Interreg
Danube Transnational Programme
SIMONA

QUESTIONNAIRE FOR EXISTING SAMPLING, LABORATORY AND EVALUATION METHODS

0.0. State your institution and country.
Croatian Geological Survey.

0.1. State institution(s) from which you got data to fill this questionnaire.
Hrvatske vode (water management public authority). Ministry of Environment and Energy.

I.LEGISLATIVE FRAMEWORK

I.1Enumeration of national or European legislation (laws, governmental orders, emergency ordinances) that regulates the concentrations of dangerous substances posing a risk to the health of the population or aquatic life, in soils, surface waters, drinking water, river sediments, marine sediments, sewage, therapeutic sludge, air and biota.

[PLEASE, SUPPORT YOUR ANSWERS WITH REFERENCES (NATIONAL LEGISLATIVE DOCUMENTS AND/OR WEB LINKS)]

No.	Title (in national language)	Title (in English)	Link	Country
1	Pravilnik o zaštiti radnika od izloženosti opasnim kemikalijama na radu, graničnim vrijednostima izloženosti i biološkim graničnim vrijednostima	Ordinance on protection of workers from exposure to hazardous chemicals at work, threshold values of exposure and biological threshold values	https://narodne-novine.nn.hr/clanci/sluzbeni/full/2018_10_91_1774.html https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32017L0164&from=EN	CRO
2	Pravilnik o zaštiti poljoprivrednog zemljišta od onečišćenja	Ordinance on the protection of agricultural land from pollution	https://narodne-novine.nn.hr/clanci/sluzbeni/2014_01_9_167.html	CRO
3	Uredba o razinama onečišćujućih tvari u zraku	Regulation on levels of pollutants in the air	https://narodne-novine.nn.hr/clanci/sluzbeni/2012_10_117_2521.html	CRO
4	Uredba o graničnim vrijednostima	Regulation on emission limit	https://narodne-novine.nn.hr/clanci/sluzbeni	CRO

	emisija onečišćujućih tvari u zrak iz nepokretnih izvora	values for pollutants in air from immovable sources	/2017_08_87_2073.html https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0050&from=EN, https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:023:0003:0016:EN:PDF https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:334:0017:0119:EN:PDF	
5	Pravilnik o zdravstvenoj ispravnosti vode za piće	Directive on the quality of water intended for human consumption	https://narodne-novine.nn.hr/clanci/sluzbeni/2008_04_47_1593.html http://www.voda.hr/sites/default/files/council_directive_98-83-ec.pdf	CRO
6	Uredba o kakvoći voda za kupanje	Bathing water quality	https://narodne-novine.nn.hr/clanci/sluzbeni/2014_04_51_978.html https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32006L0007&from=HR	CRO
7	Pravilnik o kakvoći slatkih voda kojima je potrebna zaštita ili poboljšanje kako bi bile pogodne za život riba	Directive on the quality of fresh waters needing protection or improvement in order to support fish life	http://www.voda.hr/sites/default/files/council_directive_2006-44-ec.pdf	CRO
8	Pravilnik o kakvoći voda za život i rast školjkaša	Directive on the quality required of shellfish waters	http://www.voda.hr/sites/default/files/council_directive_2006-113-ec.pdf	CRO
9	Uredba o standardu kakvoće voda	Directive on environmental quality standards in the field of water policy	https://narodne-novine.nn.hr/clanci/sluzbeni/2010_07_89_2502.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2013_06_73_1463.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2015_07_78_1504.html; https://narodne-novine.nn.hr/clanci/sluzbeni	CRO

			/2014_12_151_2829.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2016_07_61_1528.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2018_09_80_1610.html https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2008L0105:20130913:EN:HTML	
10	II. akcijski program zaštite voda od onečišćenja uzrokovanog nitratima poljoprivrednog podrijetla	II. action program for water protection against pollution caused by nitrates of agricultural origin	https://narodne-novine.nn.hr/clanci/sluzbeni/2017_06_60_1368.html	CRO
11	Pravilnik o graničnim vrijednostima emisija otpadnih voda	Ordinance on threshold values for waste water emissions	https://narodne-novine.nn.hr/clanci/sluzbeni/2013_06_80_1681.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2010_07_87_2460.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2014_04_43_801.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2016_01_3_22.html; https://narodne-novine.nn.hr/clanci/sluzbeni/2015_03_27_579.html	CRO
Croatia is in the process of setting up methodology for sediment sampling and analysis. Croatia doesn't have laws or any other official directives for mentioned sample media, except the obligation to implement EU WFD in the next years.				

I.2List of dangerous (hazardous) substances (metals, non-metals, PAHs, PCBs, other parameters) concentration levels, their significance (*definition of terms used for thresholds*) in waters, solids or biota, in accordance with the national legislative framework.

Alert threshold = concentrations of pollutants in air, water, soil or in emissions/discharges, which, when reached, warn the competent authorities on a potential impact on environment and trigger an additional monitoring and/or reduction of pollutant concentrations in emissions/discharges.
Intervention threshold = concentrations of pollutants in air, water, soil or in emissions/discharges, which, when reached, determine the competent authorities to order risk assessment studies and reduction of pollutant emissions from emissions/discharges.

Each country, please deliver the definition of specific terms in the respective law.

Soil

Croatia has the threshold limit values only for agricultural soil.

Table 1 Threshold values for metals in agricultural soil

mg/kg	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Sandy soil	0,0-0,5	0-40	0-60	0,0-0,5	0-30	0-50	0-60
Silty-clayey soil	0,5-1,0	40-80	60-90	0,5-1,0	30-50	50-100	60-150
Clayey soil	1,0-2,0	80-120	90-120	1,0-1,5	50-75	100-150	150-200

For Cd, Zn and Ni, if pH of clayey soil is under 6, than threshold limit value for silty-clayey soil is applied and if pH of silty-clayey soil is under 6, than threshold limit value for sandy soil is applied.

For Pb and Cr, if pH of clayey soil is under 5, than threshold limit value for silty-clayey soil is applied and if pH of silty-clayey soil is under 5, than threshold limit value for sandy soil is applied.

For Hg and Cu, if organic content of clayey soil is under 3%, than threshold limit value for silty-clayey soil is applied and if organic content of silty-clayey soil is under 3%, than the threshold limit value for sandy soil is applied.

