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SIMONA

SIMONA DEMONSTRATION AT 3 TEST AREAS

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Sediment-quality Information, Monitoring and Assessment System to support transnational cooperation for joint Danube Basin water management

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Authors (in alphabetical order):

DRAVA TEST AREA

HUNGARY: Győző Jordán (SZIE), Katalin Mária Dudás (NARIC), Zsófia Kovács (OVF)

UPPER TISA TEST AREA

ROMANIA: Gheorghe Damian (TUCN), Daniel Nasui (TUCN), Szolt Szakacs (TUCN), Gheorghe Iepure (TUCN)

SOUTH DANUBE TEST AREA

BULGARIA: Atanas Hikov (GI-BAS), Irena Peytcheva (GI-BAS), Milena Vetseva (GI-BAS), Petyo Filipov (GI-BAS), Zlatka Milalovska (GI-BAS).

ROMANIA: Veronica Alexe (IGR), Albert Baltres (IGR), Anca-Marina Vijdea (IGR)

SERBIA: Vladica Cvetković (UB-FMG), Marko Marjanović (JCI), Prvoslav Marjanović (JCI), Kristina Sarić (UB-FMG), Dragica Vulić (JCI)

Responsible(s) of the deliverable: Anca-Marina Vijdea (RO-IGR)

Co-responsible(s) of the deliverable: Gyozo Jordan (HU-SZIE)

Contents

1. INTRODUCTION

This Output summarises the results of Activity 3.4 "Evaluation of field data and implementing case studies"for each of the test areas (Drava, Upper Tisa and Lower Danube).

The three test areas have distinct characteristics. Drava test area is an agricultural plain, where pollution from agricultures is expected. Upper Tisa on Somes River and its tributaries is a mining region with closed base metal mines in the NE part of Romania, East Carpathians. South Danube represents an extended region where Danube reaches its largest widths and depths and where pollution (industrial, mining, agricultural, waste etc.) from tributaries and countries where it flowed are supposed to accumulate in the sediments it carries.

In each of the three test areas, during project previus periods, 10 sampling stations were selected (30 in total), where suspended sediment, bottom sediment and floodplain sediment were collected according to SIMONA Quality Sampling Protocol. The samples were stored and transported to the selected SIMONA Reference Laboratory, BalintAnalitika in Budapest. The analysed substances and the analytical standards are described in SIMONA Quality Laboratory Protocol. All these activities were described in detail in the project deliverables D.3.2.1 " Table of sampling sites providing details for Drava, Upper Tisa and South Danube areas", D.3.3.1 "Sampling report collection of the 10 sampling sites from test area" and D.3.3.2 "Laboratory report collection of the 10 sampling sites from test area"

The present report contains in chapter 2 a revision of the thresholds values for maximum admissible pollution in soils stipulated in the legislation of countries from the test areas (Bulgaria, Hungary, Romania, Serbia) for the analysed substances in SIMONA project, as well as the thresholds limits in sediments exitent in Serbia. The comparion was done also to other European and American standards for soils and/or sediments (the Dutch Pollution List, Elbe lower and upper limits, and US EPA standards).

Chapters 3, 4 and 5 contain the interpretation of the analysed values in the collected sediments from each test area and the conclusions regarding the observed level of pollution, together with identification of possible sources that determined values higher than the "normal limits" for some of the analysed substances.

2. ENVIRONMENTAL QUALITY STANDARDS

In each of the 3 Test Area there were collected sediment samples in 10 stations, whose locations were selected based on criteria listed in ISO standards and Guidelines and further developed in SIMONA Sampling Protocol., which also describes the sampling methodology for suspended, bottom and floodplain sediments. The samples were stored at 4-5°C and transported to SIMONA Reference Laboratory, where they were analyzed for the subtances listed in SIMONA Laboratory Protocol:

- 8 metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn)
- 6 polycyclic aromated hydrocarbons (PAHs: Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene+Benzo(k)fluoranthene, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene)
- 6 organoclorurated pesticides (Dicofol, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Hexachloro cyclohexane and Quinoxyfen).

The results were compared to national thresholds in the Test Areas countries:

- Drava Test Area (Hungary)
- Upper Tisa Test Area (Romania)
- South Danube Test Area (Bulgaria, Romania and Serbia).

Other European and international standards were also taken into consideration in analysing the data, for comparison:

- Dutch standards
- Elbe Lower and Upper limit
- US EPA standards.

Hungary

The alert values for soil (and groundwater) are specified in the Hungarian legislation nr. 6/2009 (IV. 14)

From this list, the values referring only to the substances analysed in SIMONA project are listed in Table 1.

Table 1: Alert values in soils in Hungary for the subtances/elements analysed in SIMONA project

	VALUES IN SOILS (mg/kg)
SUBSTANCE/ELEMENT	**Alert value**
Metals	
As	15
Cd	1
Cr	75
Cu	75
Hg	0.5
Ni	40
Pb	100
Zn	200
PAHs (sums of 10)	**1**
Anthracene	
Fluoranthene	
Benzo(a)pyrene	
Benzo(b)fluoranthene+Benzo(k)fluoranthene	
Benzo(g,h,i)perylene	
Indeno(1,2,3-cd)pyrene	
Organoclorurated pesticides	
Dicofol	
Heptachlor	
Heptachlor epoxide	
Hexachlorobenzene	
Hexachloro cyclohexane	
Quinoxyfen	

Romania

In Romania there is Order nr. 756/03.11.21997, updated 28.11.2011, issued by the Ministry of Waters, Forests and Environmental Protection for approving the Reglementation regarding environmental pollution.

This Order establishes the normal, alert and intervention values for pollutants in soils, air, surface water and groundwater. From the list of pollutants, in this study only the substances listed in SIMONA Laboratory Protocol were extracted and presented in Table 2.

Table 2: Normal, alert and intervention values in soils in Romania for the subtances/elements analysed in SIMONA project, expressed in mg/kg

	VALUES IN SOILS				
		SENSITIVE LAND USE CATEGORIES		LEAST SENSITIVE LAND USE CATEGORIES	
SUBSTANCE/ELEMENT	Normal Value	Alert Value	Intervention Value	Alert Value	Intervention Value
Metals					
As	5	15	25	25	50
Cd	1	3	5	5	10
Cr	30	100	300	300	600
Cu	20	100	200	250	500
Hg	0.1	1	2	4	10
Ni	20	75	150	200	500
Pb	20	50	100	250	1000
Zn	100	300	600	700	1500
PAHs					
Anthracene	0.05	5	10	10	100
Fluoranthene	0.02	5	10	10	100
Benzo(a)pyrene	0.02	2	5	5	10
Benzo(b)fluoranthene+Benzo(k)fluoranthene	0.02	2	5	5	50
Benzo(g,h,i)perylene	0.02	5	10	10	100
Indeno(1,2,3-cd)pyrene	0.02	2	5	5	50
Organoclorurated pesticides					
Dicofol					
Heptachlor					
Heptachlor epoxide					
Hexachlorobenzene					
Hexachloro cyclohexane	0.005	0.25	0.75	0.5	2
Quinoxyfen					

Sensitive and less sensitive land use categories are types of land uses, which involve a certain quality of soils, characterized by a maximum accepted level of pollutants.

Alert threshold values indicates concentrations of pollutants in air, water, soil or in emissions/discharges, which have the role of alerting the competent authorities to a potential impact on the environment and which trigger additional monitoring and/or reduction of pollutant concentrations from emissions/discharges.

The provisions on alert thresholds are as follows:

a) the alert thresholds warn the competent authorities about the existence, in a certain situation, of a potential pollution in air, water or soil;

b) when the concentration of one or more pollutants exceeds an alert threshold, the competent authorities may, if deemed necessary, have additional monitoring provided by the holders of activities potentially responsible for pollution, either through their own systems or through specialized units. At the same time, the competent authorities will request and follow the introduction of measures to reduce the concentrations of pollutants in emissions / discharges.

Intervention threshold indicates concentrations of pollutants in air, water, soil or in emissions/discharges, at which the competent authorities will order the execution of risk assessment studies and reduction of concentrations of pollutants in emissions/discharges.

Intervention thresholds are the pollution thresholds at which the competent authorities:

a) assesses the opportunity and requests, if necessary, the execution of risk assessment studies;

b) investigates the consequences of pollution on the environment;

c) impose the reduction of pollution, so that the concentrations of pollutants in emissions/discharges are reduced to the values provided by the regulations in force.

The importance of soil pollution with chemicals and other pollutants that are not included in the list of this Order will be assessed by the competent authorities on the basis of studies carried out by specialized units.

These regulations on soil pollution refer to both sensitive and least sensitive land use, identified as follows:

a) the sensitive use of the lands is represented by their use for residential and leisure areas, for agricultural purposes, as protected areas or sanitary areas with restricted regime, as well as the land surfaces provided for such uses in the future;

b) the less sensitive land use includes all existing industrial and commercial uses, as well as the land areas provided for such future uses;

c) in case there are uncertainties on the classification of a land use, the concentrations of the alert and intervention thresholds for the sensitive land uses will be considered.

Regarding pesticides, the Romanian Order 756/1997 indicates threshold values for soils for sums of DDTs and DDT, DDE, DDD and other types of pesticides, total HCH (Hexachloro cyclohexane) and alfa-HCH, beta-HCH, gamma-HCH, delta-HCH, polychlorinated biphenyls (PCB), total organoclorurated pesticides and triazine.

Bulgaria

As shown in the QUESTIONNAIRE FOR EXISTING SAMPLING, LABORATORY AND EVALUATION METHOD (D311) there are no Environmental Quality Standard (EQS) for river sediments that are applied in Bulgaria. In the same document, the EQS for soils (D311, BG Table 1, HSs-metals and Table 7 HSs-others/organic) and river water (Table 2 – metals; Table 9 – other/organic HSs) are provided in full. In this report, there were used only the EQS for soil as the closest natural matrix for river sediments, and the maximum/upper-limit and minimum/lower-limit values of HSs. The lower limit values correspond to the natural (background) concentrations of the corresponding element/substance in mg/kg, whereas the upper limit is used for the intervention threshold values in mg/kg.

Table 3: Normal and intervention thresholds values for metals in soils in Bulgaria, background and maximum allowable concentration for PAHs and pesticides in soil – for the substances / elements analysed in SIMONA project

	VALUES IN SOILS (mg/kg)	
SUBSTANCE/ELEMENT	**Normal Value**	**Intervention Value**
Metals		
As	10	90
Cd	0.4	12
Cr	65	550
Cu	34	500
Hg	0.03	10
Ni	46	300
Pb	26	500
Zn	88	900
PAHs	**Background Concentration in Soils**	**Maximum Allowable Concentration in Soils**
Anthracene	0.005	0.5
Fluoranthene	0.015	0.1
Benzo(a)pyrene	0.005	0.1
Benzo(b)fluoranthene+Benzo(k)fluoranthene		
Benzo(g,h,i)perylene	0.004	0.1
Indeno(1,2,3-cd)pyrene	0.011	0.2
Organoclorurated pesticides		
Dicofol		
Heptachlor		
Heptachlor epoxide		
Hexachlorobenzene		0.25
Hexachloro cyclohexane		0.01
Quinoxyfen		

Republic of Serbia

EQS standards for sediments are surrently regulated only in the Republic of Serbia from all the countries in the test areas. EQS for sediments are regulated in the RS by REGULATION ON LIMIT VALUES OF POLLUTANTS IN SURFACE AND GROUNDWATER AND SEDIMENT AND DEADLINES FOR REACHING THEM ("Official Gazette of RS", No. 50/2012)

Limit values of pollutants for assessment of sediment quality status and trend, i.e. target value, maximum allowed concentration and remediation value, are given in Table 4. "Limit values for sediment quality assessment" and Table 5. "Limit values for status and trend assessment sediment quality".

Limit values from for metals and organic matter refer to standard sediment containing 10% organic matter and 25% clay.

When assessing the quality of sediment, the limit values shall be corrected for a given sediment according to the measured content of organic matter and clay content in a given sediment in the manner defined in the regulations.

If surveillance monitoring exceeds the maximum permissible concentration or remediation value for one or more pollutants in a volume of 25 m^3 of sediment at a given site, or when there is a suspicion that the value of pollutant concentration between the target and maximum permissible value causes harmful ecotoxic effects on residential biota , the competent authority initiates the implementation of research monitoring within which the existence of harmful ecotoxic effects on residential biota is determined and the actual risk is assessed.

When the monitoring referred to confirms the existence of harmful ecotoxic effects on residential biota and/or the existence of a real risk, measures shall be implemented in accordance with the plan for protection of water from pollution.

In case of exceeding the remediation value for one or more pollutants in the volume of 25 m^3 of sediment at a given site, dislocation and/or remediation of sediment is performed and measures are taken in accordance with the plan for protection of water from pollution.

Quality assessment is performed for each specified pollutant or group of pollutants.

The final assessment of sediment quality is determined on the basis of the worst rated pollutant or group of pollutants.

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Table 4: Sediment Quality Limit values (EQS)

Sediment Quality Parameter	Unit of measure	EQS for sediment quality Target Concentration	Maximum allowable concentration	Concentration at which remediation of sediments is required
Arsenic (As)	mg/kg	29	42	55
Cadmium (Cd)	mg/kg	0,8	6,4	12
Chrome (Cr)	mg/kg	100	240	380
Copper (Cu)	mg/kg	36	110	190
Mercury (Hg)	mg/kg	0,3	1,6	10
Lead (Pb)	mg/kg	85	310	530
Nickel (Ni)	mg/kg	35	44	210
Zinc (Zn)	mg/kg	140	430	720
Mineral oils	mg/kg	50	3000	5000
Polycyclic Aromatic Hydrocarbons (PAH) (1)	mg/kg	1	10	40
Naphthalene	mg/kg	0,001	0,1	
Anthracene	mg/kg	0,001	0,1	
Phenanthrene	mg/kg	0,005	0,5	
Fluoranthenes	mg/kg	0,03	3	
Benzo (a) anthracene	mg/kg	0,003	0,4	
Crisis	mg/kg	0,1	11	
Benzo (k) fluoranthene	mg/kg	0,02	2	
Benzo (a) pyrene	mg/kg	0,003	3	
Benzo (g, h, i) perylene	mg/kg	0,08	8	
Indeno (1,2,3-cd) pyrene	mg/kg	0,06	6	
Polychlorinated Biphenyls (PCBs) (2)	µg/kg	20	200	1
DDD	µg/kg	0,02	2	
DDE	µg/kg	0,01	1	
DDT	µg/kg	0,09	9	
DDT total (3)	µg/kg	10	-	4000
Aldrin	µg/kg	0,06	6	
Dieldrin	µg/kg	0,5	450	
Endrin	µg/kg	0,04	40	
Cyclodien pesticides (4)	µg/kg	5	-	4000
α-HCH	µg/kg	3	20	
β-HCH	µg/kg	9	20	
γ-HCH (lindane)	µg/kg	0,05	20	
HCH total (5)	µg/kg	10	-	2000
Alpha-endosulfan	µg/kg	0,01	1	4000
Heptachlor	µg/kg	0,7	68	4000
Heptachlor-epoxide	µg/kg	0,0002	0,002	4000

Indices:

1 - parameter refers to the sum of the following compounds: naphthalene, anthracene, phenanthrene, fluoranthene, benzo (a) anthracene, chrysene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (g, h, i) perylene, indeno, 1, 2,3-cd) pyrene

2 - parameter refers to the sum of the following individual compounds: PCBs 28, 52, 101, 118, 138, 153 and 180.

3 - parameter refers to the sum of DDT, DDD and DDE

4 - parameter refers to the sum of aldrin, dieldrin and endrin

5 - parameter refers to the sum of four isomers of hexachlorocyclohexane: α-HCH, β / HCH, γ-HCH, δ-HCH

Soil quality EQS is regulated in Serbia by REGULATION ON LIMIT VALUES OF POLLUTANTS, HARMFUL AND HAZARDOUS SUBSTANCES IN THE LAND ("Official Gazette of RS", No. 30/2018 and 64/2019).

Limit values of pollutants, harmful and hazardous substances in the soil whose exceeding indicates the level of contamination that disturbs the ecological balance, imposes additional tests of that soil as well as limitations in the management, as well as values of pollutants, harmful and hazardous substances in the soil.

Levels that are safe for use are given in Table 5 - Limit maximum and remediation values of pollutants, harmful and dangerous substances in the soil,

In case of exceeding the limit values, additional research is performed on contaminated sites in order to determine the degree of soil pollution and prepare remediation and reclamation projects.

The remediation and reclamation project is always implemented when the average concentration of any polluting, hazardous and harmful substances in more than 25 m^3 of soil volume exceeds the remediation value given in Annex 1 or in more than 100 m^3 of aquifer volume at contaminated sites exceeds the remediation value.

