentially toxic trace elements from river and bottom sediments and assessment of the risks of their entry into the environment under different sediment management methods. Dissertation (Pažická, 2018)
- Monitoring of river sediments in Slovakia. Mineralia Slovaca, 44 (Kordík et al., 2012)
- Assessing the impact of environmental loads on groundwater and sediments in the Sereď area. Podzemná voda. Vol. 22, no. 2. (Kordík et al., 2016)
- Qualitative assessment of river sediments of selected Slovakia streams and rivers – toxic elements. Final report. (Bodiš et al., 2013).

III. INVENTORY OF SAMPLING METHODOLOGIES

For sediments, the Geochemical mapping programme (in SGIDS), notably at large regional scales, requires the selection of an optimum geological material to be sampled. The sampled material should not only have suitable geochemical properties but also should be available more or less throughout the mapped area. Another very important fact that should be borne in mind is that equal sampling procedures must be used throughout the sampling campaign and all over the sampled area. Each collected sample is stored in a separate polyethylene bag. Where it is possible, 1.2 kg of the finest clay material were collected from at least three points over a distance of about 20 m along the stream.

UWITEC Core tube sampler (and its components) working on the gravity principle, using a telescopic rod and the possibility of driving straight into the sediment, is used by Water Research Institute for bottom sediments sampling.

Slovakia participated on the project „ Geochemical Atlas of Europe". A precised and detailed sampling strategy was established and "Foregs geochemical mapping field manual" was created (stream sediments, floodplain sediments). Details can be found at:

http://weppi.gtk.fi/publ/foregsatlas/index.php

V. INVENTORY OF EVALUATION METHODS

Quality standards for priority substances and other specific pollutants are defined with Regulation of the Ministry of the Environment, Slovakia. They refer to surface water and groundwater, whereas for sediments there are no such standards.

Data (groundwater and surface water) is published in annual reports released by Slovak hydrometeorological institute which contained the resulted interpretation (data comparison with standards). The reports are available to the public: www.shmu.sk.

Presentation of the results of the stream sediment monitoring is difficult to interpret because of the complexity of the conditions of their chemical composition (weathering, sedimentation, migration of substances). The composition of the stream sediment represents the natural features of the river basin area, as well as the anthropogenic effect. Interpretation of results in SGIDS takes into account the following approaches:

- application of statistical analysis (descriptive statistics, temporal variability),
- legislative approach (comparing the measured contents of the elements with specific limit concentrations),
- combined legislative and geostatistical approach (legislative assessment of the pollution parameters and the subsequent geostatistical treatment of the results in the map of the distribution of the contamination index).

SLOVENIA

I.LEGISLATIVE FRAMEWORK

In Slovenia, monitoring of water, sediment and biota is carried out by Slovenian Environment Agency (ARSO) in accordance with EU Water Framework Directive (WFD) which sets out uniform principles for the monitoring and assessment of water status for all Member States of the European Union.

II PRACTICES, EXPERIENCES

Programs for monitoring are prepared by ARSO, which is also responsible for their implementation, data control and assessment. The program for the period 2016 - 2021 has been prepared in accordance with national and European legislations and in accordance with international conventions and interstate agreements with neighbouring countries and contains three types of monitoring: Surveillance, operational and investigative monitoring.

For the general chemical status in Slovenia, sediments are monitored at most surveillance measuring points. In addition, they are also monitored at sites where pollution loads are detected (e.g. PCBs in Krupa, Lahinja, Kolpa). Sampling of sediments is carried out only for bottom sediments at 20 measuring points. Sampling for water quality is carried out at 125 monitoring points in the area of Danube River Basin. Slovenia is also involved in the Transnational Monitoring Network (TNMN) on the Danube tributaries, on the Sava and the Drava Rivers. These two locations are on the border profiles with Croatia, which are also included in the national program and in the bilateral monitoring with Croatia. The TNMN biological monitoring program is adapted to the requirements of the WFD.

III. INVENTORY OF SAMPLING METHODOLOGIES

Sediments are monitored in order to find out trends every 3 years, in accordance with WFD, Decree on the status of surface waters and the Rules on the monitoring of surface waters, while water is monitored at least monthly and biota yearly.