Table 2 Threshold values for organic compounds in agricultural soil

Particular and total threshold limit value for polycyclic aromatic hydrocarbons - PAHs [mg/kg]	**Threshold limit value**
Naphthalene	0,1
Acenaphthylene	0,1
Fluorene	0,1
Fenantrene	0,2
Anthracene	0,1
Fluoranthene	0,2
Benz(a)anthracene	0,2
Benzo(a)pyrene	0,2
Benzo(b)fluoranthene	0,2
Benzo(k)fluorantene	0,2
Benzo(g,h,i)perylene	0,2
Krizen	0,2
Dibenz(a,h)anthracene	0,1
Indeno(1,2,3,-c,d)pyrene	0,2
Pyrene	0,2
Sum of PAHs for light and skeletal soil	1
Sum of PAHs for heavy soil	2
Total concentration of polychlorinated biphenyls –PCB [mg/kg]	
PCB= PCB 28+PCB 52+PCB 101+PCB 118+PCB 138+PCB 153+PCB 180	0,2
Insecticides based on chlorinated hydrocarbon [mg/kg]	
DDT7DDD/DDE (total concentrationa=DDT+DDD+DDE)	0,1
Drini (total concentration= aldrines+dieldrines+endrines)	0,1
HCH compounds (total concentration= alpha-HCH+beta-HCH+gamma-HCH+delta-HCH)	0,1
Herbicides [mg/kg]	
Atrazine	0,01
Simazine	0,01

I.3Quality objectives for hazardous substances (please complete the tables of HSs according to national documents)

Water

Table 3 Threshold limit values for groundwater

Indicator	Threshold limit value
arsenic (As)* [µg/l]	10
cadmium (Cd) [µg/l]	5
lead (Pb)* [µg/l]	10
mercury (Hg) [µg/l]	1
ammonium (NH_4)* [mg/l]	0,5
chlorides (Cl) [mg/l]	250
sulphates (SO_4) [mg/l]	250
orthophosphates (PO_4) [mg/l]	0,2
nitrites (NO_2) [mg/l]	0,5
total phosphorus (P)*/** [mg/l]	0,35
trichloroethylene and tetrachloroethylene sum [µg/l]	10
conductivity [µS/cm]	2 500

Table 4 Threshold limit values for groundwater in particular regions

Area	*arsenic [µg/l]	*ammonium [mg/l]	*phosphorus [mg/l]	*lead [µg/l]
East Slavonija, Drava i Danube catchment	200	5	2	
East Slavonija, Sava catchment	150	10		
Legrad – Slatina	35	2,5		
Lekenik – Lužani		10	1,5	
Lonja – Ilova – Pakra	60	15		
Zagreb		5		20

Table 5 Yearly average threshold limit values for surface water and quality standards for water biota

Substance	Land surface water [µg/l]	Other surface water [µg/l]	Quality standard for water biota [µg/kg]
Alachlor	0,7	0,7	
Anthracene	0,1	0,1	
Atrazine	2,0	2,0	
Benzene	50	50	
Brominated diphenylethers	0,14	0,014	0,0085
Cadmium and its compounds	≤ 0,45 (< 40 mg CaCO3/l) 0,45 (40 do < 50 mg CaCO3/l) 0,6 (50 do < 100 mg CaCO3/l) 0,9 (100 do < 200 mg CaCO3/l) 1,5 (≥ 200 mg CaCO3/l)	≤ 0,45 (< 40 mg CaCO3/l) 0,45 (40 do < 50 mg CaCO3/l) 0,6 (50 do < 100 mg CaCO3/l) 0,9 (100 do < 200 mg CaCO3/l) 1,5 (≥ 200 mg CaCO3/l)	
Chloralkanes	1,4	1,4	
Chlorfenvinphos	0,3	0,3	
Chlorpyrifos (chlorpyrifos-ethyl)	0,1	0,1	
Diuron	1,8	1,8	
Endosulfan	0,01	0,004	
Fluoranthene	0,12	0,12	30
Hexachlorbenzene	0,05	0,05	10
Hexachlorbutadiene	0,6	0,6	55
Hexachlorocyclohexane	0,04	0,02	
Izoproturon	1,0	1,0	
Lead and its compounds	14	14	
Mercury and its compounds	0,07	0,07	20
Naphtalene	130	130	
Nickel and its compounds	34	34	
Nonilphenols (4-Nonylphenol)	2,0	2,0	
Pentachlorophenol	1	1	
Benzo(a)pyrene	0,27	0,027	5

Benzo(b)fluoranthene	0,017	0,017	
Benzo(k)fluoranthene	0,017	0,017	
Benzo(g, h, i)perylene	8,2 × 10–3	8,2 × 10–4	
Simazine	4	4	
Tributyltin compounds (-cation tributyltin)	0,0015	0,0015	
Dicofol	not applicable	not applicable	33
Perfluorooctane sulfonic acid and its derivatives (PFOS)	36	7,2	9,1
Quinoxyfen	2,7	0,54	
Dioxins and dioxin-like compounds	not applicable	not applicable	Sum PCDD + PCDF +PCB-DL 0,0065 $\mu g kg^{-1}$ TEQ
Aclonifen	0,12	0,012	
Bifenox	0,04	0,004	
Cibutrin	0,016	0,016	
Cipermetrin	6 × 10–4	6 × 10–5	
Dichlorvos	7 × 10–4	7 × 10–5	
Hexabromocyclododecane (HBCDD)	0,5	0,05	167
Heptachlor and heptachlor epoxide	3 × 10–4	3 × 10–5	6,7 × 10–3
Terbutryn	0,34	0,034	

Table 6 Yearly average threshold limit values of eutrophication indicators in nearshore water

Indicator	**very good**	**good**	**moderate**	**bad**
Transparency [m]	> 10	< 10	< 3	< 3
Oxygen saturation [%]	80 – 120	surface layer: 120 – 170 bottom layer: 30 – 80	surface layer: > 170 bottom layer: 30 – 80	surface layer: > 170 bottom layer: 0 – 30
Dissolved anorganic nitrogen [µmol/l]	< 2	< 10	< 20	> 20

Dissolved phosphorous [µmol/l]	< 0,3	< 0,6	< 1,3	> 1,3
Chlorophyll a [µ/l]	< 1	< 5	< 10	> 10
TRIX	2 – 4	4 – 5	5 – 6	6 – 8

Table 7 Yearly average threshold limit values of eutrophication indicators in lakes

Indicator	very good	good
Total phosporus [mgP/l]	0,009 – 0,03	1,2 – 4,0
Chlorophyll a [µg/l]	0,02 – 0,07	2,5 – 7,0

Table 8 Yearly average threshold limit values of eutrophication indicators in rivers

Indicator	very good	good
Nitrates [mgN/l]	0,4 – 1,0	0,7 – 2,5
Total phosporus [mgP/l]	0,02 – 0,15	0,06 – 0,35
Chlorophyll a [µg/l]	5,9 – 20,0	10,0 – 40,0

Table 8 Microbiological threshold limit values for drinking water

Indicator	Unit for tap water	Threshold value	Unit for bottled water
Escherichia coli	broj/100 ml	0	number/250 ml
Enterococci	broj/100 ml	0	number /250 ml
Total coliformi	broj/100 ml	0	number /250 ml
Clostridium perfringens (including spores)	broj/100 ml	0	broj/100 ml
Number of colonies	broj/1 ml	100	broj/1 ml
Number of colonies	broj/1 ml	20	broj/1 ml
Salmonella spp.	broj/1000 ml	0	broj/1000 ml
Shigella spp.	broj/1000 ml	0	broj/1000 ml
Vibrio cholerae	broj/1000 ml	0	broj/1000 ml