The remediation and reclamation project can be realized in case of exceeding the limit values, as well as in case the concentrations of pollutants, hazardous and harmful substances in less than 25 m^3 of soil volume exceed the remediation values, if additional research at contaminated sites indicates significant consequences for human health and the environment.

Table 5: Soil Quality Limit values (EQS) in the Republic of Serbia – Limit, maximum and remediation values of pollutants, harmful and dangerous substances in the soil

Parameter	Soil concentration (mg/kg absolute dry matter)	
	Maximum allowable Concentration Limit value (EQS)	Concentration Limit value at which remediation is to be initiated
Metals		
Cadmium (Cd)	0,8	12

Parameter	Soil concentration (mg/kg absolute dry matter)	
	Maximum allowable Concentration Limit value (EQS)	Concentration Limit value at which remediation is to be initiated
Chrome (Cr)	100	380
Copper (Cu)	36	190
Nickel (Ni)	35	210
Lead (Pb)	85	530
Zinc (Zn)	140	720
Mercury (Hg)	0,3	10
Arsenic (As)	29	55
Barium (Ba)	160	625
Cobalt (Co)	9	240
Molybdenum (Mo)	3	200
Antimony (Sb)	3	15
Beryllium (Be)	1,1	30
Selenium (Se)	0,7	100
Tellurium (Te)	-	600
Thallium (Th)	1	15
Tin (Sn)	-	900
Vanadium (V)	42	250
Silver (Ag)	-	15
Inorganic substances		
yanides - free	1	20
Cyanides - complex (pH <5) 1 *	5	650
Cyanides - complex (pH ≥ 5)	5	50
Thiocyanates (total)	1	20
Bromides (mgBr / l)	20	-
Fluorides (mgF / l)	500*	-

Parameter	Soil concentration (mg/kg absolute dry matter)	
	Maximum allowable Concentration Limit value (EQS)	Concentration Limit value at which remediation is to be initiated
Organic Substances		
Benzene	0,01	1
Ethylbenzene	0,03	50
Toluene	0,01	130
Xylenes	0,1	25
Styrene (vinyl benzene)	0,3	100
Phenol	0,05	40
Cresols (total)	0,05	5
Catechol (o-dihydroxybenzene)	0,05	20
Resorcinol (m-dihydroxybenzene)	0,05	10
Hydroquinone (p-dihydroxybenzene)	0,05	10
Dodecylbenzene	-	1000
Aromatic solvents	-	200
Polycyclic aromatic compoundsi (PAH)		
AH (total) 2 *	1	40
Chlorinated hydrocarbons		
Vinyl chloride	0,01	0,1
Dichloromethane	0,4	10
1,1-dichloroethane	0,02	15
1,2-dichloroethane	0,02	4
1,1-dichloroethene	0,1	0,3

Parameter	Soil concentration (mg/kg absolute dry matter)	
	Maximum allowable Concentration Limit value (EQS)	Concentration Limit value at which remediation is to be initiated
1,2-dichloroethene (cis, trans)	0,2	1
Dichloropropane	0,002	2
Trichloromethane (Chloroform)	0,02	10
1,1,1- trichloroethane	0,07	15
1,1,2-trichloroethane	0,4	10
Trichloroethene	0,1	60
Tetrachloromethane	0,4	1
Tetrachloroethene	0,002	4
Chlorobenzenes (total) 3 *	0,03	30
Chlorophenols (total) 4 *	0,01	10
Chloronaphthalene	-	10
Monochloraniline	0,005	50
Polychlorinated biphenyls (total) 5 *	0,02	1
Extractable halogenated organic compounds (EOX)	0,3	-
Dichloroaniline	0,005	50
Trichloroaniline	-	10
Tetrachloraniline	-	30
Pentachloroaniline	-	10
4-chloromethylphenol	-	15

Parameter	Soil concentration (mg/kg absolute dry matter)	
	Maximum allowable Concentration Limit value (EQS)	Concentration Limit value at which remediation is to be initiated
Dioxin	-	0,001
Pesticides		
DDT / DDD / DDE (total)	0,01	4
Drini6 *	0,005	4
Aldrin	0,00006	-
Dieldrin	0,0005	-
Endrin	0,00004	-
HCH compounds7 *	0,01	2
α-HCH	0,003	-
β-HCH	0,009	-
γ-HCH	0,00005	-
Atrazin	0,0002	6
Carbaryl	0,00003	5
Carbofuran	0,00002	2
Chlordan	0,00003	4
Endosulfan	0,00001	4
Heptachlor	0,0007	4
Heptachlorepoxide	0,0000002	4
Maneb	0,002	35
MCPA8 *	0,00005	4
Organo tin compounds (total)	0,001	2,5
Azinphosmethyl	0,000005	2
Other substances		
Cyclohexanone	0,1	45
Phthalates (total) 9 *	0,1	60

Parameter	Soil concentration (mg/kg absolute dry matter)	
	Maximum allowable Concentration Limit value (EQS)	Concentration Limit value at which remediation is to be initiated
Total petroleum hydrocarbons (fractions C6-C40)	50	5000
Pyridines	0,1	0,5
Tetrahydrofuran	0,1	2
Tetrahydrothiophene	0,1	90
Tribromomethane	-	75
Acrylonitrile	0,000007	0,1
Butanol	-	30
1,2 butyl acetate	-	200
Ethyl acetate	-	75
Diethylene glycol	-	270
Ethylene glycol	-	100
Formaldehyde	-	0,1
Isopropanol	-	220
Methanol	-	30
Methyl tertiary butyl ether (MTBE)	-	100
Methyl ethyl ketone (MEK)	-	35

Indices:

1 * - The pH is determined in 0.01 M $CaCl_2$.

2 * - Sum of ten polycyclic aromatic hydrocarbons (anthracene, benzo (a) anthracene, benzo (k) fluoranthene, benzo (a) pyrene, chrysanthemum, phenanthrene, fluoranthene, indeno (1,2,3-cd) pyrene, naphthalene and benzo (ghi) perilen).

3 * - The sum of all chlorobenzenes (mono-, di-, tri-, tetra-, penta- and hexachlorobenzenes).

4 * - The sum of all chlorophenols (mono-, di-, tri-, tetra- and pentachlorophenols).

5 *- In case of remediation values, the sum of congeners of polychlorinated biphenyls is taken into account: PCB 28, 52, 101, 118, 138, 153 and 180; and in the case of maximum limits, the sum of the same congeners except PCB 118 is taken into account.

6 * - By "drins" is meant the sum of aldrin, dieldrin, and endrin.

7 * - HCH (hexachlorocyclohexane) means the sum of α-HCH, β-HCH, γ-HCH and δ-HCH.

8 * - MCPA - 4-chloro-o-toluxyacetic acid ($C_9H_9ClO_3$).

9 * - The sum of all phthalates.

- differentiation by clay content: (F) = 175 = 13 · L (L =% clay)..

Dutch standards (pollution list)

From the Dutch pollution lists the thresholds corresponding to subtances/elements analyzed in SIMONA Reference Laboratory were extracted in Table 6.

Table 6: Dutch target and intervention values in soils for the subtances/elements analysed in SIMONA project

	VALUES IN SOILS (mg/kg)	
SUBSTANCE/ELEMENT	**Target Value**	**Intervention Value**
Metals		
As	29	55
Cd	0.8	12
Cr	100	380
Cu	36	190
Hg	0.3	10
Ni	35	210
Pb	85	530
Zn	140	720
PAHs (sums of 10)		40
Anthracene		
Fluoranthene		
Benzo(a)pyrene		
Benzo(b)fluoranthene+Benzo(k)fluoranthene		
Benzo(g,h,i)perylene		
Indeno(1,2,3-cd)pyrene		
Organoclorurated pesticides		
Dicofol		
Heptachlor		4
Heptachlor epoxide		4
Hexachlorobenzene		2
Hexachloro cyclohexane		
Quinoxyfen		

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Elbe Lower and Upper Limit in Sediments

From the Elbe EQSs the thresholds corresponding to subtances/elements analyzed in SIMONA Reference Laboratory were extracted in Table 7.

Table 7: Elbe limits in sediments for the subtances/elements analysed in SIMONA project

	VALUES IN SEDIMENTS (mg/kg)	
SUBSTANCE/ELEMENT	**Lower Limit**	**Upper Limit**
Metals		
As	7.9	40
Cd	0.22	2.3
Cr	26	640
Cu	14	160
Hg	0.15	0.47
Ni		3
Pb	25	53
Zn	200	800
PAHs (sums of 10)	**0.6**	**2.5**
Anthracene	0.03	0.31
Fluoranthene		0.18
Benzo(a)pyrene	0.01	0.6
Benzo(b)fluoranthene+Benzo(k)fluoranthene		
Benzo(g,h,i)perylene		
Indeno(1,2,3-cd)pyrene		
Organoclorurated pesticides		
Dicofol		
Heptachlor		
Heptachlor epoxide		
Hexachlorobenzene	0.0004 µg/kg	17 µg/kg
Hexachloro cyclohexane		
Quinoxyfen		

US EPA TEC and PEC

From the US EPA TEC and PAC lists, the thresholds corresponding to subtances/elements analyzed in SIMONA Reference Laboratory were extracted in Table 8.

Table 8: US EPA TEC and PEC values for soils for the substances/elements anallysed in SIMONA project

	VALUES IN SOILS (mg/kg)	
SUBSTANCE/ELEMENT	**US EPA TEC**	**US EPA PEC**
Metals		
As		
Cd	0.99	4.98
Cr		
Cu	31.6	149
Hg		
Ni		
Pb	35.8	128
Zn	120	459
PAHs		
Anthracene		
Fluoranthene		
Benzo(a)pyrene		
Benzo(b)fluoranthene+Benzo(k)fluoranthene		
Benzo(g,h,i)perylene		
Indeno(1,2,3-cd)pyrene		
Organoclorurated pesticides		
Dicofol		
Heptachlor		
Heptachlor epoxide		
Hexachlorobenzene		
Hexachloro cyclohexane		
Quinoxyfen		

3. DRAVA TEST AREA

4. UPPER TISA TEST AREA

4.1 INTRODUCTION

The Upper Tisa test area comprises the Lăpuș Catchment, including the Lăpuș River, 2 of its tributaries and 2 points on the Someș River, also a tributary of Tisa – one upstream and one downstream of Lăpuș River's outlet. The area is characterized with present and past mining activity, industrial and agricultural activities, and a rising degree of urbanization which contributes to the overall sediment pollution. A schematic of the sampling sites is shown in Fig 4.1 and Fig. 4.2.

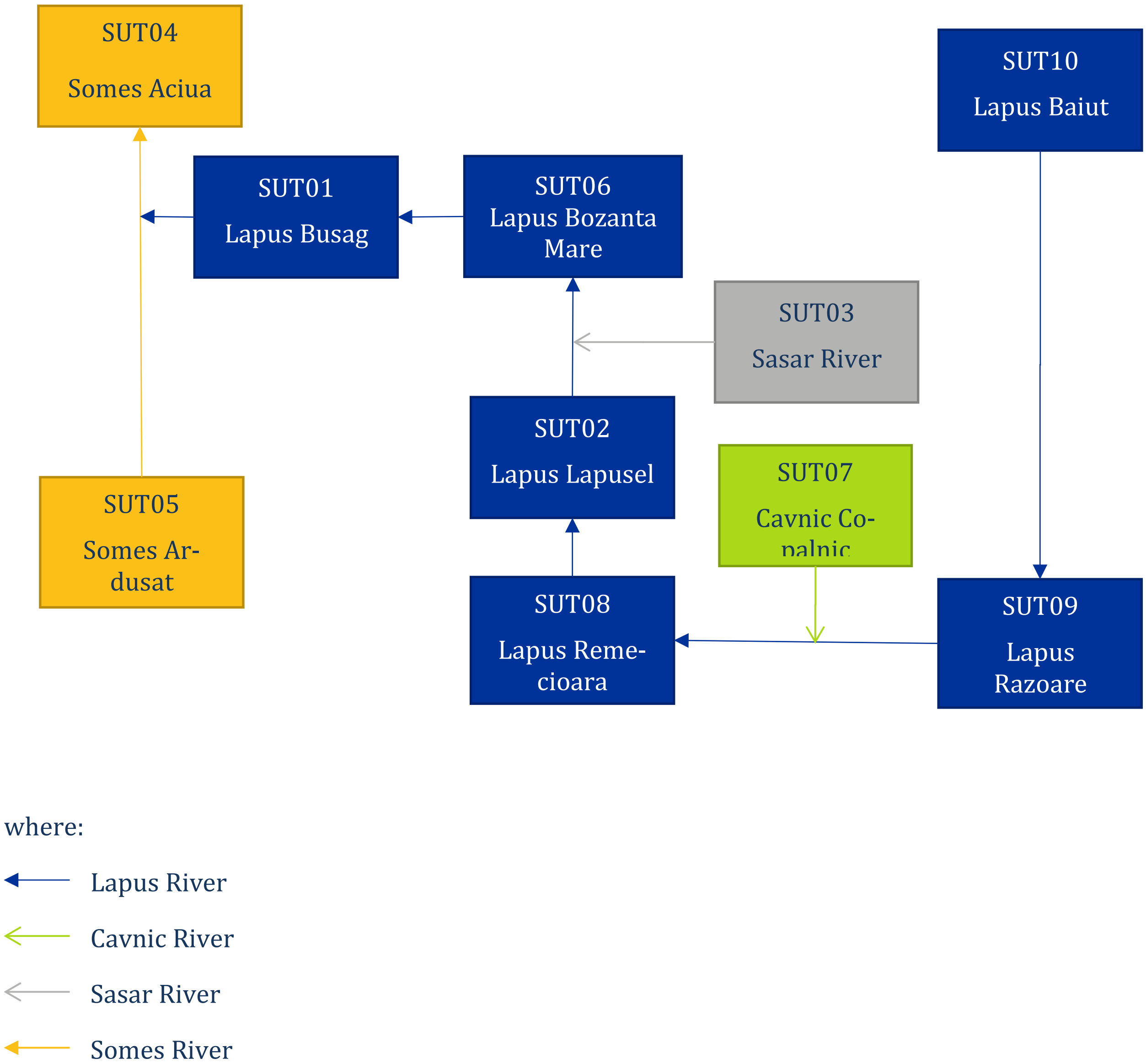

Fig. 4.1: Upper Tisa Sampling sites schematic

For each representative sampling site from Fig. 4.2 suspended sediment, bottom sediment from the 0-5cm layer and floodplain sediment from the 0-5cm and 40-50cm layer was sampled. The analysis of selected HS's was performed in SIMONA accredited laboratory. The measured data was then tabulated and processed. The determined values, together with the Project name, sample ID, sampling method and date, unit of measure and laboratory internal codes for As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene + Benzo(k)fluoranthene, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene, Dicofol, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Hexachloro cyclohexane and Quinoxyfen can be found in Chapter 4.5.

The data in these tables were compared to the following EQS's:

1.) Dutch target and intervention values for soils

2.) Hungarian EQS for soils

3.) Elbe lower limit and upper limit values for sediments

4.) Romanian normal, alert and intervention thresholds for sensitive and less sensitive soils

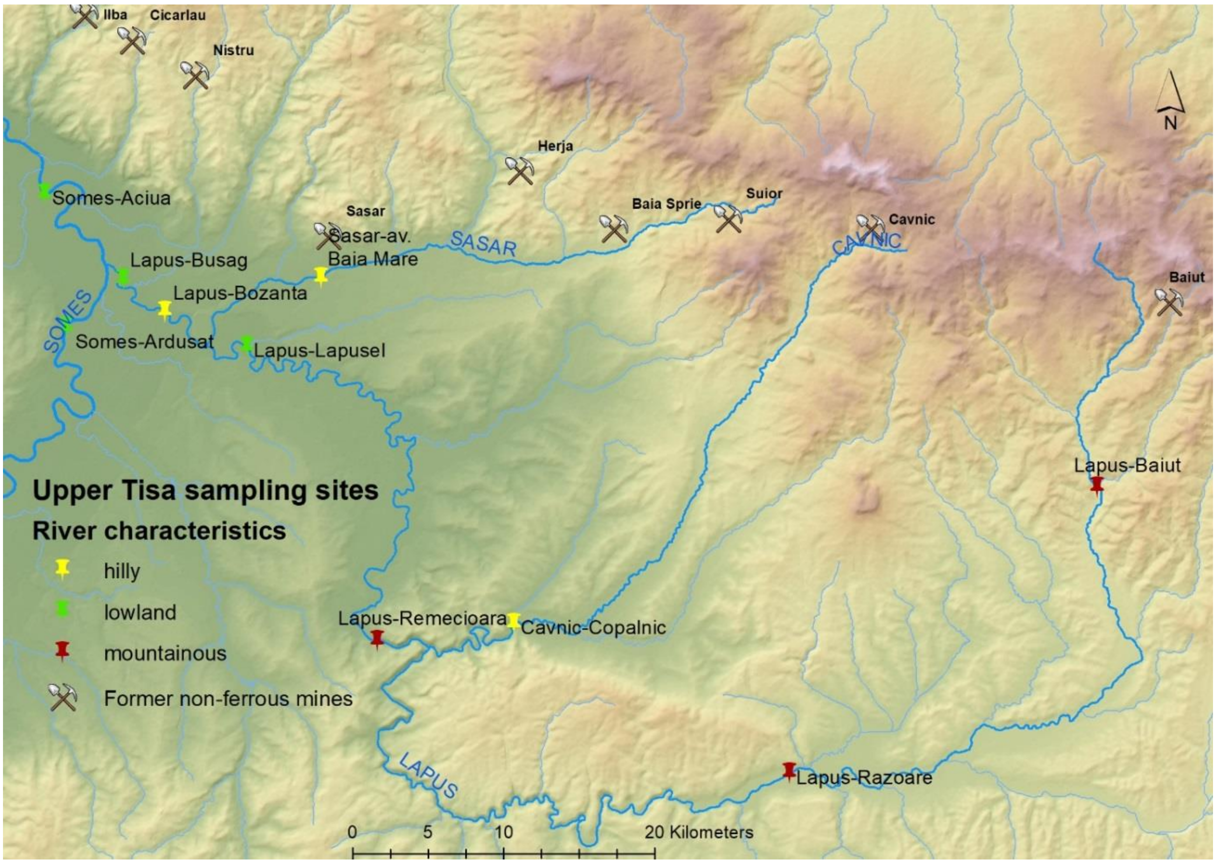

Fig. 4.2: Localisation of sampling points and mines in Upper Tisa test area

4.2. DESCRIPTION OF POSSIBLE SOURCES OF CONTAMINATION AT EACH SITE

The possible sources of contamination for the Upper Tisa Test Area sampling sites are presented in the order from upstream to downstream, considering also the tributaries. This way spatial distribution and evolution of the selected HS concertation and possible sources of contamination can be identified.