Sampling and most of the analyses are performed by accredited (for sampling and most of the analyses) external laboratory, ARSO only carries out analyses of metals in water, which has accreditation for those analyses.

For sampling river water standards SIST ISO 5667-6 and ISO 5667-3 are used, while for sampling bottom sediments standards SIST ISO 5667-12 and ISO 5667-15 are used. For the chemical analysis of sediments, the wet sieved fraction < 63 µm is used.

IV.INVENTORY OF LABORATORY METHODOLOGIES

River water monitoring includes 45 priority substances of which 21 are priority hazardous substances (e.g. cadmium, mercury, endosulfan, nonylphenol, etc.). For these substances a uniform Environmental quality standards (EQS) are set up for water and organisms (fish) in accordance with WFD. EQS are generally fixed. Some metals also consider the natural background (Cd, B, Hg, Cu, Zn, Co, Sb) and bioaccumulation (Ni and Pb). For some elements such as Cd, Cu, Zn EQS vary depending on the water hardness.

The assessment of the chemical status of river water bodies represents the pollution of rivers with priority substances for which the uniform EQS are set up in WFD for EU territory. The chemical status of the surface water body is determined at a single measuring point based on the calculation of the annual average value of the parameters of the chemical status.

V. INVENTORY OF EVALUATION METHODS

Evaluation of the ecological status and definition of categories is done according to WFD and Decree on the status of surface waters. Additional data about the methodology for ecological status evaluation are available at: http://www.mop.gov.si/fileadmin/mop.gov.si/pageuploads/podrocja/voda/ekolosko_stanje/metod_vredn_ekoloskega_st_vodotokov_rib.pdf.

The results of monitoring are available in the web site of Slovenian Environment Agency http://www.arso.gov.si/en/.

The original data (concentrations) are available in MS Excel files also in the web site: http://www.arso.gov.si/vode/podatki/arhiv/kakovost_arhiv2018.html.

The Environmental Agency of Slovenia suggests that uniform methodology for determining trends of sediments, which now is not yet prescribed, should be developed.

UKRAINE

I.LEGISLATIVE FRAMEWORK

In Ukraine existing normative documents are, in their majority, the analogues of those developed in the former USSR. Normative documents on the limits of concentration of hazardous substances in bottom sediments of rivers and lakes are lacking. Only maximum allowable concentrations for air of populated areas and for drinking water are available.

II PRACTICES, EXPERIENCES

The monitoring in Ukraine, along the Tisza River (of surface water levels, hydrochemical composition of surface water) is carried out by the Basin Department of the Water Resources of the Tisza River.

In 2000 it was created an automated information and measurement system for forecasting floods and for water resources management in the Tisza River Basin (AIVS-Tisza), in cooperation with Hungary. Eight hydrological stations in the Tisza basin were built and put into operation in the Transcarpathian region.

III. INVENTORY OF SAMPLING METHODOLOGIES

For sediment sampling, the locations were selected according to DSTU ISO 5667-12-2001. Sampling takes place during the summer low water period, once a year. For thicker muddy sediments (0.3 - 3.0 m) the Giller peat drill is used.

For laboratory measurements it was applied DSTU ISO 5667-12/2001.

IV.INVENTORY OF LABORATORY METHODOLOGIES

Analytical methods follow DSTU B V.2.1-19: 2009; DSTU CEN ISO / TS 17892: 2007; DSTU B V.2.7-232: 2010; DSTU B V.2.7-131: 2007; DSTU B V.2.7-71-98 norms.

V. INVENTORY OF EVALUATION METHODS

There are methods for a complex environmental assessment, but they are not approved at state level. To estimate the level of contamination, the gross concentrations of elements in the bottom sediments are mainly used. Only the method of MPC for the toxic elements in food products is used. A tentative scale for estimation of pollution of rivers by the level of accumulation of technogenic chemical elements in bottom sediments was proposed following Yanin E.P., “Technogenic geochemical associations in the bottom sediments of small rivers”, M., IMGRE, 2002.

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