Parasites	broj/1000 ml	0	broj/1000 ml
Enteroviruses	broj/5000 ml	0	broj/5000 ml
Pseudomonas aeruginosa	broj/100 ml	0	broj/250 ml

Table 9 Threshold limit values for chemical substances in drinking water

Indicator	**Threshold value**
Acrylamide [µg/l]	0,10
Aluminium [mg/l]	0,2
Ammonia [mg/l]	0,50
Antimony [µg/l]	5,0
Arsenic [µg/l]	10,0
Copper [µg/l]	2000
Barium [µg/l]	700
Benzene [µg/l]	1,0
Benzo(a)pyrene [µg/l]	0,01
Beryllium [µg/l]	
Color [mg/PtCo scales]	20
Boron [µg/l]	1000,0
Bromate [µg/l]	10,0
Cyanides [µg/l]	50,0
Zinc [µg/l]	3000
Detergents - anionic[µg/l]	200,0
– neionski [µg/l]	200,0
Epichlorohydrin [µg/l]	0,10
Fenoles [µg/l]	
Fluorides [µg/l]	1500
Phosphates [µg/l]	300
Evaporation residue [mg/l/105^{o}C]	<1000
Cadmium [µg/l]	5,0
Calcium [mg/l]	
Potassium [mg/l]	12

Chlorides [mg/l]	250,0
Chlorite [µg/l]	400
Cobalt [µg/l]	
Concentration of hydrogen ions [pH unit]	6,5-9,5
Chromium [µg/l]	50,0
Magnesium [mg/l]	
Manganes [µg/l]	50,0
Mineral oil [µg/l]	20,0
Smell	without
Dullness [^{o}NTU]	4
Sodium [mg/l]	200,0
Nickel [µg/l]	20,0
Nitrates [mg/l]	50,0
Nitrites [mg/l]	0,50
taste	without
Lead [µg/l]	10,0
PAH [µg/l]	0,10
Pesticides single/total [µg/l]	0,1/0,5
Selenium [µg/l]	10,0
Silicates [mg/l]	50
Free chlor [mg/l]	0,5
Silver [µg/l]	10
Sulphates [mg/l]	250,0
Temperature [^{o}C]	25
THM – total [µg/l]	100,0
1,2-dichloroethane [µg/l]	3,0
Tetrachlorethene and trichlorethene sum [µg/l]	10,0
TOC [mg/l]	
$CaCO_3$ [mg/l]	
Total suspensions [mg/l]	10
Consumtion of $KMnO_4$[µg/l of O_2]	5,0

Vanadium [µg/l]	5,0
Vinyl chloride [µg/l]	0,50
hydrogen sulphide	without
Conductivity [µS/cm/20°C]	2500
Iron [µg/l]	200,0
Mercury [µg/l]	1,0

Table 11 Threshold limit values for bathing water after each testing

Indicator	Perfect	Good
Intestinal Enterococci [CFU /100 ml]	≤200	≤400
Escherichia coli [CFU/100 ml]	≤500	≤1000

Table 10 After season and three-year average threshold limit values for bathing water

Indicator	Perfect	Good	Adequate
Intestinal Enterococci [CFU/100 ml]	≤200	≤400	≤330
Escherichia coli [CFU/100 ml]	≤500	≤1000	≤900

I.4Listing of analytical standards (national analytics and international e.g. USEPA, ASTM, etc.) recommended in documents for chemical, physical, microbiological analyzes of samples

Element	National analytical standards	International analytical standards	"in-house" developed methods"
Mercury in surface water, underground water and waste water		EPA Method 245.7 – Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry	
Advisory norm for phytoplankton counting by inverse microscope		HRN EN 15204:2008 (Utermöhl tehnic)	
Guidelines for quantitative and qualitative investigation of see phytoplankton.		HRN EN 15972:2011	
Measurement of an iochemical indicators – spectrophotometric determination of concentrations of the chlorophyll a norm for the macrophytes and phytobenthos.		HRN ISO 10260:2001	
Advisory norm for testing of the macrophytes in lakes.		HRN EN 15460:2008	
Guidelines for testing of the aquatic macrophytes in rivers.		HRN EN 14184:2014	
Guidelines for identification and counting Diatomae in samples of the river and lake bentos.		HRN EN 14407:2014	
Directive for assessment of fish quantity by mobile hydroaqustic methods		HRN EN 15910:2014	
TP - Application of inductively coupled plasma mass spectrometry (ICP-MS)		HRN EN ISO 17294-2:2016 (2mL of conc. H_2SO_4 in 500mL sample volume)	
Metals - Application of inductively coupled plasma mass spectrometry (ICP-MS)		HRN EN ISO 17294-2:2016 (4mL of HCl (1:1) in 1L sample volume)	
TN - Determination of nitrogen — Determination of bound nitrogen (TNb), following oxidation to nitrogen oxides		HRN EN 12260:2008 (2mL of conc. H_2SO_4 in 500mL sample volume)	
PI - Determination of permanganate index		HRN ISO 8467:2001 (2mL of conc. H_2SO_4 in 500mL sample volume)	

I.5. List of chronic or acute toxicity tests and determination of bioaccumulation or persistence in biota according to the specificity of the dangerous substance in the trophic chain (Ex: Microtox test - The potential ecological impacts of anaerobic degradation of vegetable oil on freshwater sediments; Hyalella Azteca etc).

Couldn't find any info on this.

I.6List of national, and international guides of techniques on the design of sampling,transport, storage, samples preparation (sieving, fraction extraction, separation, etc.) recommended in documents

No.		sediment	soil	water	Biota
1	sampling	HRN ISO 5667-12:2017 (Guidance on sampling of bottom sediments from rivers, lakes and estuarine areas)	HRN ISO 18400-102:2017 (Selection and application of sampling techniques)	HRN ISO5667-1:1999 (Guidance on the design of sampling programmes and sampling techniques)	HRN EN ISO 16665 (Guidelines for quantitative sampling and sample processing of marine soft-bottom macrofauna)
2				HRN EN ISO 5667-3:2012 (Preservation and handling of water samples)	HRN EN 14757:2015 (Fish sampling with net)
3					HRN EN 14011:2005 (Sampling of fish with electricity)
4					HRN EN 14962:2007 (Guidance on the scope and selection of fish sampling methods)
5					HRN EN ISO 16665:2014 (Guidelines for quantitative sampling and sample processing of marine soft-bottom macrofauna)
6					HR EN ISO