SUT10 Lapus Baiut

The test point is located in the upstream area of the Lapus River in a former mining area. Although this activity stopped, the river is still heavily polluted. The analyzed heavy metals (Cu Pb, Hg, Zn, Cd, Cr, Ni, As) exceed the EQS limits, as well as those in Romanian Soil Standards. The source of these metals in soil and sediments is the mining activity. In the suspended sediment sample the contents are below EQS's and Romanian Soil Standard. This happens because the heavy metals existing in the sediments were taken over and transported, dissolved in the water solution. The insoluble ones, such as Pb and its compounds, were deposited together in the floodplain or in the bottom stream sediment. This trend continues in all samples examined indicating that there is no transport of heavy metals in suspension. In the suspended sediment the contents are below all EQS limits, although the water has a reddish yellow color. The color is given by the high contents of iron oxyhydroxides which were not analyzed. The Ni and Cr contents are only partially exceeded. Upstream of this point there are no deposits containing Ni and Cr. Their source is represented by the petrographic background consisting of eruptive rocks represented mostly by pyroxene andesites. These elements can be present as minor elements in pyrite, which is a very abundant mineral in the metal base deposits in the Baiut area. Benzo(a)pyrene has high contents only in the sample of barrel-suspended sediment and could come from the previous industrial activity of mineral processing or from the domestic activity. Another source of pollution is the production of mangal (charcoal) which is common in this area.

SUT09 Lapus Razoare

This test point is placed downstream of SUT10 Lapus Baiut. The lower contents of heavy metals compared to the previous point are explainable because of two tributaries (Cisma and Suciu River) which have unpolluted sediments and are clean mountain waters. Decrease of heavy metal concentrations can be observed in every case, through the intake of clean water and dilution of the previous content. Although there has been a dilution, there are contents that exceed the limits of EQS and Romanian Soil Standard. For Hg the contents fall below the limits of EQG and Romanian Soil Standard. The contents of Ni and Cr are not diluted, due to the contribution of the new sediments brought by the tributaries, which contain approximately equal amounts and come also from source areas with eruptive rocks. The low pollutant content in the bottom sediment is due to the deepening of the river bottom in the last 20 years by 47cm. In the SUT09SS/BR suspended sediment samples (barrel), the contents of benzo (a) pyrene, fluoranthene and anthracene are above EQS limits, and are highlighted in the concentration tables (chapter 4.5). These would probably originate from the domestic activity, because the industrial activity is extremely low. The heating of the houses is made with wood and methane gas, while these installations achieve a less efficient combustion.

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SUT07 Cavnic Copalnic

The test point is located on the Cavnic River which is tributary to the Lapus River after the test point SUT09 Lapus Razoare and before SUT08 Lapus Remecioara. Heavy metal contents, except Hg, largely exceed EQS limits and Romanian Soil Standard. The source of metals is the mining activity in the Cavnic area located upstream the test point. The source of Ni and Cr are the eruptive rocks represented by pyroxenic and amphibole andesites, because there are no Ni and Cr deposits in the area. In the SUT07SS/BR barrel-suspended sediment sample, the contents of benzo(a)pyrene, fluoranthene and anthracene are above the limits of EQS, coming, probably, from the domestic activity, because the industrial activity is extremely low. The heating of the houses is made with wood and methane gas with a less efficient combustion.

SUT08 Lapus Remecioara

The test point is located after the confluence of the Lapus River with the Cavnic River at the exit from the gorges. Heavy metals contents are slightly higher than at the previous sampling sites (SUT09 and SUT10), because of the additional contribution of the Cavnic River. Contents exceed EQS's, except for Hg. Ni and Cr contents are low, but exceed some EQS's. Their sources are represented by the petrographic background in the source area. In this location, the sample SUT07SS/BR suspended sediment (barrel) has high contents of benzo(a)pyrene, fluoranthene and anthracene, above the limits of EQS. Its source comes especially from domestic activities, because industrial activity is extremely low. The heating of the houses is made with wood and methane gas with less efficient combustions.

SUT02 Lapus Lapusel

The test point is located downstream of SUT08 Lapus Remecioara and before the Sasar River flows into the Lapus River. At this site heavy metals concentrations (excepting Hg) exceed EQS's and Romanian Soil Standard limits. The contents are kept at about the same level as the previous point with decreases for some metals. Ni and Cr have the same tendency as in the previous point. The contents of benzo(a)pyrene, fluoranthene and anthracene are kept within normal limits.

SUT03 Sasar River

The Sasar River collects sediments from the center of a mining area and crosses the city of Baia Mare. Heavy metal contents exceed all limits, including Hg, which has contents that exceed normal values. High heavy metal values are due to industrial mining and metallurgical activities in Baia Mare. Ni and Cr come from the petrographic background of the area where pyroxene andesites are predominant. High values of benzo(a)pyrene, exceeding the *Elbe lower limit* are due to the ore processing activities that previously existed in Baia Mare, car traffic of a municipal city and household use of heating.

SUT06 Lapus, Bozanta Mare

The test site is on the Lapus River after the confluence with the Sasar River. The contents are higher than in the previous point SUT02, on the same Lapus River. Heavy metal contents exceed EQS's and Romanian Soil Standard limits. Hg content exceeds *Elbe lower limit* in the stream sediment sample at a depth of 5 cm. Ni and Cr exceed only *Elbe lower limit*, but not because pollution. Most of their contents come from the petrographic background of the area. Pyrites processing and pyrite ash could also be considered as a possible source. Benzo(a)pyrene exceeds the *Elbe lower limit* in the SUT06SS/BR (barrel-suspended sediment) sample and is due to the ore processing activities, car traffic of a municipal city and household use of heating that exists or existed in Baia Mare.

SUT01 Lapus Busag

The test point is located after the confluence with the Baita River, a tributary of the Lapus River, but before the confluence with the Somes River. The heavy metal contents are high and mostly exceeding EQS and Romanian Soil Standard limits. Mercury contents do not exceed the EQS limits, except for two samples SUT01FS/SP/TS (spade floodplain sediment 5 cm) and SUT01FS/SP /CK (cake sampler-floodplain sediment 5 cm), which exceed *Elbe lower limit*. When compared to the Romanian Soil Standard, the normal values are exceeded in the samples SUT01BS/CR/TL (vacuum core stream sediment 5 cm), SUT01FS/SP/TS (spade floodplain sediment 5 cm) and SUT01FS/SP/CK (cake sampler-floodplain sediment 5 cm). As in the previous sampling sites, in the SUT01SS/BR (barrel-suspended sediment) sample, the contents in heavy metals have normal values. Benzo(a)pyrene exceeds the *Elbe lower limit* value in sample SUT01FS/SP/CK (floodplain cake sampler sediment 5 cm) and SUT01SS/BR (barrel-suspended sediment) and is due to the activities from the municipal city of Baia Mare.

SUT05 Somes Ardusat

None of the heavy metals contents in the samples collected from this location exceed the EQS limits. This is because the sampling site is placed on the Somes River before the confluence with the Lapus River, which accumulates the waters from the Baia Mare Mining Basin. There are insignificant exceedances for As, Cd and Cu according to *Elbe lower limit*. Also, according to Romanian Soil Standard, the contents are within normal values. There are small exceeds for Cr with regard to the *Elbe lower limit* and for Ni according to the *Elbe upper limit*. But for these metals there are no pollution sources, because they result from the geochemical background of the area crossed by Somes River. There is also a small exceedance of benzo(a)pyrene according to *Elbe lower limit* in sample SUT05SS/BR (barrel suspended sediment), which is still maintained at the next sampling site SUT04 Somes Aciua.

SUT04 Somes Aciua

This is the most downstream site after the confluence of the Somes and the Lapus Rivers. In this location the limits for heavy metals are not exceeded. Mercury is in all samples at normal values according to all standards. The limits for heavy metals are exceeded in accordance with the *Elbe lower limit*. For some samples the limits for cadmium, copper and zinc are partially exceeded according to *Dutch intervention* and sometimes *Hungarian limit*. There are some exceeds of the Romanian Soil Standard's alert threshold for sensitive soil. Heavy metal contents have much lower values than in the SUT01 Lapus Busag sampling site. This is explained by the dilution of the waters of the Lapus River, which is more polluted, with waters of the river Somes which are cleaner and have a much higher flow. Ni and Cr have similar values as point SUT05 Somes Ardusat.

Other than those named and discussed above, the organic substances are in all sites below the detection limits.

4.3. CORRELATION ANALYSIS OF HEAVY METAL CONCENTRATION BEHAVIOURS

The behavior of each Heavy Metal concentration in all sampling sites considered together as a whole, can be used as an input to identify the contamination sources. For this purpose, a regression analysis was done. Beside the correlation coefficient, the significance of this correlation was computed. The adjusted R-squared can be used to explain the variance of the dependent variables with regard to the variance of the independent ones, also taking into account the degrees of freedom.

As can be seen in table 4.1, strong and significant correlations can be identified between the following groups of metals:

1.) Zn, Cd, Cu, Pb, As

2.) Cu, As, Hg,

3.) Ni, Cr

Table 4.1 Correlation analysis of heavy metal concentration behavior

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
As								
p								
adj R^2								
Cd	0.6913							
p	3.8E-08							
adj R^2	0.467							
Cr	0.3237	0.2791						
p								
adj R^2								
Cu	0.8552	0.8097	0.4605					
p	5.2E-15	1.9E-12						
adj R^2	0.726	0.648						
Hg	0.8975	0.5499	0.4462	0.7833				
p	2.5E-18			2.9E-11				
adj R^2	0.801			0.605				
Ni	0.2952	0.2736	0.9727	0.4175	0.4190			
p			1.8E-31					
adj R^2			0.945					
Pb	0.7041	0.7782	0.2621	0.8227	0.5866	0.1793		
p	1.7E-08	4.7E-11		4.1E-13				
adj R^2	0.485	0.597		0.670				
Zn	0.7079	0.9698	0.2701	0.8246	0.5682	0.2663	0.7970	
p	1.3E-08	1.9E-30		3.3E-13			7.3E-12	
adj R^2	0.491	0.939		0.673			0.627	

In Table 4.1, correlations above 0.68 were marked with different shades of green, respectively up to 0.86 and above 0.95. Correlations above 0.98 cannot be found. In every case when a strong correlation was found, the significance was computed. These p values are well bellow 0.001, so that the correlations are very significant. It can also be seen that the adjusted R-squared value is, in most cases, much higher, or at least very close to 0.5, so that the behavior of the three HM groups is more than a simple coincidence by chance.

To illustrate the good correlation of each group the Line-fit plots of the tested Heavy Metal concentration behaviors groups are attached in chapter 4.5 as follows:

1.) c_{Zn} as a function of c_{Cd}, c_{Cu}, c_{Pb}, c_{As}

2.) c_{Hg} as a function of c_{As}, c_{Cu}

3.) c_{Ni} as a function of c_{Cr}

The above grouping of Heavy Metal concentrations is in very good accordance with the expert opinion and the expert local knowledge on the sources of possible contamination sources. It also describes well the spatially correlated behaviour of those groups.

4.4 CONCLUSIONS

The preliminary analysis shows moderate to high values of heavy metal concertation values in most of the sites, whereas all the other contaminants show moderate to low values, almost for all EQS's taken into account during the study. The most polluted sites are placed on the Lapus River tributaries: SUT03 Sasar River and SUT10 Lapus Baiut, while the least polluted are placed on Somes River (SUT05 Somes Ardusat) and on Lapus River (SUT09 Lapus Razoare).

Regression and correlation analysis of different heavy metal concentrations taken for the whole sampling area shows that these can be divided in three categories based on their behaviour, and together with the local expert knowledge, can give a hint on the contamination sources. These categories are:

1.) Zn, Cd, Cu, Pb, As are a result of the mining activity in the described catchment. The behaviour of this group can be very well modeled by multivariate regression.

2.) Hg, As, Cu do also result from mining and nonferrous ore preparation and metals production. Because the behaviour of this group can be very well modeled by multivariate regression, Hg can also be considered to come from the above described activities.

3.) The high and significant correlation of Ni only to Cr, together with the local expert knowledge proves that these metals come mainly from the geological background, but that they can also result from the pyrite processing and pyrite ash, a mineral which is very abundant in this mining region.

The identified organic compounds are generated during incomplete or low temperature combustion processes occurring in households (mainly in rural areas) or during road transportation (in urban areas or where the rivers flow near heavy traffic on national and express roads).

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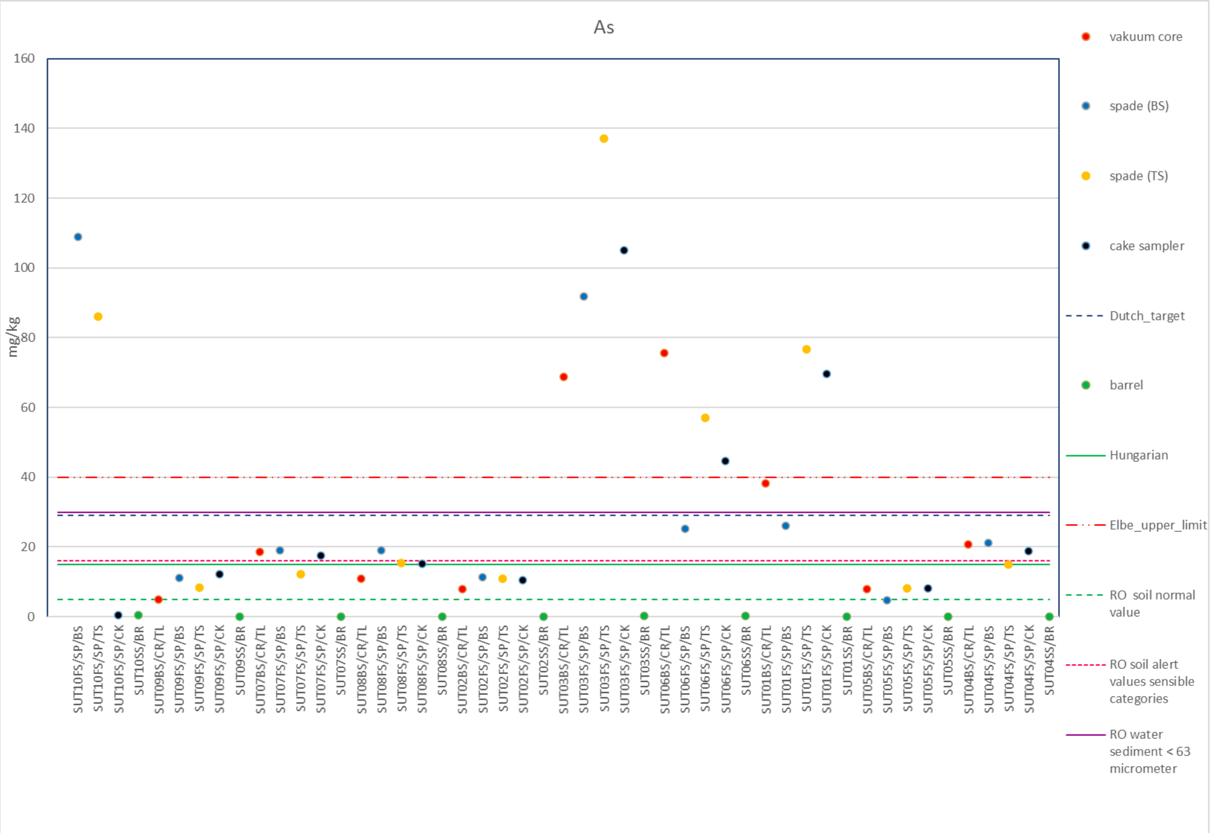
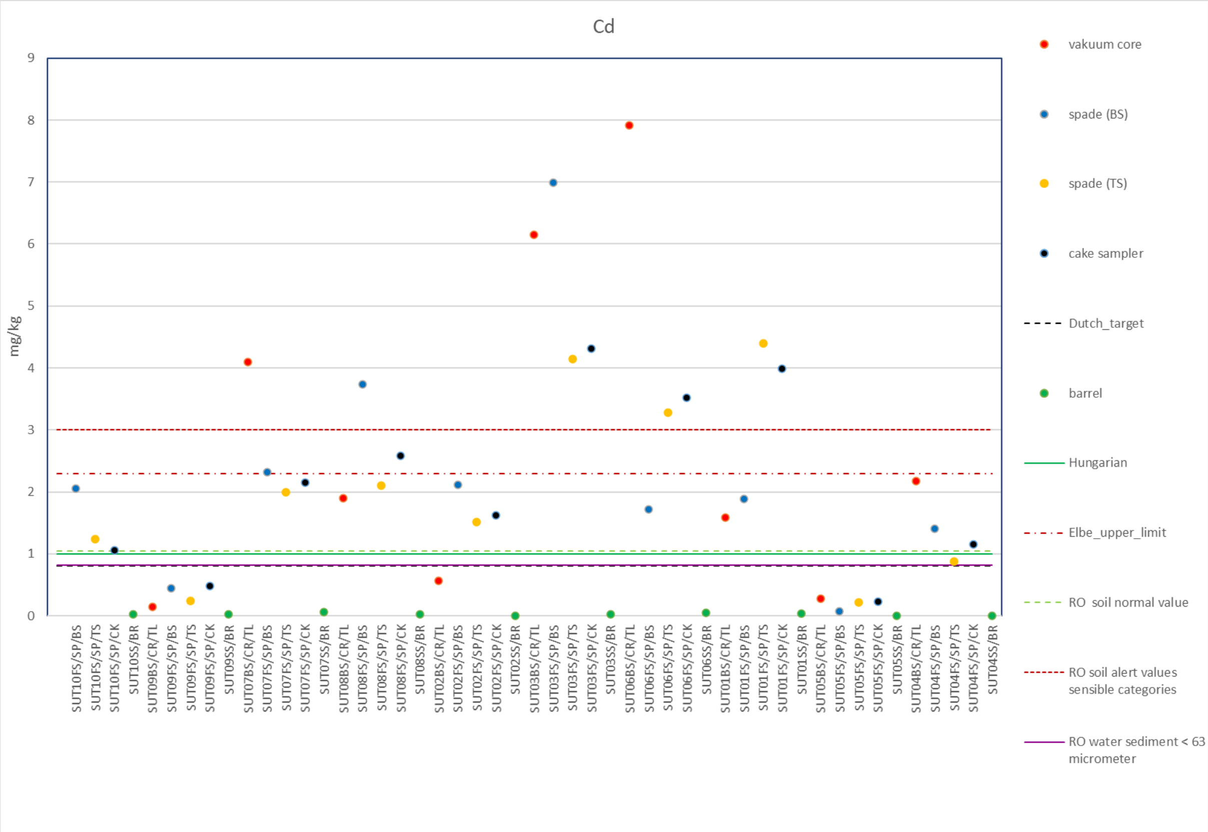
4.5 GRAPHS

Fig. 4.3: Graphics for measured values compared to EQS's data and National Standard in the Upper Tisa Test Area sites. Graphs were made for the following parameters: As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, Anthracene, Fluoranthene, Benzo(a)pyrene.
Used abbreviations: SUT: Sampling Upper Tisa; CR: vakuum core; TL: top layer; SP: spade; FS: floodplain sediment; BS: bottom sediment; TS: top sediment; CK: cake sampler; SS: suspended sement; BR: barrel.




Cd
mg/kg
0
1
2
3
4
5
6
7
8
9
SUT10FS/SP/BS
SUT10FS/SP/TS
SUT10FS/SP/CK
SUT10SS/BR
SUT09BS/CR/TL
SUT09FS/SP/BS
SUT09FS/SP/TS
SUT09FS/SP/CK
SUT09SS/BR
SUT07BS/CR/TL
SUT07FS/SP/BS
SUT07FS/SP/TS
SUT07FS/SP/CK
SUT07SS/BR
SUT08BS/CR/TL
SUT08FS/SP/BS
SUT08FS/SP/TS
SUT08FS/SP/CK
SUT08SS/BR
SUT02BS/CR/TL
SUT02FS/SP/BS
SUT02FS/SP/TS
SUT02FS/SP/CK
SUT02SS/BR
SUT03BS/CR/TL
SUT03FS/SP/BS
SUT03FS/SP/TS
SUT03FS/SP/CK
SUT03SS/BR
SUT06BS/CR/TL
SUT06FS/SP/BS
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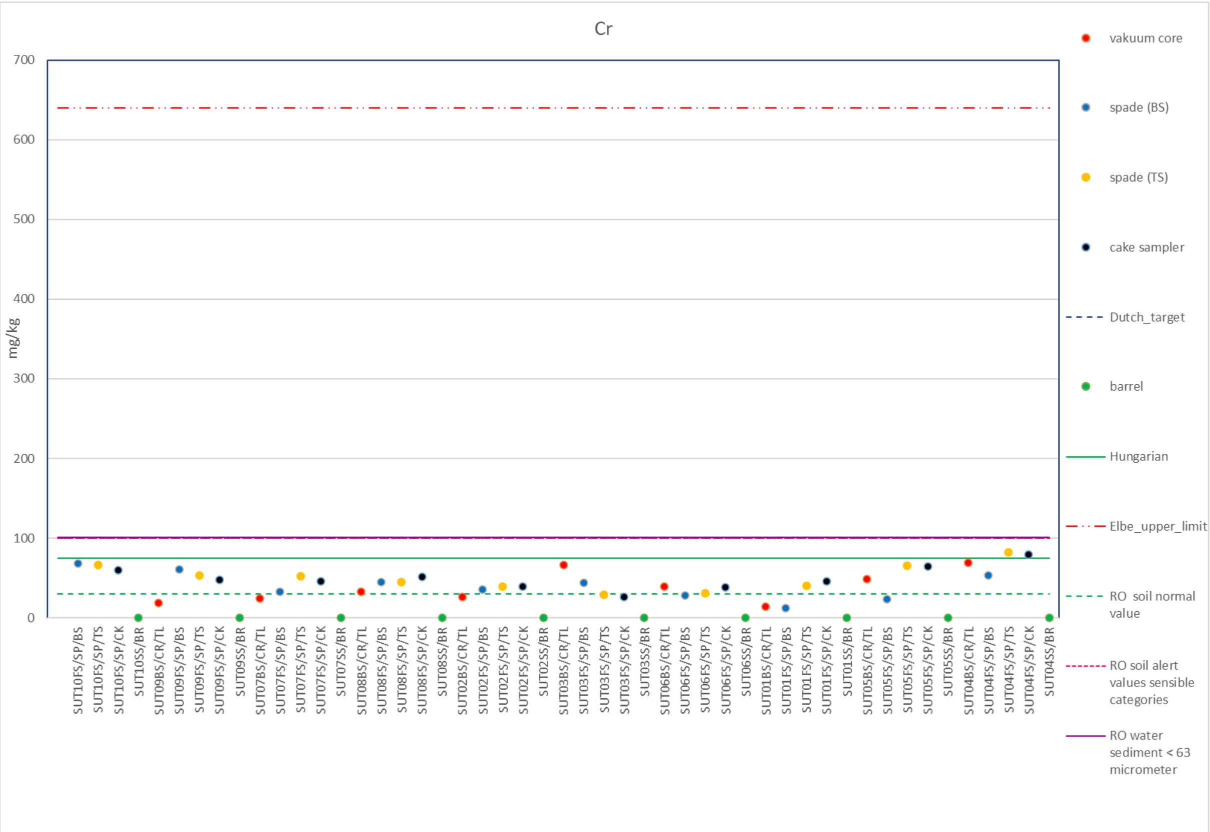
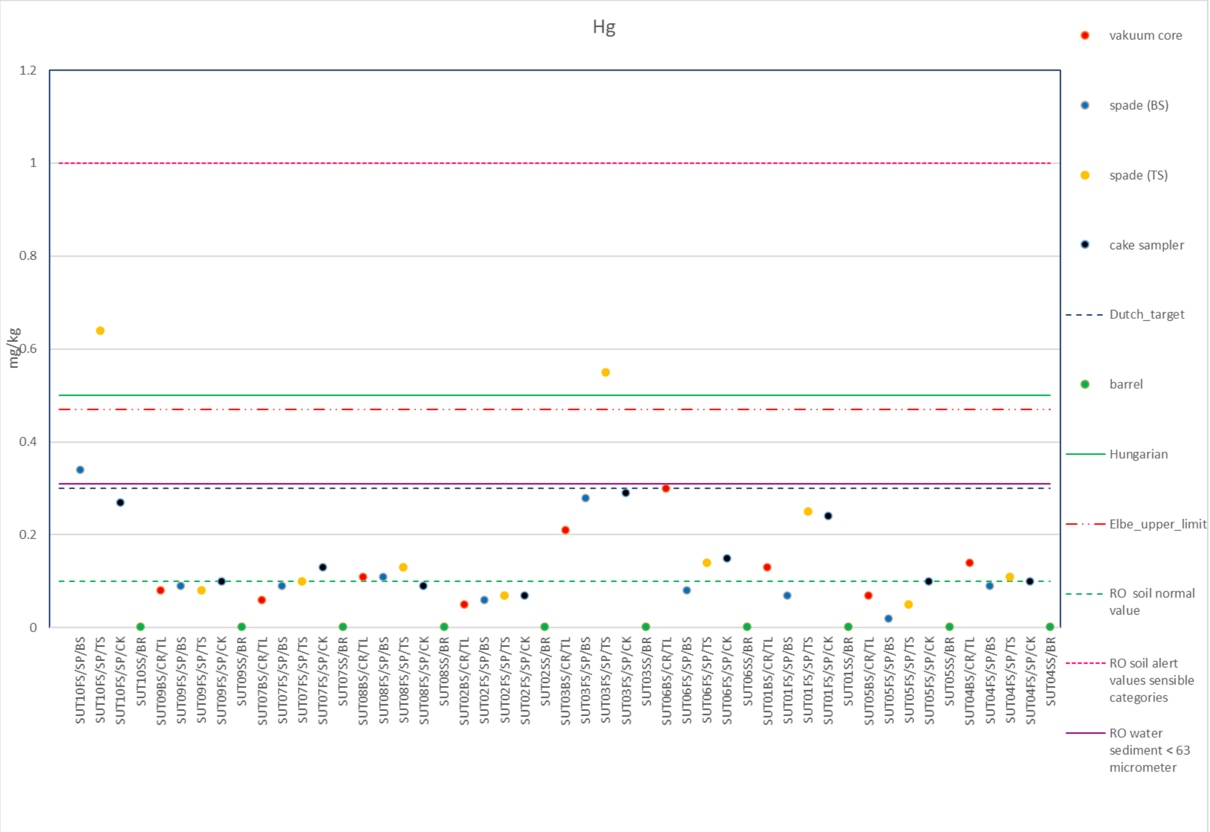
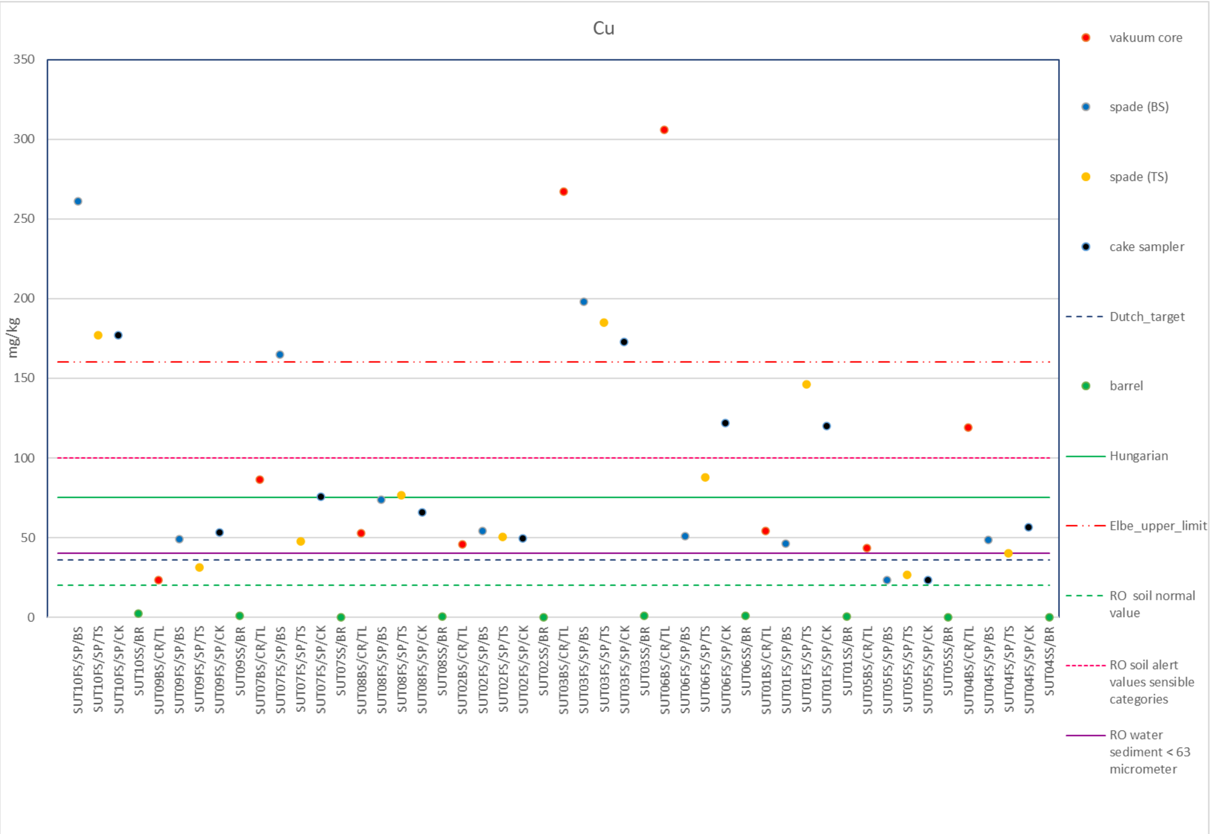
SUT06SS/BR
SUT01BS/CR/TL
SUT01FS/SP/BS
SUT01FS/SP/TS
SUT01FS/SP/CK
SUT01SS/BR
SUT05BS/CR/TL
SUT05FS/SP/BS
SUT05FS/SP/TS
SUT05FS/SP/CK
SUT05SS/BR
SUT04BS/CR/TL
SUT04FS/SP/BS
SUT04FS/SP/TS
SUT04FS/SP/CK
SUT04SS/BR
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
RO soil normal value
RO soil alert values sensible categories
RO water sediment < 63 micrometer


Cr
mg/kg
0
100
200
300
400
500
600
700
SUT10FS/SP/BS
SUT10FS/SP/TS
SUT10FS/SP/CK
SUT10SS/BR
SUT09BS/CR/TL
SUT09FS/SP/BS
SUT09FS/SP/TS
SUT09FS/SP/CK
SUT09SS/BR
SUT07BS/CR/TL
SUT07FS/SP/BS
SUT07FS/SP/TS
SUT07FS/SP/CK
SUT07SS/BR
SUT08BS/CR/TL
SUT08FS/SP/BS
SUT08FS/SP/TS
SUT08FS/SP/CK
SUT08SS/BR
SUT02BS/CR/TL
SUT02FS/SP/BS
SUT02FS/SP/TS
SUT02FS/SP/CK
SUT02SS/BR
SUT03BS/CR/TL
SUT03FS/SP/BS
SUT03FS/SP/TS
SUT03FS/SP/CK
SUT03SS/BR
SUT06BS/CR/TL
SUT06FS/SP/BS
SUT06FS/SP/TS
SUT06FS/SP/CK
SUT06SS/BR
SUT01BS/CR/TL
SUT01FS/SP/BS
SUT01FS/SP/TS
SUT01FS/SP/CK
SUT01SS/BR
SUT05BS/CR/TL
SUT05FS/SP/BS
SUT05FS/SP/TS
SUT05FS/SP/CK
SUT05SS/BR
SUT04BS/CR/TL
SUT04FS/SP/BS
SUT04FS/SP/TS
SUT04FS/SP/CK
SUT04SS/BR
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
RO soil normal value
RO soil alert values sensible categories
RO water sediment < 63 micrometer