					19493:2008 (Guidance on marine biological surveys of hard-substrate communities)
7					HRN EN 16150:2012 (Guidance on pro-rata Multi-Habitat sampling of benthic macro-invertebrates from wadeable rivers)
8					HRN EN 15196:2008 (Guidance on sampling and processing of the pupal exuviae of Chironomidae (Order Diptera) for ecological assessment)
9					HRN EN ISO 10870:2012 (Guidelines for the selection of sampling methods and devices for benthic macroinvertebrates in fresh waters)
10					HRN EN 13946:2014 (Guidance standard for the routine sampling and pretreatment of benthic diatoms from rivers)
11					HRN EN 15708:2010 (Advisory norm for testing, sampling and laboratory analysis of phytobenthos in shallow streams)

12	Transport, storage	HRN ISO 5667-12:2017 (Guidance on sampling of bottom sediments from rivers, lakes and estuarine areas)	HRN ISO 18400-102:2017 (Selection and application of sampling techniques)	HRN ISO 5667-3:1999 (Guidance on the preservation and handling of water samples)	
13	Sample preparation	ISO 11466 (Soil quality- Extraction of trace elements soluble in aqua regia)			

I.7 Specify the recommended remedy measures associated with the contents of the hazardous substances (alert threshold, intervention threshold)

These actions are defined according to the situation. All information regarding actions is stated in Croatian legislative:
https://narodne-novine.nn.hr/clanci/sluzbeni/1999_08_82_1487.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2008_10_113_3297.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2008_12_145_3992.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2011_01_5_82.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2014_04_44_813.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2015_08_87_1727.html

Operational plan of Croatian Waters:
https://www.voda.hr/sites/default/files/dokumenti/operativni_plan.pdf

Croatia is also part of the International Commission for the Protection of the Danube River (ICPDR). International Organisation consists of 14 cooperating states and the European Union. Commission has a manual for accident warning system which also applies for Croatia. AEWS - International Operations Manual for Principal International Alert Centres of the Danube Accident Emergency Warning System.

https://www.icpdr.org/main/icpdr
https://www.icpdr.org/main/activities-projects/aews-accident-emergency-warning-system

II PRACTICES, EXPERIENCES

II.1.Significant national, European, finalized or ongoing projects related to geochemistry of waters, soils, sediments in the Danube basin

No.	Project title (national language, if available)	Project Title (EN)	Year	Country	Project coordinators,Partners
1	Osnovna geokemijska karta Republike Hrvatske	Basic Geochemical Map of Croatia	1998-2009	Croatia	Croatian Geological Survey
2	Sustainable management of sediment resources (SedNet)		2002-2004	Europe	SedNetwork (https://sednet.org/)
3	FOREGS Geochemical mapping of Europe		1998-2005	Europe	European Geological Surveys (EGS)
4	Monitoring aluvijalnih sedimenata rijeke Drave	Monitoring of Drava alluvial sediments	2004-2008	Croatia	Croatian Geological Survey
5	Origin, fate and Transport modelling of Nitrate in the Varaždin Alluvial aquifer - TRANITAL		2017-2021	Croatia	Croatian Geological Survey. Partners: Institute Ruđer Bošković (Zagreb), Croatian Waters (Zagreb) and Faculty of Natural Sciences-Department for biology (Zagreb)
6	Sava River Basin: Sustainable Use, Management and Protection of Resources		2004-2007	Slovenia, Croatia, B&H, Serbia	Jožef Stefan Institute (Slovenia), University of Ljubljana, Faculty of Civil and Geodetic Engineering (Slovenia), Rudjer Bošković Institute (Croatia), University of Zagreb, Faculty of Food Technology and Biotechnology (Croatia), Hydro-Engineering Institute (B&H), Mihailo Pupin Institute (Serbia), University of Banja Luka, Faculty of Agriculture (B&H),

					International Centre for Science and High Technology (Italy), University of Natural Resources and Applied Life Sciences Vienna, Institute for Agrobiotechnology (Austria), Norwegian Institute for Water Research (Norway), Imos Geateh, Planners and Engineers (Slovenia)
7	Geochemical Mapping of Agriculture and Grazing Land Soil in Europe (GEMAS)		2008-2014	Europe	European Geological Surveys (EGS)
8.	Ocena in modeliranje čezmejnega razširjanja onesnaženosti z namenom trajnostne rabe tal, varnosti hrane in varovanja naravnega obrečnegahabitata na poplavnem območju reke Drave	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	Geological Survey of Slovenia. Partner: Department of Chemistry, Institute of Environmental Sciences Szent Istvan University (Hungary)
9	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	Geological Survey of Slovenia (Slovenia), Faculty of Mining and Geology (Serbia), Johann Wolfgang Goethe University of Frankfurt (Germany)
10	HydroMorphological assessment and management at basin scale for the Conservation of Alpine Rivers and related Ecosystem		2016-2019	Alps	Civil protection Agency-Autonomous Province of Bolzano (Italy) and 13 different partners

	Services (HyMoCARES) (https://www.alpine-space.eu/projects/hymocares/en/home)				

II.2. Significant scientific papers, books, related to geochemistry of waters, soils, sediments in the Danube basin

No.	Paper title (national language, if available)	Title (EN)	Year	Country	Authors
1	FOREGS Geochemical Mapping Field manual		1998	Europe	Salminen, R. et al.
2	Geochemical Atlas of Europe-Part 1		2005	Europe	Salminen, R. et al.
3	Geochemical Atlas of Europe-Part 2		2006	Europe	De Vos, W. et al.
4	EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) - Field manual		2008	Euope	EuroGeoSurveys Geochemistry Working Group
5	Sediment quality and impact assessment of pollutants		2007	Europe	Barcelo, D, & Petrovic, M.
6	Chemistry of Europe's Agricultural Soils-Part A		2014	Europe	Reimann, C. et al.
7	Chemistry of Europe's Agricultural Soils-Part B		2014	Europe	Reimann, C. et al.
8	EuroGeoSurveys Geochemical mapping of agricultural and grazing land soil of Europe (GEMAS) - Field manual		2008	Euope	EuroGeoSurveys Geochemistry Working Group
9	Geokemijski atlas Hrvatske	Geochemical Atlas of Croatia	2009	Croatia	Halamić, j. & Miko, S. (eds)
10	Geokemijski atlas Siska	Geochemical Atlas of Sisak	2014	Croatia	Šorša, A. & Halamić, J.
11	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.

12	Handbook for Sediment Qulity Assessment		2005		Simpson et al.
13	Monitoring Pesticide Residues in Surface and Ground Water in Hungary: Surveys in 1990–2015		2015	Hungary	Székács, A., Mörtl, M. & Darvas, B.
14	2nd Sava River Basin Analysis Report		2016	Croatia	International Sava River Basin Commission

II.3Existent waterbodies and sampling sites (Ramsar, Natura2000 etc.) and current quality monitoring stations of the Danube River

Croatian Geological Survey has already provided locations of monitoring stations in the Croatian part of the Danube River Basin.

II.4.Data and metadata availability (including information on ambient or natural concentrations of HSs for establishing intervention measures)
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.

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

In addition, it should be noted 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.