Hg
mg/kg
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
RO soil normal value
RO soil alert values sensible categories
RO water sediment < 63 micrometer


Cu
mg/kg
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
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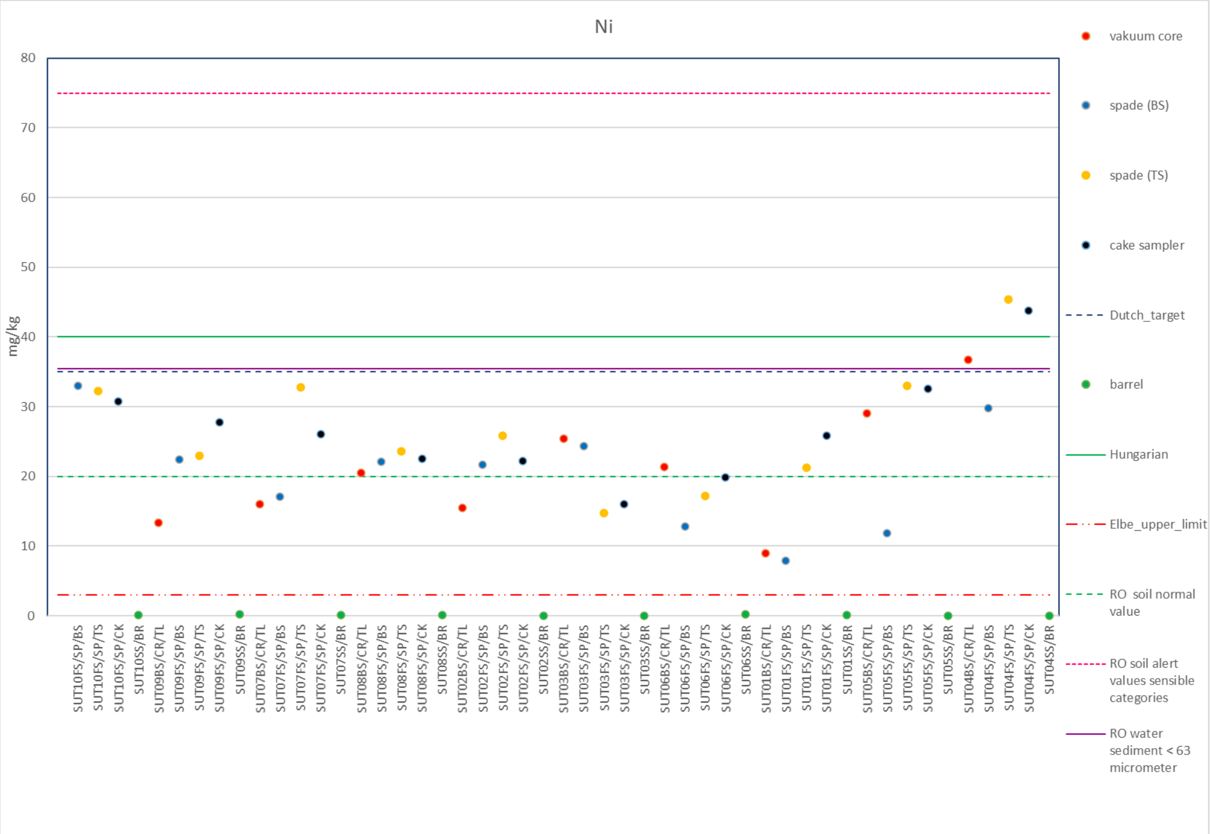
RO soil alert values sensible categories
RO water sediment < 63 micrometer


Ni
mg/kg
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
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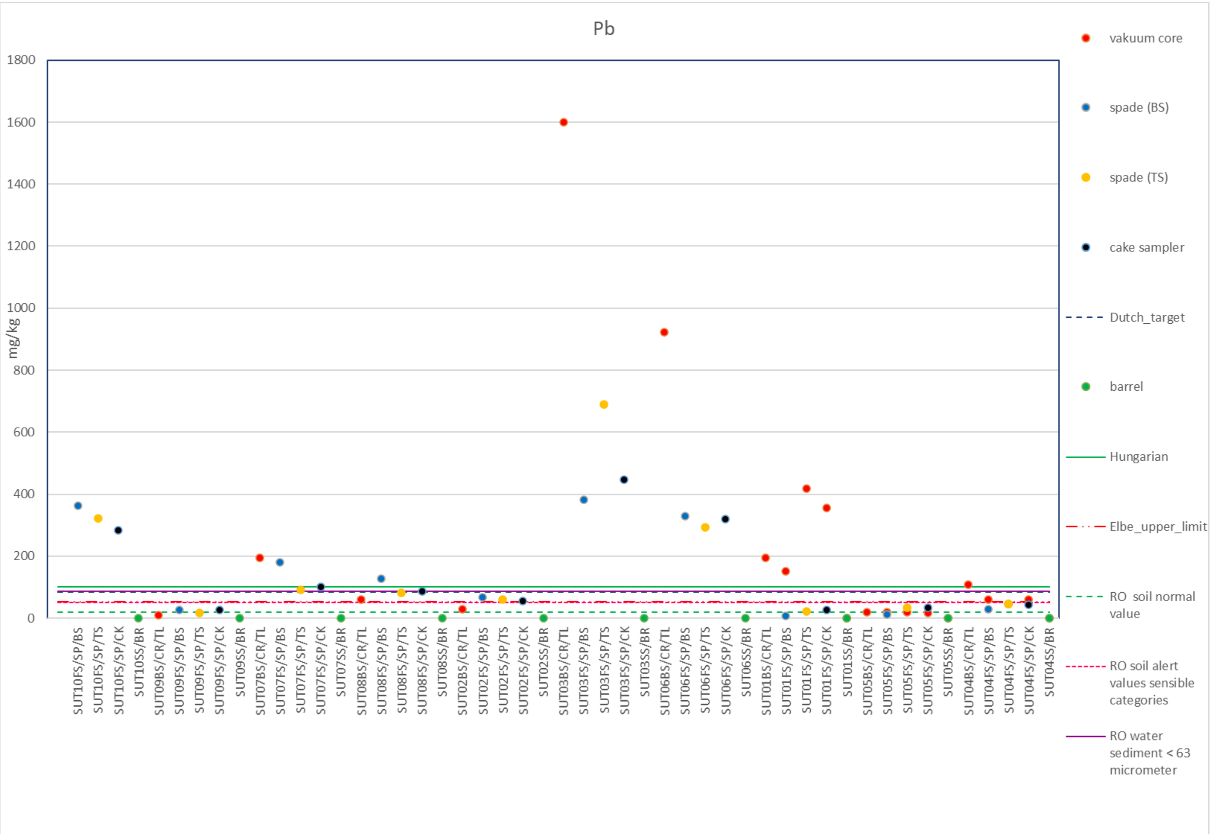
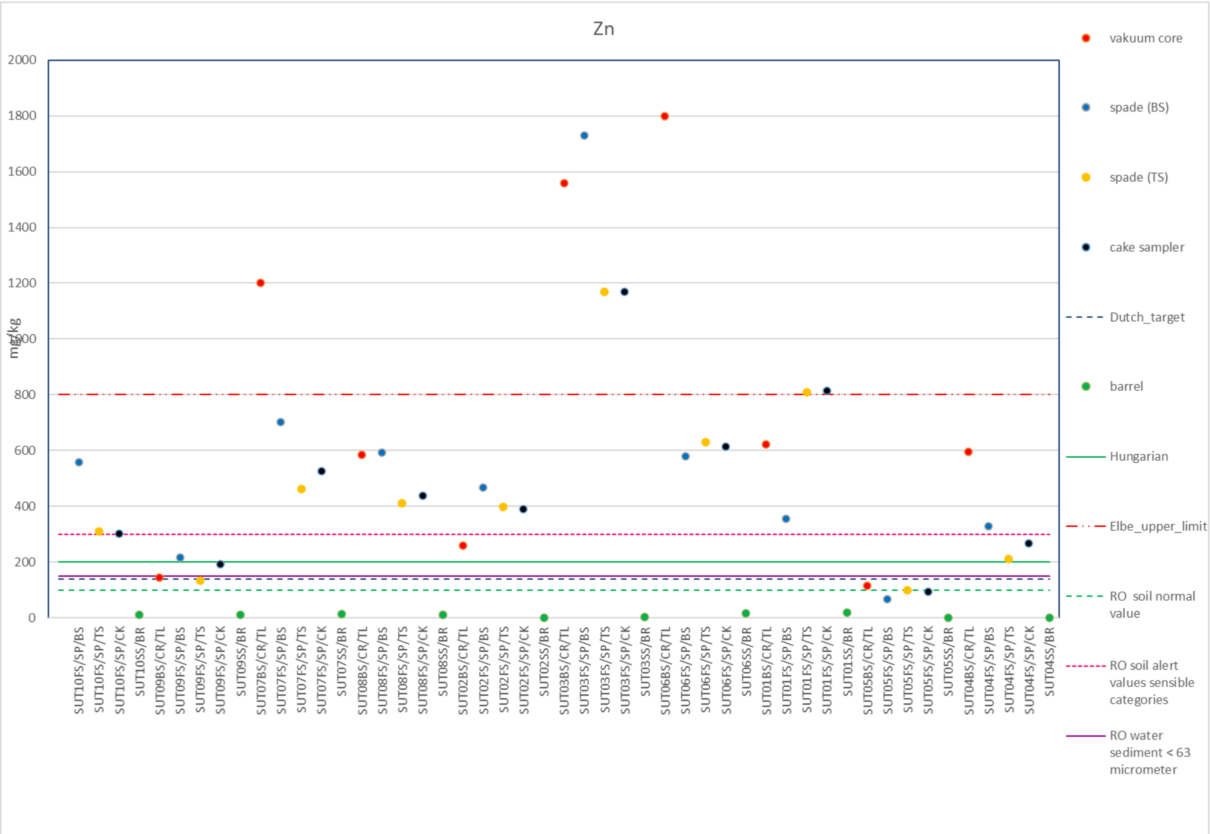
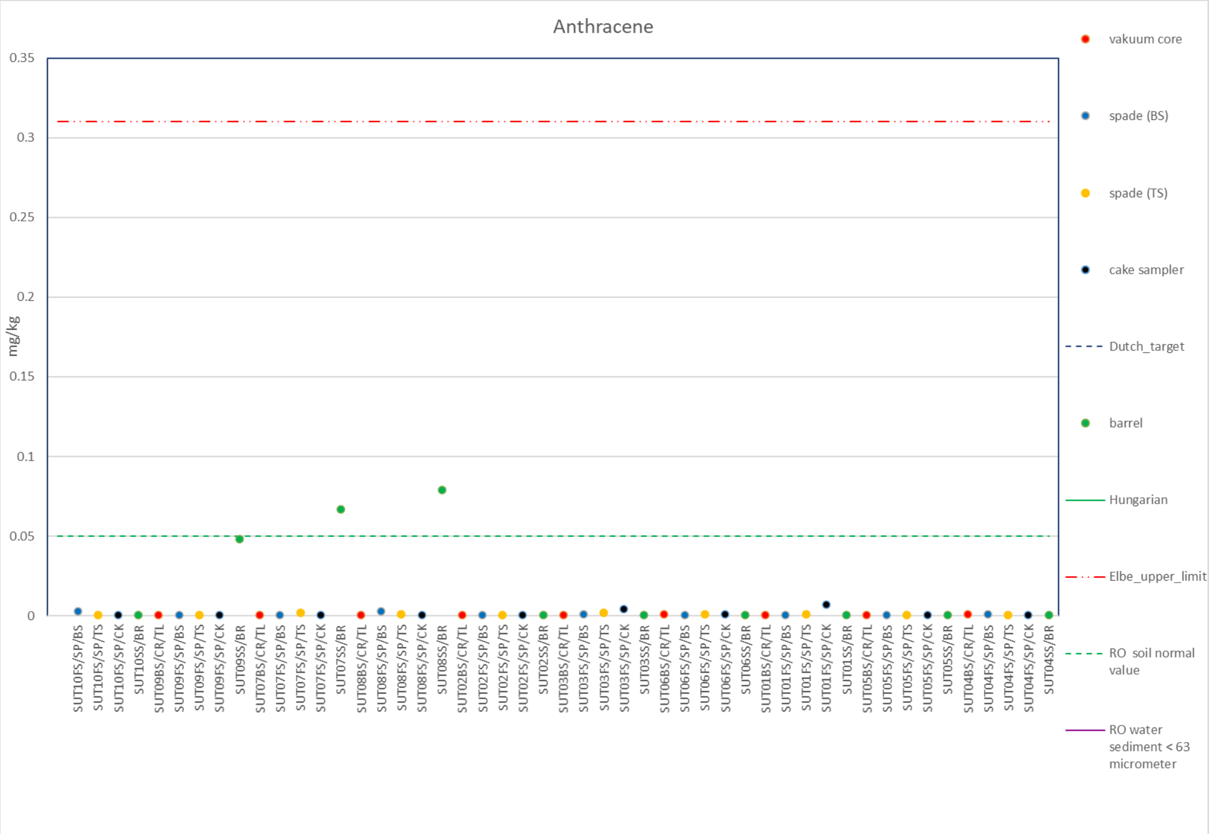
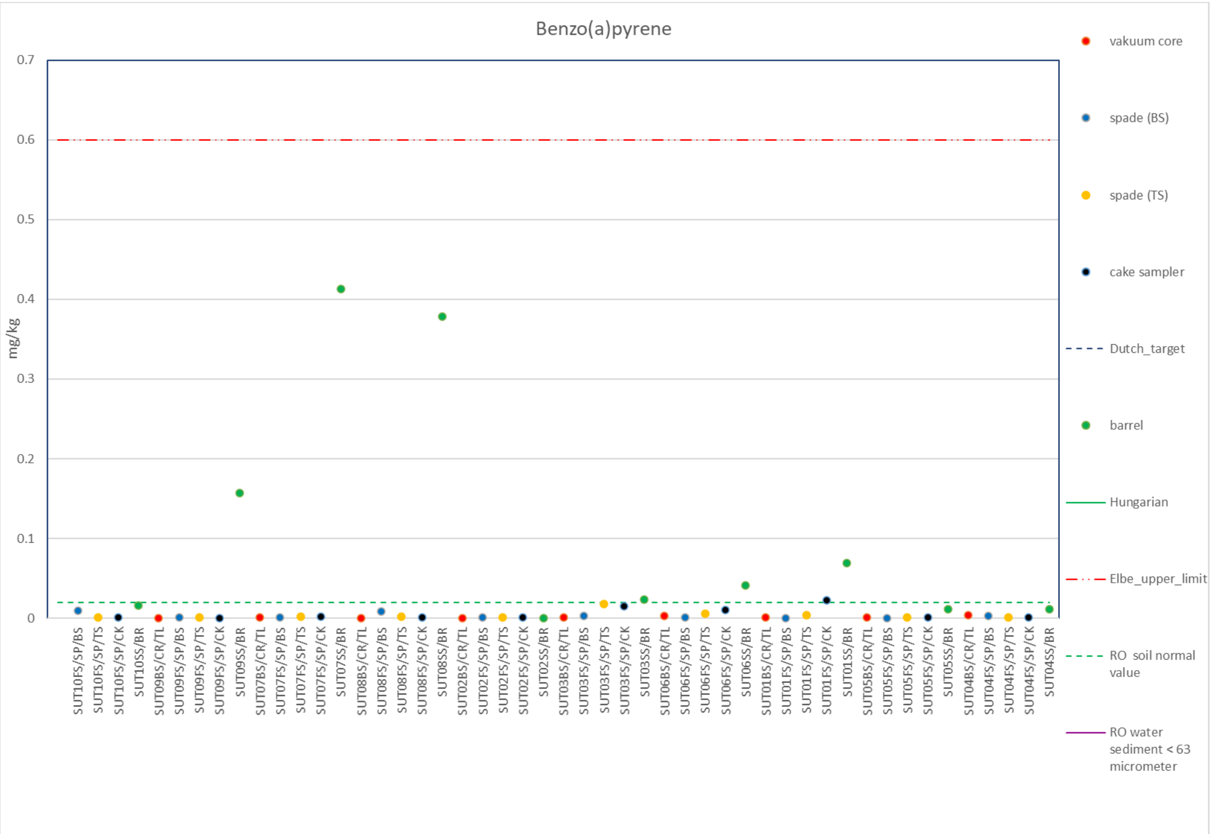
RO water sediment < 63 micrometer


Pb
mg/kg
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
RO soil normal value
RO soil alert values sensible categories
RO water sediment < 63 micrometer


Zn
mg/kg
2000
1800
1600
1400
1200
1000
800
600
400
200
0
SUT10FS/SP/BS
SUT10FS/SP/TS
SUT10FS/SP/CK
SUT10SS/BR
SUT09BS/CR/TL
SUT09FS/SP/BS
SUT09FS/SP/TS
SUT09FS/SP/CK
SUT09SS/BR
SUT07BS/CR/TL
SUT07FS/SP/BS
SUT07FS/SP/TS
SUT07FS/SP/CK
SUT07SS/BR
SUT08BS/CR/TL
SUT08FS/SP/BS
SUT08FS/SP/TS
SUT08FS/SP/CK
SUT08SS/BR
SUT02BS/CR/TL
SUT02FS/SP/BS
SUT02FS/SP/TS
SUT02FS/SP/CK
SUT02SS/BR
SUT03BS/CR/TL
SUT03FS/SP/BS
SUT03FS/SP/TS
SUT03FS/SP/CK
SUT03SS/BR
SUT06BS/CR/TL
SUT06FS/SP/BS
SUT06FS/SP/TS
SUT06FS/SP/CK
SUT06SS/BR
SUT01BS/CR/TL
SUT01FS/SP/BS
SUT01FS/SP/TS
SUT01FS/SP/CK
SUT01SS/BR
SUT05BS/CR/TL
SUT05FS/SP/BS
SUT05FS/SP/TS
SUT05FS/SP/CK
SUT05SS/BR
SUT04BS/CR/TL
SUT04FS/SP/BS
SUT04FS/SP/TS
SUT04FS/SP/CK
SUT04SS/BR
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
RO soil normal value
RO soil alert values sensible categories
RO water sediment < 63 micrometer


Anthracene
mg/kg
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
RO soil normal value
RO water sediment < 63 micrometer


Benzo(a)pyrene
mg/kg
vakuum core
spade (BS)
spade (TS)
cake sampler
Dutch_target
barrel
Hungarian
Elbe_upper_limit
RO soil normal value
RO water sediment < 63 micrometer

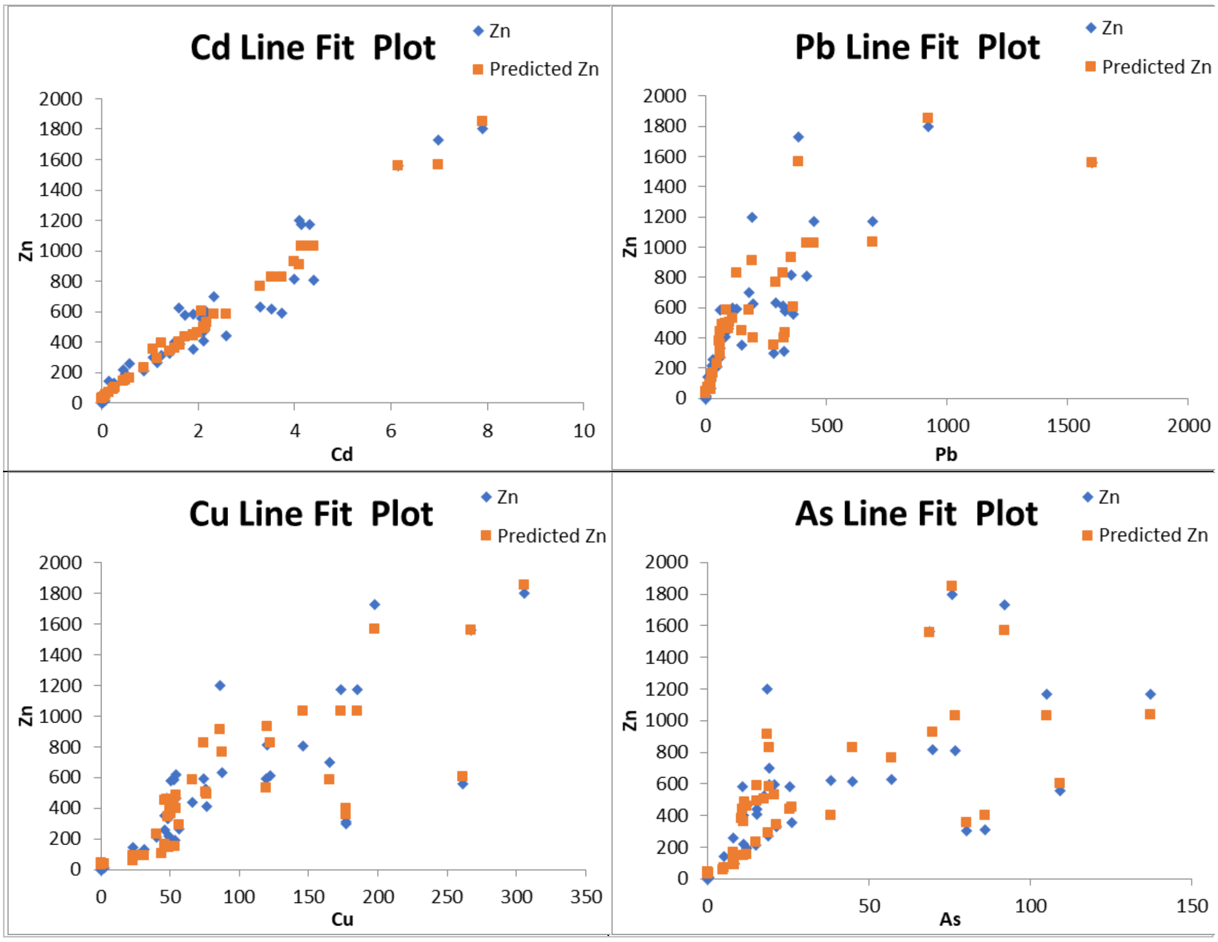


Fig. 4.4: Line fit plots determined using multivariate linear regression for Zn, Cd, Pb, Cu, As exhibit good correlation between measured and modeled results in the correlograms

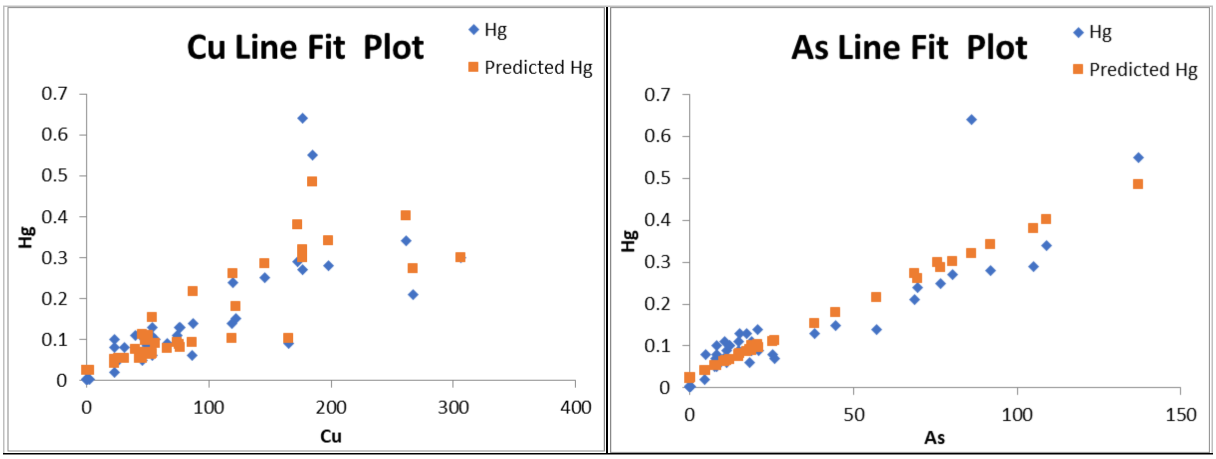


Fig. 4.5: Line fit plots determined using multivariate linear regression for Hg, Cu, As exhibit good correlation between measured and modeled re-sults in the correlograms

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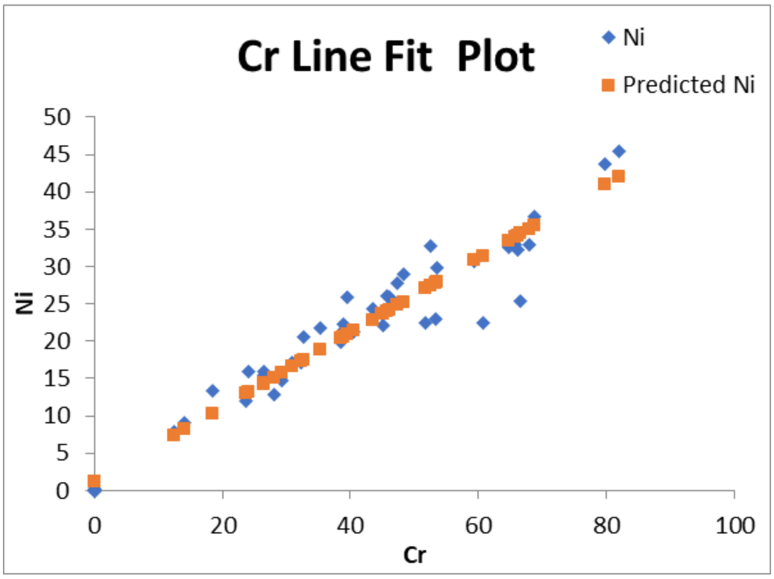

Fig. 4.6: Line fit plot determined using linear regression for Ni and Cr exhibits good correlation between measured and modeled results in the correlogram

5. SOUTH DANUBE TEST AREA

5.1 INTRODUCTION

The South Danube test area comprises the part of the Lower Danube River from the border between Serbia, Romania and Bulgaria to Silistra (Călărași) and northward to Hârșova, including a number of large and small tributaries. The area is characterized by present and past mining activityies and industrial and agricultural activities which could contribute to the overall sediment pollution.

Sampling sites in the South Danube test area were selected upon the following major criteria:

- Trans-national character;
- Covering river of different size (small, medium, and large), including the Danube River;
- Existing sediment/water monitoring sites;
- Different geology;
- Diverse pollution sources;
- Good infrastructure.

Serbian, Romanian, and Bulgarian Project Partners (PPs) from the South Danube Catchment area countries (Fig. 5.1) agreed about the following sites:

- 1 sampling point at the Borska Reka trubitary (SRB);
- 1 sampling point at the Timok River in its transboundary part (BG/SRB);
- 1 sampling point at the Ogosta River (BG);
- 2 points in the Iskar River basin (BG) – one above the confluence with the Danube and one at its tributary Malak Iskar River;
- 1 sampling point at the Lower Jiu River (RO);
- 1 sampling point at the Lower Olt River (RO);
- 3 transnational sampling points/transects (RO/BG) on the Danube River: one near Pristol (Romania), one near Svishtov (Bulgaria) and one near Oltenita (Romania).

The pre-sampling survey of the Bulgarian part of the SDTA on 12-13.08.2020 revealed that the Iskar River monitoring point near the village of Orehovitsa has been discredited by local contamination with waste from quatz-kaolinite processing plant at the site. Another point for sediment sampling located near the village of Baykal/Gigen was surveyed and chosen to replace the Orechovitsa site. The Ogosta River site was found dangerous for the sampling staff and the site was moved upstream to the Mizia town. The pre-sampling survey of the Serbian part of the SDTA was done on 07.09.2020 and resulted in a slightly moved position of the Rgotina (Borska Reka) and Timok River sampling points, too.

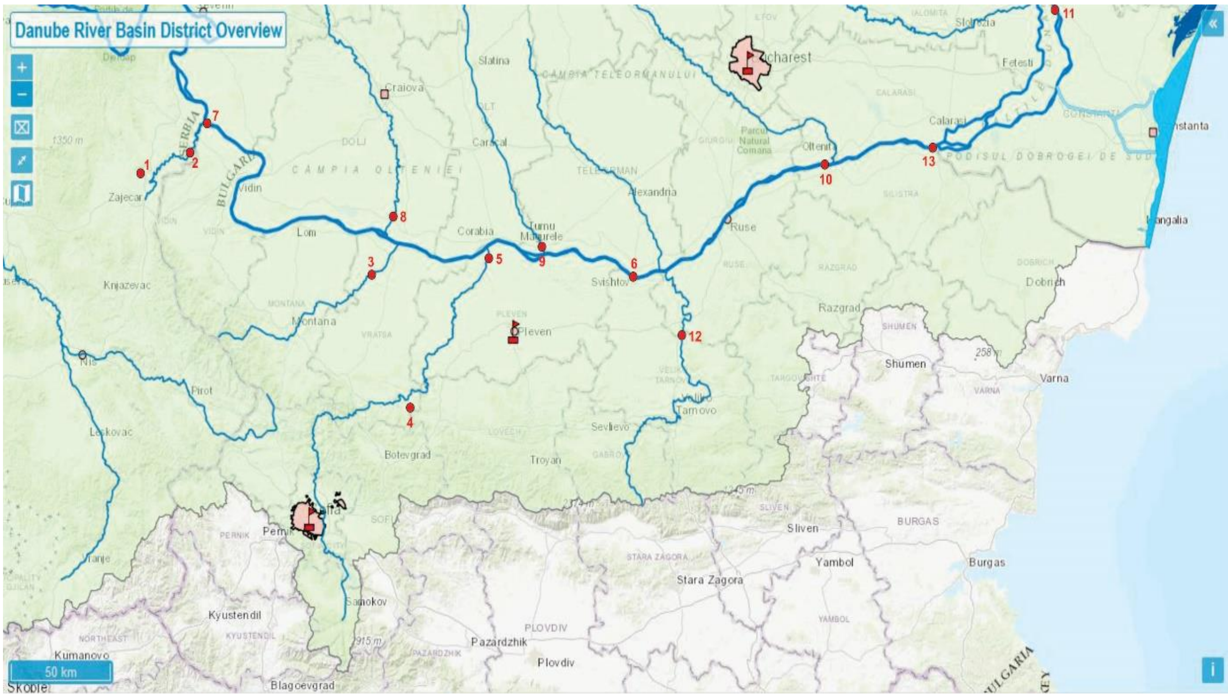

Fig 5.1: Sampling stations in South Danube test area

In addition, a station at Hârșova was added in order to check the "good status" of water body in this part of the Danube Basin, in contrast with the "bad status" of the Danube upstream of Silistra-Călărași.

For each representative sampling site 2 bottom sediment samples (0-5 cm layer) and 2 floodplain sediment samples 0-15 (20) cm layer were taken, with either stainless tools (for analyses of organic substances) or with plastic tools (for inorganic component). The samples were stored in brown and white jars, respectively, and kept at around 4 °C, then sent to the accredited laboratory. At a site with higher turbidity of the river water (Svishtov) suspended sediment samples were taken from the whole water column (around 1 m) and stored in 20 L barrels. The water from the samples was decanted after 24 h rest and the 2 L plastic bottles were sent to Balint Analytics Laboratory in Hungary.

The samples were processed as described in the corresponding Laboratory Report (Deliverable D.3.3.2 – version 1.0). The analytical results were provided in the second half of December 2020. The determined values, together with the sample ID, sampling method, unit of measure and laboratory internal codes for As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene + Benzo(k)fluoranthene, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene, Dicofol, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Hexachloro cyclohexane and Quinoxyfen can be found in the graphs in chapter 5.5.

Hg was also measured in IGR laboratory using Analizer Hydra IIC, Teledyne Leeman Labs, using the analytical standard US EPA 7473 (TDGA-AAS). The instrument had the detection limit of 0.005mg/kg.

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The data in the above-mentioned graphs (chapter 4.5) were compared to the following EQS's:

1.) Bulgarian normal and intervention thresholds for sensitive and less sensitive soils

2.) Romanian normal, alert and intervention thresholds in soils for sensitive and less sensitive land uses

3.) Dutch target and intervention values for soils

4) Elbe lower limit and upper limit values for sediments

5) US EPA TEC

6.) US EPA PEC

7) Republic of Serbia EQS limit values (see Chapter 2 of this document). Comparison to be completed when data from SIMONA Reference Laboratory is available.

5.2. DESCRIPTION OF POSSIBLE SOURCES OF CONTAMINATION AT EACH SITE

The probable sources of contamination for the SD Test Area sampling sites are presented in order from west to east and from up to downstream of the studied water bodies' basins (Fig. 5.1), considering also the tributaries. In this way spatial distribution and evolution of the selected HSs concertation and possible sources of contamination can be identified.