II.5.Problems of current monitoring procedures in DRB

There are not known problems in addition to ones listed in Application Form for all countries. The area of the Danube River Basin is shared among many countries, so unique system is necessity for reliable water, biota and sediment quality monitoring and interpretation of results.

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

III.INVENTORY OF SAMPLING METHODOLOGIES

Croatia adopted Directive 2000/60/EC of the European Parliament and Council, establishing a framework for Community action in the field of water policy. Croatia is still not monitoring sediment but is monitoring water and biota. Answers to the most of the following questions regarding monitoring water and biota can be found in EU WFD Guidance Documents - http://ec.europa.eu/environment/water/water-framework/facts_figures/guidance_docs_en.htm

1. Directive 2000/60/EC –
https://eur-lex.europa.eu/resource.html?uri=cellar:5c835afb-2ec6-4577-bdf8-756d3d694eeb.0004.02/DOC_1&format=PDF

2. Directive 2014/101/EU - http://extwprlegs1.fao.org/docs/pdf/eur140065.pdf

3. Summary in Croatian language –
http://www.voda.hr/sites/default/files/metodologija_uzorkovanja_laboratorijskih_analiza_i_odredivanja_omjera_ekoloske_kakvoce_bioloskih_elemenata_i_odluka.pdf

III.1. Water

III.1.1. Sampling design strategy. How do you choose sampling locations, number of sites, sampling position within the national Danube sector, distance from confluence points, distance from point industry/agriculture polluters, distance from big cities, sampling depth, distance from the water course/bodies banks? How do you decide about temporal frequency of collecting samples?

According to the methodology requested by Water Framework Directive.

III.1.2. Which parameters of water **quality**/**quantity** are measured ***in situ***?

Dissolved oxygen.

III.1.3. Which **instruments** are used for ***in situ*** measurements (include manufacturer and type)?

HACH HQ40D Portable Dissolved Oxygen Meter.

III.1.4. Please, describe **methodology** for ***in situ*** measurements.

Immerse the probe of dissolved oxygen meter in the water and read the value.

III.1.5. Which **tools** are used for collecting samples for **laboratory** measurements (include manufacturer and type)?

Telescopic sampling pole, with an adjustable holder for different sample containers and bottles.

III.1.6 Sample preservation (samples chemical preservation according to their type and used analysis method).

Parameter	Method	Sample preservation
PI	HRN ISO 8467:2001	2mL of conc. H_2SO_4 in 500mL sample volume
TN	HRN EN 12260:2008	
TP	HRN EN ISO 17294-2:2016	
Metals	HRN EN ISO 17294-2:2016	4mL of HCl (1:1) in 1L sample volume

III.1.7 Please, describe a **methodology** for collecting samples

Sampling is conducted according to the methodology requested by Water Framework Directive. Parameters and sampling frequency depend on the measuring station type i.e. if it is surveillance, operative or investigative measuring station.

III.2 Sediment

III.2.1. Which type(s) of sediment do you sample/measure **bottom**, **suspended**, **floodplain**?

Bottom and floodplain.

III.2.2. Sampling design strategy. How do you choose sampling locations?
How do you decide about temporal frequency of collecting samples?

According to the methodology requested by Water Framework Directive.

III.2.3. Which parameters of sediment **quality**/**quantity** are measured ***in situ***?

None.

III.2.4. Which appropriate sampling devices (e.g. GRAIFER, CAROTIER etc.) and instruments are used for ***in situ*** measurements (include manufacturer and type)?

None.

III.2.5. Please, describe **methodology** for ***in situ*** measurements.

Not applicable.

III.2.6. Which **tools** are used for collecting samples for **laboratory** measurements (include manufacturer and type)?

PVC or ceramic spoons.

III.2.7. Please, describe a **methodology** for collecting samples for **laboratory** measurements.

Sampling is conducted according to the parameters intended to analyze later on.

a) sampling for polar parameters (pesticides, pharmaceuticals, hormones, personal care products…) is conducted only after the water has withdrawn to watercourse and as close as possible to the point where the water flow before the withdrawal was minimal. Sediment sample is grabbed with the clean plastic spatula/spoon (inert plastics), to the depth of maximum of 2 cm. Sample is stored in the dark glass bottle.

b) sampling for all other parameters is conducted from the watercourse, using polyethylene spoon. Sample is taken from the sediment surface or up to 1 cm deep. Sample should be composite, taken from the three different points within the perimeter of 2 m. Sample is stored in the 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.

III.2.8. Please, describe a **transport** methodology for samples intended for laboratory measurements.

Transport of the samples is done with cooling at the 2°C - 8°C.
For storing of samples up to 24 hrs, for cooling at this temperature laboratory refrigerators could be used.
For sample storing during longer periods (more than a month) it is recommended to freeze sample at -20°C. Before the analysis of such sample, care should be taken to thaw the sample thoroughly.

III.2.9. Do you **archive** samples? If yes, please describe how.

No.

III.3 . **Biota**

Monitoring of biota for the evaluation of chemical status of surface water bodies is done according to the Common Implementation Strategy for the Water Framework Directive (2000/60/EC) Guidance document No.32 on biota monitoring.

III.3.1. Which type(s) of **biota** do you sample/measure: **flora**, **fauna** (name species)?

Selected organism is chosen according to the parameters analyzed. Priority substances (WFD) are measured usually in the fish tissue.
Specifically, polyaromatic hydrocarbons are analyzed in the shellfish and gammaridae tissue, but problem is to find appropriate number of those organisms since they live in clean water (family gammaridae) and sandy bottom (shellfish).

III.3.2. Sampling design strategy. How do you choose sampling locations? How do you decide about temporal frequency of collecting samples?

Sampling design is done in order to fulfill WFD requirements. During 2017,. methodology has been developed for the first time. 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 1x per year. The

same parameters are planned to be analyzed in the sediment on all those stations, as well.

III.3.3. Which parameters of biota **quality**/**quantity** are measured ***in situ***?

During sampling, collected fish is visually inspected and counted; species and age are also determined and fish are selected accordingly.

III.3.4. Which **instruments** are used for ***in situ*** measurements (include manufacturer and type)?

Visual inspection.

III.3.5. Please, describe **methodology** for ***in situ*** measurements.

Visual inspection.

III.3.6. Which **tools** are used for collecting samples for **laboratory** measurements (include manufacturer and type)?

Fish samples are collected using direct current electro-aggregate, with at least 2,5 kW (for fishing from the shore) and at least 5 kW (for fishing from the boat). Aggregate have to allow the use of pulse current. For fishing in big rivers aggregate with 7,5 kW and 11 kW were used.

Invertebrate: shellfish are collected by hand and Gammaridae were sampled using Surber net.

III.3.7. Please, describe a **methodology** for collecting samples for **laboratory** measurements.