Ogosta

Ogosta sampling site is one of the points where bottom sediments are monitored by the Bulgarian Water Authority. It is situated on the Ogosta River right bank, 5 km before the confluence with the Danube. This sampling site was selected because of possible source of pollution from past mining activity in the Chiprovtsi region. Agricultural pollution sources are also suspected. The analyzed heavy metal content (*Cu, Pb, Hg, Zn, Cd, Cr, Ni, As*) is higher in floodplain sediments than in bottom sediments, especially for *As, Cu and Pb* (chapter 5.4). It is most probably a result of past mining activity in the catchment area. The most elevated is the content of *As* which exceeds the EQS limits both for bottom and floodplain sediments. This is in agreement with previous studies concerning *As* contamination of soils around the Ogosta basin (Bird et al., 2010). Some other metals (*Cd, Cr, Cu, Ni* and *Pb*) content exceeds the EQS of *Elbe limits*. *As, Cd, Pb* and *Zn* content is higher than the normal content of trace elements in soils. The content of all metals is lower than the maximum content in soils in regard to Bulgarian Soil Standards (Aquachim report). The measured organic substances content is below the EQS limits.

Danube at Pristol

This site is very close to the border between Bulgaria and Serbia (on the right bank of the Danube), downstream of the confluence with Timok River. It was selected in order to check pollution from mining sites in Serbia and Bulgaria.

Regarding the metal content in Floodplain Topsoil (FS-TS: 0-5 cm) and Floodplain Bottomsoil (FS-BS: 40-50 cm), it was observed that *As* content of Pristol is comparable between FS-TS and FS-BS

(7.3mg/kg, respectively 8mg/kg), and both values are above RO soil normal values (5mg/kg), but under RO soil alert values (15mg/kg). This higher content in *As* is probably caused by mining activity in neighbouring countries, since it is known that the pollution source of *As* is generally natural. What should be evaluated would be the ratio As^{2+}/As^{5+}, because the toxicity of the first for organisms is 10 times stronger (Oros, 2008). *Cd* content is in the limits of RO soil normal values (1mg/kg), both in FS-TS and FS-BS. *Cr* in FS-TS is above RO soil normal values (30mg/kg), and close to RO soil alert values (100mg/kg). It is also above BG soil normal values and *Dutch target values*. *Cr* content is significantly lower in FS-BS (60.6mg/kg) as compared with FS-TS (96mg/kg). *Cr* in FS-BS is above RO soil normal values (30mg/kg), and relatively close to BG soil normal values. *Cu* in FS-TS is lower than RO soil normal values (20mg/kg), but slightly higher than in FS-BS. Comparatively, *Cu* in FS-TS (12.9mg/kg) is half the content in FS-BS (29.4mg/kg). *Hg* could be measured only in FS-TS, and is below RO soil normal values (0.1mg/kg).In FS-BS the *Hg* values are below the detection limit. *Hg* measured at IGR indicated 0.04mg/kg in FS-TS and 0.005mg/kg in FS-TS. *Ni* content is near twice in FS-TS as in FS-BS (38.6mg/kg versus. 21.4mg/kg), and slightly above RO soil normal values. In FS-TS it is higher than RO soil normal values (20mg/kg) and than the *Dutch target*. *Pb* is low both in FS-TS and FS-BS, and below RO and BG soil normal values (20mg/kg), as well as all other EQS. *Zn* shows the same situation as *Pb*.

All the values for PAHs in FS-TS of Pristol are below RO soil normal values, also below BG and EQS. In FS-BS all PAHs values were below detection limit, except for *Anthracene*, which could be determined and is below all EQS.

Pesticides are below detection limits in both FS-TS and FS-BS of Pristol.

Jiu at Zaval

The sampling station was selected downstream the bridge near Zaval locality, where there is also a water and sediment monitoring station of the National Administration Romanian Waters. The site was selected due to suspicion of pollution from the coal mines on the Valley of Jiu River, as well as agriculture.

Metal content: *As* is very slightly above RO soil normal values (5.26mg/kg for FS-TS and 5.33mg/kg for FS-BS). *Cd* is below BG, RO and all other standards. *Cr* is above RO soil normal values in both FS-TS and FS-BS (60.1mg/kg, respectively 55.4mg/kg), but below BG soil normal values (65mg/kg). *Cu* is slightly above the RO normal values (20mg/kg), being 26.3mg/kg in FS-TS and 29.8mg/kg in FS-BS. *Hg* is above the BG, Dutch and RO normal values, with 0.55mg/kg (FS-TS), respectively 0.57mg/kg (FS-BS). *Hg* determined at IGR is 0.57mg/kg in FS-TS and 0.205mg/kg in FS-BS.

As it is known, the main sources of *Hg* pollution are metallurgy, cement factories, burning of oil, coal and wood.The sampling site is at the confluence with the Jiu River, a river associated with the coal processing industry and the location of the series of high-power thermal power plants in the country (Lăcătușu et al., 2008). This could be the explanation for the higher values recorded for mercury at this sampling site.

Ni is above the RO soil normal value (20mg/kg), with the values of 30mg/kg in both FS-TS and FS-BS, but below the BG soil normal values (46mg/kg). *Pb* is below all standars in both FS-TS and FS-BS (10.4mg/kg, respectively 10.5mg/kg), approximately half of the limit for BG and RO nomal values (26mg/kg, respectively 20mg/kg). *Zn* is following the same pattern, being also under all standarsds, and approximately half (45.5mg/kg and 47mg/kg) of BG and RO normal values (88mg/kg and 100mg/kg).

PAHs: *Anthracene* is below RO normal values (0.05mg/kg) and *Elbe lower limit* (0.03mg/kg) being 0.023mg/kg in FS-TS and 0.021mg/kg in FS-BS. *Floranthene* is twice above BG and RO soil normal values (0.053mg/kg in FS-TS, respectively 0.05mg/kg in FS-BS), but below *Elbe lower limit*. *Benzo(a)pyrene* content is around the RO soil normal values (0.02mg/kg), being 0.023mg/kg in FS-TS, respectively 0.021mg/kg in FS-BS, around twice as much as E*lbe lower limit* (0.01mg/kg). *Benzo(b)fluoranthene+Benzo(k)fluoranthene* has the same pattern regarding RO soil normal values (0.02mg/kg), with 0.025mg/kg in FS-TS and 0.022mg/kg in FS-BS. *Benzo(g,h,i)perylene* is slightly twice as much as RO soil normal values (0.02mg/kg), being 0.052mg/kg in FS-TS and 0.046mg/kg in FS-BS. *Indeno(1,2,3-cd)pyrene* is nearly at 0.02mg/kg, which is the RO soil normal value, respectively 0.019mg/kg in FS-TS and 0.017mg/kg in FS-BS.

For the pesticides, the values are below the detection limit, except for *Hexachlorobenzene*, where the values are 0.002mg/kg in FS-TS and 0.001mg/kg in FS-BS.

Malak Iskar

Malak Iskar sampling site is the other point where bottom sediments are monitored by the Bulgarian Water Authority. It is situated on the Malak Iskar River right bank at the town of Roman, before the confluence with the Iskar River. This sampling site was selected because of possible pollution from recent mining activity (Elatsite copper mine) and less from agriculture. The analyzed heavy metals show that *Cu* and *Ni* content is elevated in both bottom and floodplain sediments compared to some of EQS limits (chapter 5.4). This is in agreement with previous studies of heavy metal contamination in the Malak Iskar River (Cholakova, 2004, 2006; Bird et al., 2010). Among the other metals, the content of *Cd* and *Cr* only in floodplain sediments is slightly higher than *Elbe lower limits*. The measured values of the organic substances are below the EQS limits.

Iskar

Iskar sampling site is a point where bottom sediments are monitored by the Bulgarian Water Authority and is also a part of the Trans National Monitoring Network (TNMN). It is situated on the Iskar River, between the villages Baykal and Gigen, 5 km before the confluence with the Danube. Possible pollution from industrial and agricultural activity is expected. The analyzed heavy metals content both in the bottom and floodplain sediments is comparatively low. The values for some elements (*As*, *Cd*, *Cr*, *Cu*, *Ni*) are slightly higher compared only to *Elbe lower limit*. The values for *Cu* especially in floodplain sediments are higher than *Dutch target* (chapter 5.4). The organic substance content is below the EQS limits, only *Benzo(a)pyrene* in floodplain sediments exceeds *Elbe lower limit*.

Olt at Islaz

The station on Olt River was placed upstream of its confluence with the Danube, with the purpose of identifying pollution from the industry in Slatina and/or agriculture. In this zone there is a Natura 2000 Special Protection Area ROSPA0024, which has been monitored monitored since a long time.

Metals: *As* content is above RO normal values (5mg/kg), being 6.73mg/kg in FS-TS, respectively 7.3mg/kg in FS-BS. It is below the BG and Dutch standards. *Cd* is below the RO soil normal values (1mg/kg), and also below BG soil normal values (0.4mg/kg), varying between 0.25mg/kg (FS-TS) and 0.37mg/kg (FS-BS). *Cr* is twice as much as the RO soil normal values (30mg/kg), being 61.1mg/kg (FS-TS) and 64.2mg/kg (FS-BS), slightly under BG soil normal values. *Cu* is almost at the RO soil normal values (19.7mg/kg versus 20mg/kg) in FS-TS, but 50% higher in FS-BS (30.5mg/kg). It is below the BG and other standards. *Hg* is around the RO soil normal value

(0.1mg/kg), being 0.07mg/kg in FS-TS and 0.12mg/kg in FS-BS, but consistently above the BG soil normal values (0.03mg/kg). *Hg* values determined at IGR were 0.081mg/kg in FS-TS and 0.207mg/kg in FS-BS.

The contents detected both in the Balint laboratory and in the IGR laboratory show a pollution in the case of the FS-TS sample compared to the RO threshold of the normal value, which is not found in the case of the FS-TS sample. Olt River has a length of 600 km, crosses cities with heavy industry (especially before 1989), is the most hydrotechnically arranged river in the country, and passes through mountains, including volcanics. Thus the sources of pollution in the past were numerous. One of them was surely at Govora (Sodium Plants), which used Hg in technologies, however, after 1989 its capacity was reduced, and from 2020 it is dramatically reduced to 33%. Probably the remediation occurs naturally, because the surface samples do not show pollution.

Ni presents higher values than the RO soil normal values (20mg/kg), being 32.1mg/kg in FS-TS and 38.2mg/kg in FS-BS (the latter being also higher than the *Dutch target*, but below the BG soil nomal values). The values for *Pb* are below all standards (12.9mg/kg in FS-TS, lower than in FS-BS, where the value is 17.2mg/kg). *Zn* is below all standards (52.8mg/kg in FS-TS and 72.2mg/kg in FS-BS).

PAHs: The Romanian standard for *Anthracene* is 0.05 mg/kg. Our data shows that in FS-TS of Islaz this PAH is 0.014mg/kg, and much lower in the FS-BS (0.003mg/kg). For *Fluoranthene*, the value in FS-TS is five time greater than RO soil normal value (0.02), respectively 0.105mg/kg, in contrast with FS-BS, that is near the normal values (0.022mg/kg). The value in FS-TS is also slightly higher than BG maximum concentration in soils (0.1mg/kg). For *Benzo(a)pyrene*, the value in FS-TS is twice as the RO soil normal value (0.02mg/kg), namely 0.041mg/kg. In contrast, the FS-BS content is 0.008mg/kg, twice and haft lower than the normal value. For *Benzo(b)fluoranthene+Benzo(k)fluoranthene*, the value for FS-TS is four times greater than RO soil normal values (0.02mg/kg), namely 0.076mg/kg. In contrast, the FS-BS values are slightly under the RO normal values, i.e. 0.015mg/kg. For *Benzo(g,h,i)perylene*, the Romanian standard is 0.02mg/kg. In Islaz FS-TS, the value is slightly above this (0.024mg/kg), in contrast with FS-BS values (0.01mg/kg), ten times lower than the BG maximum allowable concentration in soils (0.1mg/kg). For *Indeno(1,2,3-cd)pyrene*, the FS-TS values are 0.022mg/kg, near the RO soil normal values (0.02mg/kg), contrasting with the FS-BS values, which are 0.006mg/kg (three times lower as the RO soil normal values).

For pesticides there are no data available (outside the detection limit).

Danube – Svishtov and Zimnicea

Danube at Svishtov sampling site is another point where water quality is monitored by the Bulgarian Water Authority and is also a part of the Trans National Monitoring Network (TNMN). It is situated on the Danube River to the east of the of Svishtov port. Possible pollution from industrial and agricultural activity is expected. In addition to bottom and floodplain sediments a sample from suspended sediments was taken. The analyzed heavy metal content, both in bottom and floodplain sediments, is comparatively low. Only the content of *Cr* and *Cu* is higher than *Elbe lower limits*. The values for *As* in floodplain sediments and for *Cd* in bottom sediments are higher than *Elbe lower limits* and some other standards (chapter 5.4). The heavy metal content is low in all suspended sediments. The measured organic substances content is below the EQS limits. The only exception is the content of *Benzo(a)pyrene* which is higher in all sediment types (chapter 5.4).

ZIMNICEA

Project co-funded by the European Union (ERDF, IPA and ENI)

For the sake of completion, floodplain sediments were collected at Zimnicea, opposite Svishtov, on the left bank of Danube River, in order o have a full profile.

Metal content: *As* is consistenly over RO soil normal value (5 mg/kg), i.e. 8.49mg/kg in FS-TS and 12.9mg/kg in FS-BS, the latter being also over BG soil normal value (10mg/kg). *Cd* is below RO soil normal value (1mg/kg), BG (0.4 mg/kg) and other standards, with the values of 0.3 mg/kg (FS-TS) and 0.24mg/kg (FS-BS). *Cr* is twice as much as RO soil normal value (30mg/kg), being 65.9mg/kg (FS-TS) and 64mg/kg (FS-BS), very close to BG soil normal value (65mg/kg). *Cu* is over the RO soil normal value (20mg/kg), being slightly over this value in FS-TS (23.3mg/kg) and almost with 1/3 greater in FS-BS (29.2mg/kg). It is, however, lower than the other standards. *Hg* content is slightly larger than the RO soil normal value (0.1mg/kg) in FS-TS (0.16mg/kg) and more than twice in FS-BS (0.25mg/kg). The *Hg* values determined at IGR showed 0.185mg/kg in FS-TS and 0.326mg/kg in FS-BS, in line with the values obtained at BalintAnalitika.The BG normal standard for *Hg* is more restrictive (0.03mg/kg), while the *Dutch target* is three times higher than the RO soil normal value, being 0.3mg/kg.

The analysis of *Hg* at BalintAnalitika and IGR shows a higher content compared to normal values. No continuous polluting sources have been identified except for a concrete factory with activity in the last 9 years. In the 2018 prefecture report on the quality of environmental factors, *Hg* pollution is not detected. The measured values are below the alert threshold.

Ni is almost twice as much as RO soil normal value (20mg/kg), namely 37.4mg/kg in FS-TS and 38.4mg/kg in FS-BS, being slightly over the *Dutch target* (35mg/kg). The content in *Pb* is lower than all standards, being 17.9mg/kg in FS-TS and 15.3mg/kg in FS-BS. The same situation occurs for *Zn* (59.2mg/kg for TS and 59.7mg/kg for BS).

PAHs: *Anthracene* is very low (0.003mg/kg in FS-TS and 0.012mg/kg in FS-BS), consistently below all standards. *Fluoranthene* is close to RO soil normal values in FS-TS (0.025mg/kg) and about five times more in FS-BS (0.098mg/kg), being close to BG maximum allowable concentration in soil (0.1mg/kg). *Benzo(a)pyrene* is twice as large in FS-BS (0.04mg/kg) than RO soil normal values (0.02mg/kg) and half than the RO soil normal values in FS-TS (0.009mg/kg). *Benzo(b)fluoranthene+Benzo(k)fluoranthene* is 0.016mg/kg in FS-TS (below the RO soil normal values) and much more in FS-BS (0.06mg/kg), as compared with the 0.02mg/kg for the RO standard. *Benzo(g,h,i)perylene* is also lower in FS-TS(0.016mg/kg) than in FS-BS (0.049mg/kg), more than twice the RO soil normal values (0.02mg/kg). A similar trend is observed for *Indeno(1,2,3-cd)pyrene*: 0.008mg/kg in FS-TS and 0.025mg/kg in FS-BS.

On the right bank of the Danube, in Svistov, there is a pulp and viscose factory that polluted heavily with sulfur until 2010. For this reason, the pollution is monitored, in addition to that carried out by the National Administration Romanian Waters, in the Zimnicea area, according to the report at the link below, which shows data regarding organic susbtances, as well as beta and gamma radiations.

https://tr.prefectura.mai.gov.ro/wp-content/uploads/sites/24/2019/06/APM-Calitatea-factorilor-de-mediu-2018.pdf

The report mentions: Directive 96/59/EEC on the elimination of polychlorinated biphenyls and triphenyls (PCBs/PCTs) transposed into national law by H.G. no. 173/2000 for the regulation of the special regime regarding the management and control of polychlorinated biphenyls and other similar compounds, modified by G.D. no. 291/2005 led to the updating of the reports on the management and control of polychlorinated biphenyls and other similar compounds. The PCB Inventory for 2016 in Teleorman County indicates a single economic operator.