Fish are handled in gloves, to protect from contamination. After sampling, fish should be frozen at -20^{o}C. Prior to analysis, muscle tissue for analysis have to be removed while fish is half-thawed and then homogenized. Also, for the analysis for some parameters, the whole fish is used.
After homogenization and lyophilization, samples are stored at -20^{o}C.

Invertebrate: collected organisms should be immediately frozen at -20^{o}C. Whole organism (soft tissue) is used for analysis. After homogenization and lyophilization, samples are stored at -20^{o}C.

III.3.8. Please, describe a **transport** methodology for samples intended for laboratory measurements.

After sampling, fish or invertebrate were kept on ice and in the laboratory they were frozen at -20^{o}C.

III.3.9. Do you **archive** samples? If yes, please describe how.

No.

[PLEASE, SUPPORT YOUR ANSWERS WITH REFERENCES (NATIONAL LEGISLATIVE DOCUMENTS AND/OR WEB LINKS)]

IV.INVENTORY OF LABORATORY METHODOLOGIES

IV.1. How do you **mechanically prepare samples** for measurement (drying, sieving, grinding, homogenization, etc.)?

a) water - **filtration**
b) sediment – **drying, sieving, homogenization**
c) biota – **homogenization, cryogen grinding**

IV.2 Chemicals.
Granulometric analysis (information on the correlation of particle sizes and the absorption of toxic metals or metal compounds in sediments).
Analytical methods (including sample preparation: e.g. acid digestion, etc.) for the hazardous substance analyzed in agreement with the matrix in which it is being analyzed (water, sediment, sludge).
Type of analytical equipments.
Description of internal procedures

IV.2.1. Organic matter. What is the **procedure** for **organic matter** content determination in water and sediment?

Organic matter content is not being determined.

IV.2.2. ICP-MS, ICP-AES systems
IV.2.2.1. Which system of analysis do you use (ICP-MS, ICP-AES, etc.)? Please, include manufacturer and type.

ICP-MS, Perkin Elmer ELAN 9000 and ICP QQQ 8900 Agilent Technologies.

IV.2.2.2. Which **elements (HSs)** do you measure by this system? Please, state **detection limits** for measured elements (HSs).

In water:

Elements	Unit	Detection limit
Copper	(µg /L)	0,011
Zink	(µg /L)	0,01
Chromium	(µg /L)	0,01
Cadmium	(µg /L)	0,003
Nickel	(µg /L)	0,011
Lead	(µg /L)	0,003
Arsenic	(µg /L)	0,011

In sediment:

Elements	Unit	Detection limit
Copper	(mg/kg)	0,041
Zink	(mg/kg)	0,038
Chromium	(mg/kg)	0,016
Cadmium	(mg/kg)	0,002
Nickel	(mg/kg)	0,15
Lead	(mg/kg)	0,114
Arsenic	(mg/kg)	0,112

IV.2.2.3. Please, describe **sample preparation and procedure** for these measurements (microwave acid digestion, another disintegration procedure, gas velocity, temperature of atomization, mirrors position, nebulizer type, excitation power, wavelengths etc.).

Sediments are wet-sieved using water from sampling sites by standard sieves Retsch AS 200 to obtain the fraction of <63µm which is recommended in Guidance Document No: 25 (Guidance on chemical monitoring of sediment and biota under the WFDirective 2000/60/EC). The obtained fraction is then dried in an oven at 40°C. Aliquots of approximately 0.1 g of the dried sediment sample are digested with 2.5 mL of suprapur nitric acid and 7.5 mL of puriss hydrochloric acid and heated in Anton Paar Multiwave 3000 oven according to HRN ISO 11466:2004 (Soil quality -- Extraction of trace elements soluble in aqua regia). The elements in sediments are detected by inductively coupled plasma-mass spectrometry with solution of 20 µg/L Ge, Rh, In, Tb, Re and Y as internal standard according to HRN EN ISO 17294-2:2016. Each instrument has a standard nebulizer type from its manufacturer. Gas flow is around 1 L/min, but every time before measuring instruments are adjusted for the best performance with tuning solution so for that reason the gas flow can slightly be changed.

IV.2.2.4. How do you calculate **accuracy and precision** (references)?

The accuracy of the ICP-MS analytical method are performed by the analysis of the elements of interest in certified reference material which are analyzed at the beginning and after analysis. The certified reference material sample is digested in the same way as the sediment sample. As usual, if good agreement within 20% are observed between measured CRM data and the certified values, measurements can be made. Precision is not done at each measurement, but it is done once a year as part of validation of the ICP-MS method and consists of the following measurements: repeatability of measurements, repeatability of sample preparation and intermediate precision.

IV.2.3. AAS systems

IV.2.3.1. Please, state manufacturer and type of AAS(F-AAS,GF-AAS) instrument you use.

IV.2.3.2. Which **elements (HSs)** do you measure by AAS? Please, state **detection limits** for measured elements (HSs).

IV.2.3.3. Please, describe **sample preparation and procedure** for AAS measurements (dissolution, radiation source, source temperature, wavelengths, etc.).

IV.2.3.4. How do you calculate **accuracy and precision** (references)?

IV.2.4. XRF

IV.2.4.1. Please, state manufacturer and type of XRF(EDXRF,WDXRF) instrument you use.

IV.2.4.2. Which **elements and/or compounds** (HSs) do you measure by **XRF**? Please, state **detection limits** for measured elements and/or compounds (HSs).

IV.2.4.3. Please, describe **preparation of the sample and procedure** for XRF measurements.

IV.2.4.4. How do you calculate **accuracy and precision** (references)?

IV.2.5 DC-arc –AES

IV.2.5.1. Please, state manufacturer and type of instrument you use (type of detectors etc.).

IV.2.5.2. Which **elements and/or compounds** (HSs) do you measure by **DC-arc-AES**? Please, state **detection limits** for measured elements and/or compounds (HSs).

IV.2.5.3. Please, describe **preparation of the sample and procedure** for DC-arc-AES measurements.

IV.2.5.4. How do you calculate **accuracy and precision** (references)?

ICP method is used preferably to AAS, XRF and DC-arc-AES.

IV.2.6. Radionuclides

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

IV.2.6.1. **Which instrumental method(s)** you use to detect radionuclides in water, sediment and/or biota? Please, state manufacturer and type of radionuclide detection instrument you use.

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 60Co). 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.

IV.2.6.2. **Which radionuclides** do you measure? Please, state **detection limits** for measured radionuclides.

^{40}K, ^{137}Cs, ^{134}Cs ^{232}Th, ^{238}U, ^{226}Ra, ^{228}Ra ^{210}Pb, ^{235}U. Detection limits depend on the time of analysis, media type, radionuclide itself and used instrument.

IV.2.6.3. How do you calculate **accuracy and precision** (references)?

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.

References:

- Currie, L.A., Limits for qualitative detection and quantitative determination – application to radioactivity, Anal. Chem. 40(1968)586-593
- 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
- Software for nuclear spectrometry. IAEA-TECDOC-1049, IAEA, Vienna 1998.
- GammaVision®-32. A66-B32: gamma-ray spectrum analysis and MCA emulator for Microsoft® Windows® 98,2000,NT and XP®. (computer program and manual). Version 6,09. Oak Ridge: ORTEC®; 2005.
- Validation procedures of Softvare Applied in Nuclear instruments. IAEA-TECDOC-1565, IAEA, Vienna 2006.
- Quantifying uncertaintly in nuclear analytical measurements. IAEA-TECDOC-1401, IAEA, Vienna 2004.
- JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement
- 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
- Measurement uncertainty. IAEA-TECDOC-1585, IAEA, Vienna 2008.
- Guide to expression of Uncertainty in Measurement. (GUM), 1995.ISO.

IV.2.7. Organic compounds (HSs)

IV.2.7.1. **Which instrumental method(s)** you use to detect organic compounds (HSs) in water, sediment and/or biota?

Biota: GC-MS; HRGC/HRMS for PBDE and dioxins; LC-MS/MS for PFOS and HBCDD; (CV-AAS for mercury).
Water and sediment: GC-MS, GC-MS/MS and LC-MS/MS.

IV.2.7.2. **Which organic compounds (HSs)** do you measure?
Please, state **detection limits** for measured organic compounds (HSs)

In water:

Elements	Unit	Detection limit
alachlor	µg /L	0,00019
aldrin	µg /L	0,0004
anthracene	µg /L	0,00028
atrazine	µg /L	0,00006
benzene	µg /L	0,047
carbon tetrachloride	µg /L	0,037
endrin	µg /L	0,00018

isodrin	µg /L	0,00016
para-para-DDT	µg /L	0,00013
orto-para-DDT	µg /L	0,0001
para-para-DDE	µg /L	0,00032
para-para-DDD	µg /L	0,0004
heptachlor	µg /L	0,00006
heptachlor epoxide	µg /L	0,00005
dieldrin	µg /L	0,0001
1,2- dichloroethane	µg /L	0,086
dichloromethane	µg /L	1,707
HBCDD	µg /L	0,0002
α-endosulphan	µg /L	0,00008
β-endosulphan	µg /L	0,00138
fluoranthene	µg /L	0,00007
HCB	µg /L	0,00056
hexachlorobutadiene	µg /L	0,011
α-HCH	µg /L	0,00039
β- HCH	µg /L	0,00031
γ- HCH	µg /L	0,00025
δ- HCH	µg /L	0,00019
naphthalene	µg /L	0,00012
pentachlorobenzene	µg /L	0,00033
benz(a)pyrene	µg /L	0,00011
benzo(b)fluoranthene	µg /L	0,00051
benzo(k)fluoranthene	µg /L	0,00011
benzo(g,h,i)perylene	µg /L	0,00006
indeno(1,2,3-cd)pyrene	µg /L	0,00013
simazine	µg /L	0,00051
tetrachloroethene	µg /L	0,049
trichloroethene	µg /L	0,045
1,2,3-trichlorobenzene	µg /L	0,032
1,2,4- trichlorobenzene	µg /L	0,035
1,3,5- trichlorobenzene	µg /L	0,037
chloroform	µg /L	0,048
o-xylene	µg /L	0,041
m- xylene	µg /L	0,033
p- xylene	µg /L	0,036
toluene	µg /L	0,041
chlorpyrifos	µg /L	0,00015
chlorfenvinphos	µg /L	0,00019
trifluralin	µg /L	0,00011
DEHP	µg /L	0,00141
nonylphenol	µg /L	0,00021
oktylphenol	µg /L	0,00047
pentachlorophenol	µg /L	0,0001
diuron	µg /L	0,00009
isoproturon	µg /L	0,00019
C10-13 chloroalkanes	µg /L	0,004
tributyltin	µg /L	0,00013
AOX	µg /L	6
PBDE 28	µg /L	0,00006
PBDE 47	µg /L	0,00009

PBDE 99	µg /L	0,00008
PBDE 100	µg /L	0,0001
PBDE 153	µg /L	0,00064
PBDE 154	µg /L	0,00006
PBDE 183	µg /L	0,0002
PCB-28	µg /L	0,00007
PCB-52	µg /L	0,00009
PCB-101	µg /L	0,00009
PCB-138	µg /L	0,00018
PCB-153	µg /L	0,00048
PCB-180	µg /L	0,00007
PCB-77	µg /L	0,00011
PCB-81	µg /L	0,00007
PCB-105	µg /L	0,00011
PCB-114	µg /L	0,00009
PCB-118	µg /L	0,00021
PCB-123	µg /L	0,00007
PCB-126	µg /L	0,00008
PCB-156	µg /L	0,00007
PCB-157	µg /L	0,00006
PCB-167	µg /L	0,00007
PCB-169	µg /L	0,00008
PCB-189	µg /L	0,00008
dicofol	µg /L	0,0001
PFOS	µg /L	0,00015
quinoxyfen	µg /L	0,00017
aclonifen	µg /L	0,00025
bifenox	µg /L	0,00030
cybutryne	µg /L	0,00015
cypermethrin	µg /L	0,00007
dichlorvos	µg /L	0,00007
terbutryn	µg /L	0,00012
2,3,7,8-T4CDD	µg /L	0,000001
1,2,3,7,8-P5CDD	µg /L	0,000002
1,2,3,4,7,8-H6CDD	µg /L	0,000002
1,2,3,6,7,8-H6CDD	µg /L	0,000002
1,2,3,7,8,9-H6CDD	µg /L	0,000002
1,2,3,4,6,7,8-H7CDD	µg /L	0,000005
1,2,3,4,6,7,8,9-O8CDD	µg /L	0,000003
2,3,7,8-T4CDF	µg /L	0,000005
1,2,3,7,8-P5CDF	µg /L	0,000001
2,3,4,7,8-P5CDF	µg /L	0,000002
1,2,3,4,7,8-H6CDF	µg /L	0,000001
1,2,3,6,7,8-H6CDF	µg /L	0,000002
1,2,3,7,8,9-H6CDF	µg /L	0,000002
2,3,4,6,7,8-H6CDF	µg /L	0,000002
1,2,3,4,6,7,8-H7CDF	µg /L	0,000003
1,2,3,4,7,8,9-H7CDF	µg /L	0,000003
1,2,3,4,6,7,8,9-O8CDF	µg /L	0,000003

In sediment:

Elements	Unit	Detection limit
aldrin	µg /kg	0,798
anthracene	µg /kg	0,66
endrin	µg /kg	0,893
isodrin	µg /kg	0,569
para-para-DDT	µg /kg	0,548
orto-para-DDT	µg /kg	0,521
para-para-DDE	µg /kg	0,542
para-para-DDD	µg /kg	0,362
heptachlor	µg /kg	0,728
heptachlor epoxide	µg /kg	0,732
dieldrin	µg /kg	0,502
α-endosulphan	µg /kg	0,574
β-endosulphan	µg /kg	0,363
fluoranthene	µg /kg	0,59
HCB	µg /kg	0,187
α-HCH	µg /kg	0,31
β- HCH	µg /kg	0,565
γ- HCH	µg /kg	0,435
δ- HCH	µg /kg	1,502
pentachlorobenzene	µg /kg	0,305
benz(a)pyrene	µg /kg	0,726
benzo(b)fluoranthene	µg /kg	0,825
benzo(k)fluoranthene	µg /kg	0,99
benzo(g,h,i)perylene	µg /kg	0,99
indeno(1,2,3-cd)pyrene	µg /kg	0,792
C10-13 chloroalkanes	µg /kg	0,33
DEHP	µg /kg	0,002
tributyltin	µg /kg	4,06
PBDE 28	µg /kg	0,324
PBDE 47	µg /kg	0,587
PBDE 99	µg /kg	0,486
PBDE 100	µg /kg	0,318
PBDE 153	µg /kg	0,405
PBDE 154	µg /kg	0,513
PBDE 183	µg /kg	0,3
PCB-28	µg /kg	0,226
PCB-52	µg /kg	0, 319
PCB-101	µg /kg	0, 586
PCB-138	µg /kg	0, 483
PCB-153	µg /kg	0, 288
PCB-180	µg /kg	0, 433
PCB-77	µg /kg	0, 513
PCB-81	µg /kg	0, 554
PCB-105	µg /kg	0, 196
PCB-114	µg /kg	0, 256
PCB-118	µg /kg	0,83
PCB-123	µg /kg	0, 311
PCB-126	µg /kg	0, 522
PCB-156	µg /kg	0, 446
PCB-157	µg /kg	0, 352

PCB-167	µg /kg	0, 347
PCB-169	µg /kg	0, 186
PCB-189	µg /kg	0, 285
dicofol	µg /kg	0, 542
PFOS	µg /kg	0,003
quinoxyfen	µg /kg	0,008
HBCDD	µg /kg	0,003
2,3,7,8-T4CDD	µg /kg	0,002
1,2,3,7,8-P5CDD	µg /kg	0,008
1,2,3,4,7,8-H6CDD	µg /kg	0,008
1,2,3,6,7,8-H6CDD	µg /kg	0,008
1,2,3,7,8,9-H6CDD	µg /kg	0,008
1,2,3,4,6,7,8-H7CDD	µg /kg	0,008
1,2,3,4,6,7,8,9-O8CDD	µg /kg	0,02
2,3,7,8-T4CDF	µg /kg	0,002
1,2,3,7,8-P5CDF	µg /kg	0,008
2,3,4,7,8-P5CDF	µg /kg	0,008
1,2,3,4,7,8-H6CDF	µg /kg	0,008
1,2,3,6,7,8-H6CDF	µg /kg	0,008
1,2,3,7,8,9-H6CDF	µg /kg	0,008
2,3,4,6,7,8-H6CDF	µg /kg	0,008
1,2,3,4,6,7,8-H7CDF	µg /kg	0,008
1,2,3,4,7,8,9-H7CDF	µg /kg	0,008
1,2,3,4,6,7,8,9-O8CDF	µg /kg	0,02

IV.2.7.3. How do you calculate **accuracy and precision** (references)?

The accuracy of the analytical methods are performed by the analysis of the organic compounds of interest in certified reference material which are analyzed at the beginning and after analysis. As usual, if good agreement within 20% are observed between mesaured CRM data and the certified values, measurements can be made. Precision is not done at each measurement, but it is done once a year as part of validation of the adequate method and consists of the following measurements: repeatability of measurements, repeatability of sample preparation and intermediate precision.

IV.2.8. XRD

IV.2.8.1. Please, state manufacturer and type of XRD instrument you use.
IV.2.8.2. Do you use **XRD for sediment analysis**?
IV.2.8.3. Please, describe **preparation of the sample and procedure** for XRD measurements

XRD is not being performed.

IV.3 Inventory of national laboratories where dangerous substances are analyzed, specifying whether they have accreditations on the quality of analyzes (certificate issued by the national body attesting the quality of the analyzes), price and time of analyses.

IV.4 Description of "good practices" in laboratory and “in situ” analysis. For example, ways to convert analytical data obtained from sediment analysis to water quality assessments (taking into account the high cost of water analysis compared to the sediment).

IV.5 Description of protocols for intercomparison and intercalibration between laboratories. List of national and internationals projects which had developed the Protocols.

V .INVENTORY OF EVALUATION METHODS

V.1. How **threshold values** for HSs are set in each type of media (sediment, water, biota)? (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.).
V.2. Are **threshold values fixed or variable** and do they depend on the sample form, drainage basin lithology, time of the year, etc.?

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.

V.3. Do you use **corrections for threshold values**? (amount of **quartz**, **organic matter** etc.).

No.

V.4. The environmental quality objectives are based on measuring the total metal concentration and / or some dangerous compounds of that metal in different valence states?

Total metal concentration.

V.5 How the legislation reflects the phenomenon of “bioaccumulation”? Is the type of biota correlated with the ecosystem?
V.6. Does your national legislative find **categories of environment quality** based on deviations from threshold values?

Yes. There are some specific categories (for example those stated in I.2), but only for individual indicator.

V.7. Can these categories be **defined by quality of more than one medium?**
There are no multivariate indicators.

V.8. Please, describe **algorithm** for **defining** these **categories**? (e.g. weight coefficients).

No data.

V.9. How does your legislative framework define **difference** between **contamination** and **pollution**?

No. There is only contamination. Contamination is a direct or indirect introduction, as a result of human activity, of substances, vibration, heat or noise in the air, water or soil, which can be harmful to human health or the quality of the environment, can result in damage to property or impair or diminish value and other legitimate ways of using the environment.

V.10. Do you **relate specific HSs** with **sources of contamination and pollution** and how?

No.

V.11. Please, describe **actions** in case of contamination and pollution.

These actions are defined according to the situation. All information regarding actions is stated in Croatian legislative.
https://narodne-novine.nn.hr/clanci/sluzbeni/1999_08_82_1487.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2008_10_113_3297.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2008_12_145_3992.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2014_04_44_813.html
https://narodne-novine.nn.hr/clanci/sluzbeni/2015_08_87_1727.html

V.12. How do you **present results** in your **reports**, e.g. do you use complex representation for scientific community or simple representation for target groups? Does the report include methodology, full results, QA/QC, models? Are these results public or can be obtained by request?

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

V.13. Do you have a method for **space-time risk assessment** after determination of contamination and/or pollution?

Croatian legislation incorporated 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

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Method Implementation Document for EN 14385. BS EN 14385:2004. Stationary source emissions – Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V. Measurement of metals including an option to measure mercury. Environment Agency, Version 4, December 2013.

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G. Allen Burton, Jr. Sediment quality criteria in use around the world**.** Received: December 26, 2000 / Accepted: December 28, 2001

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