All pesticides are below detection limit.

Danube at Oltenita

Oltenita station was selected at the recommendation of the National Administration Romanian Waters in order to have comparative data for upstream (this station) and other station downstream of Arges River confluence with the Danube. Arges River collects the waters of Dambovita River which passes through Bucharest, the capital of Romania, and pollution is suspected.

Metal content: *As* content is above RO soil normal value (5mg/kg), being 7.92mg/kg in FS-TS and 6.48mg/kg in Fs-BS, but below the BG and Dutch standards. *Cd* is 0.4mg/kg in FS-TS, equal to the RO soil normal value (0.4) and lower than all other standards. In FS-BS, *Cd* is lower (0.27). *Cr* content is high in FS-TS (74.9mg/kg), more than both RO standard (30mg/kg) and BG standard (65mg/kg), while in FS-BS is a little lower (59.4mg/kg). *Cu* is 29.8mg/kg in FS-TS and 26.3mg/kg in FS-BS, being above RO soil normal value (20mg/kg). Otherwise, *Cu* content is below the other standards. *Hg* is below the RO soil normal values (0.1mg/kg), being 0.05mg/kg in FS-TS and 0.06mg/kg in FS-BS, but higher than the BG soil normal values (0.03mg/kg). *Hg* values measured at IGR were 0.027mg/kg in FS-TS, respectively 0.048mg/kg in FS-TS, also below RO soil normal values.

Ni is near twice RO soil normal value in FS-TS (39mg/kg) and 1.5 higher than RO soil normal value in FS-BS (32.4mg/kg), but lower than BG soil normal values (46mg/kg). *Pb* content is 18.4mg/kg in FS-TS and 14.2mg/kg in FS-BS, lower than all standards.The same applies to *Zn* content (78.8mg/kg in FS-TS and 60mg/kg in FS-BS).

PAHs: consistently lower *anthracene* content (0.002mg/kg in FS-TS and 0.003mg/kg in FS-BS), lower than all standards. *Fluoranthene* is 0.018mg/kg in FS-TS and 0.015mg/kg in FS-BS, lower than RO soil normal value (0.02mg/kg) and the other standards. *Benzo(a)pyrene* values (0.008mg/kg in FS-TS and 0.006mg/kg in FS-BS) are much lower than the RO soil normal value (0.02mg/kg). *Benzo(b)fluoranthene+Benzo(k)fluoranthene* values are also lower than RO soil normal value (0.02mg/kg), being 0.019mg/kg in FS-TS, respectively 0.015mg/kg in FS-BS. *Benzo(g,h,i)perylene* values are also lower than RO soil normal value (0.02mg/kg): 0.008mg/kg in FS-TS and 0.006mg/kg in FS-BS. *Indeno(1,2,3-cd)pyrene* values show the same pattern regarding RO soil normal value (0.02mg/kg), being 0.006mg/kg in FS-TS and 0.005mg/kg in FS-BS.

For pesticides, 0.001mg/kg were determined in case of *Hexachlorobenzene*, for both FS-TS and FS-BS, other substances being below the detection limit.

Danube at Hârșova

The sampling site at Hârșova was added in order to check the status of Danube waters after entering entirely in the Romanian territory, changing flow direction from W-E to S-N. For this part of the Danube, the reports of basin management of the National Authority Romanian Waters indicate "good water condition", as opposed to "bad water condition" from Bazias to Silistra-Călărași segment of Danube River.

Metal content: *As* content is higher (almost 50% more) in FS-TS than RO soil normal value (5mg/kg), having a value of 7.68mg/kg. In FS-BS it is slightly over the RO standard (5.5mg/kg). *Cd* is in both FS-TS and FS-BS less than the detection limit. *Cr* is 41.7mg/kg in FS-TS, higher than RO soil normal value, whereas in FS-BS, the content is 30mg/kg (equal to RO standard). Both values are below all other EQS. *Cu* in FS-TS is 52.2mg/kg, being 2.5 higher than RO soil normal value (20mg/kg), and also higher than BG and other standards. In FS-BS, the value for *Cu* is 28.9mg/kg, almost 50% higher than RO soil normal value, but lower than the rest of the standards. *Hg* content in FS-TS coincide with RO soil normal threshold (0.1mg/kg) and is three times higher than BG soil normal value. In FS-BS, *Hg* content is only 0.067mg/kg, lower than the *Dutch target*. *Hg* values determined at IGR were below RO soil normal values, being 0.060mg/kg in FS-TS and 0.065mg/kg in FS-TS.

Ni in FS-TS (47.7mg/kg) is nearly 2.5 higher as the RO soil normal value (20mg/kg) and higher also than the *Dutch target* (35mg/kg) and BG soil normal value (46mg/kg). In FS-BS, *Ni* is lower (32.1mg/kg), higher only than RO soil normal value. *Pb* in FS-TS (26.9mg/kg) is higher than RO and BG soil normal value (20mg/kg, respectively 26mg/kg). In FS-BS *Pb* content is a little lower (20.1mg/kg). *Zn* in FS-TS (102mg/kg) is almost as RO normal value (100mg/kg), higher than BG soil normal value (88mg/kg), whereas in FS-BS the content is lower (70.1mg/kg).

PAHs: *Anthracene* content is below the detection limit for both floodplain depths. *Fluoranthene* content is near the RO threshold (0.02mg/kg), namely 0.026mg/kg in FS-TS and 0.024mg/kg in Fs-BS. *Benzo(a)pyrene* is below RO soil normal value (0.02mg/kg), namely 0.013mg/kg in FS-TS, respectively 0.012mg/kg in FS-BS. *Benzo(b)fluoranthene+Benzo(k)fluoranthene* content is equal in FS-TS and FS-BS (0.022mg/kg), almost identical with RO soil normal value (0.02mg/kg). *Benzo(g,h,i)perylene* is below the RO standard (0.02mg/kg), respectively 0.016mg/kg in FS-TS and 0.013mg/kg in FS-BS. *Indeno(1,2,3-cd)pyrene* values follow the same pattern as *Benzo(g,h,i)perylene*, i.e. 0.015mg/kg in FS-TS and 0.013mg/kg in FS-BS, being below RO standard.

Organoclorurated pesticides were below detection limit.

Sites on Timok River and Borska Reka in Serbia

The main source of pollution detected at these two sites are the mining activities in Bor copper mine and associated mineral processing activities.

Fig. 5.2 The city of Bor and the quarry in the background

Project co-funded by the European Union (ERDF, IPA and ENI)

Fig. 5.3: Bor mining and processing facilities

Fig. 5.4: Borska Reka

Fig. 5.5: Pollution at Borska Reka

Pollution by heavy metals is dominant, but also organic pollution from raw sewage discharge from the city of Bor is evident.

Discussion will be extended when laboratory data is released.

5.3. CONCLUSIONS

The preliminary analysis shows moderate to high values for some heavy metal concertation in most of the sites, whereas all the other contaminants show moderate to lower values, compared to almost all EQS's taken into account during the study.

The evaluation of the published data for HSs in the South Danube Test Area suggests the following preliminary conclusions:

1. The elevated *Zn*, *Cu*, *Pb*, and *As* values are a result of the mining activity in the described catchments. The *As*, *Pb*, *Zn* are above the target values in the Ogosta river sediments, whereas *Cu* is enriched (higher than the lower limit) in Malak Iskar, but closer to normal before the confluence with the Danube (Iskar site). The *Cd* values are normal (below the BG soil target value) at all sites except the transnational Svishtov sediment sampling point.

2.) The identified organic compounds exceeding the normal EQS values are assumed to be generated during incomplete or low temperature combustion processes occurring in households (mainly in rural areas) or during road transportation (in urban areas or where the rivers flow near heavy traffic national and express roads). These organic components are found mainly in the Danube river sites (Svishtov) and are normal in the Bulgarian BRD catchments (Ogosta and Iskar). Consequently, pollution from river transport should also come into consideration.

3) In neither sampling site the alert or intervention limits is reached. Usually there is a great difference from the alert value and the levels where the analysed elements/susbtances lie.

4) The normal value is overpassed in case of samples collected from the confluence with rivers which cross long mountaineous areas or zones where high industrialisation existed in the past (before 1990). In these case, overpassing of the normal value in case of metals (Cu, Ni, Cr, Pb) can represent the "geological background" (Fodor, 2001).

5) A tendency for natural remediation can be noted, because the content of metals in FS-TS is lower than in FS-BS.

6) Larger values in the FS-TS samples might occur in areas prone to flooding, these being accidental pollutions if continuous pollution sources are not identified in the area.

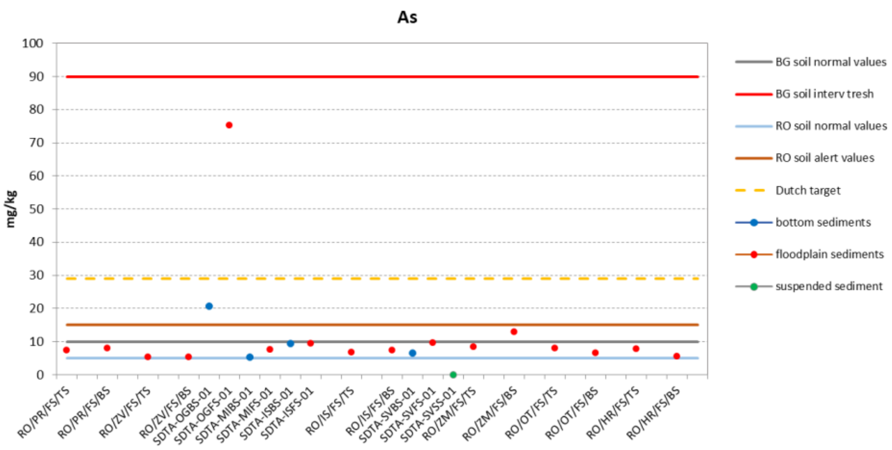
Conclusions on Borska Reka and Timok will be added when data becomes available from the laboratory.

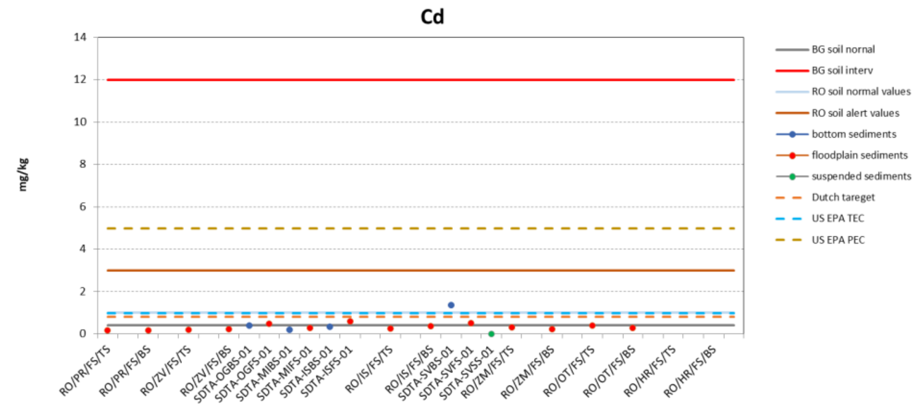
5.4. GRAPHS

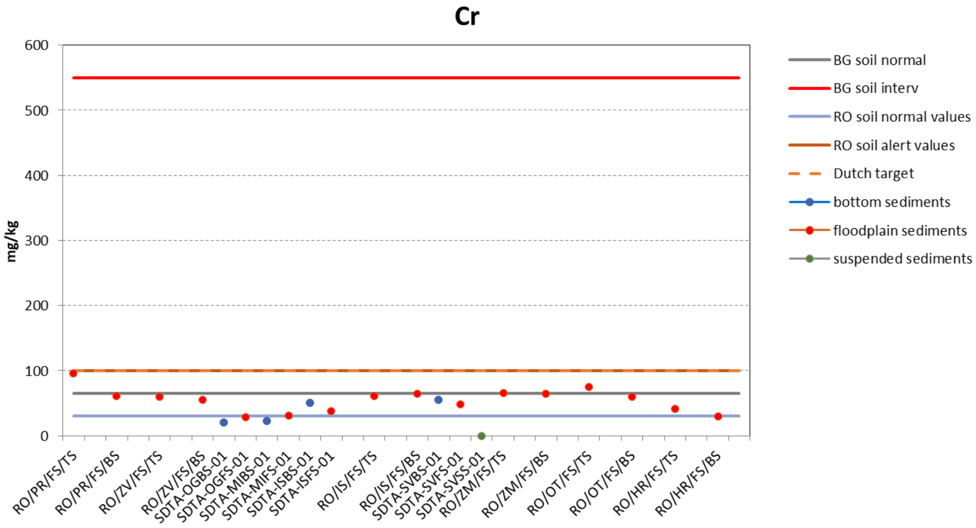
Graphics for measured values compared to EQS's data in the South Danube Test Area sites. Used abbreviations: *OG: Ogosta; MI: Malak Iskar; IS: Iskar at Baykal; SV: Svishtov; RO: Romania; Pr: Pristol; ZV: Zăval on Jiu; IS: Islaz on Olt; OT: Oltenița; HR: Hârșova; FS: floodplain sediment; BS: bottom sediment; SS: suspended sediment; FS-TS floodplain topsoil (0-5cm depth); FS-TS: floodplain bottom soil (40-50cm depth).*

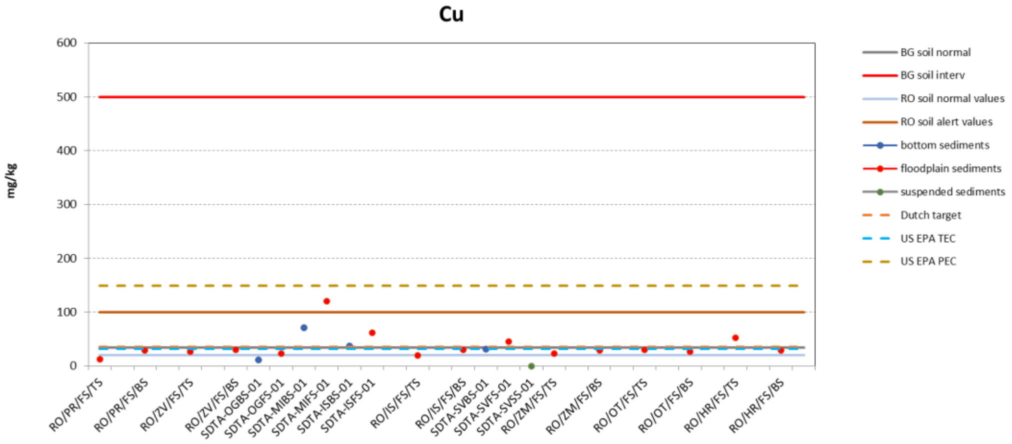
Note: Laboratory data for Borska Reka and Timok in Serbia is still not available and will be added to graphs when completed.

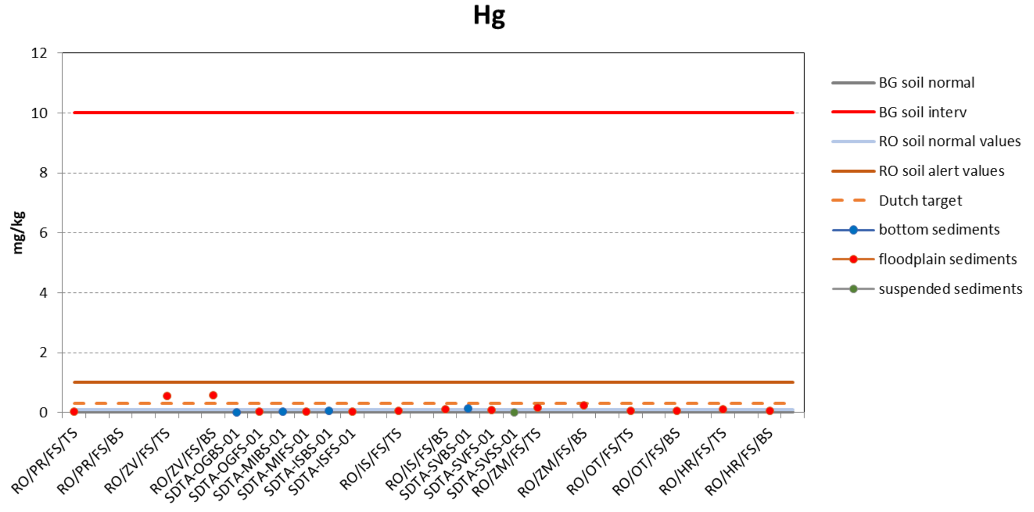
HEAVY METALS:

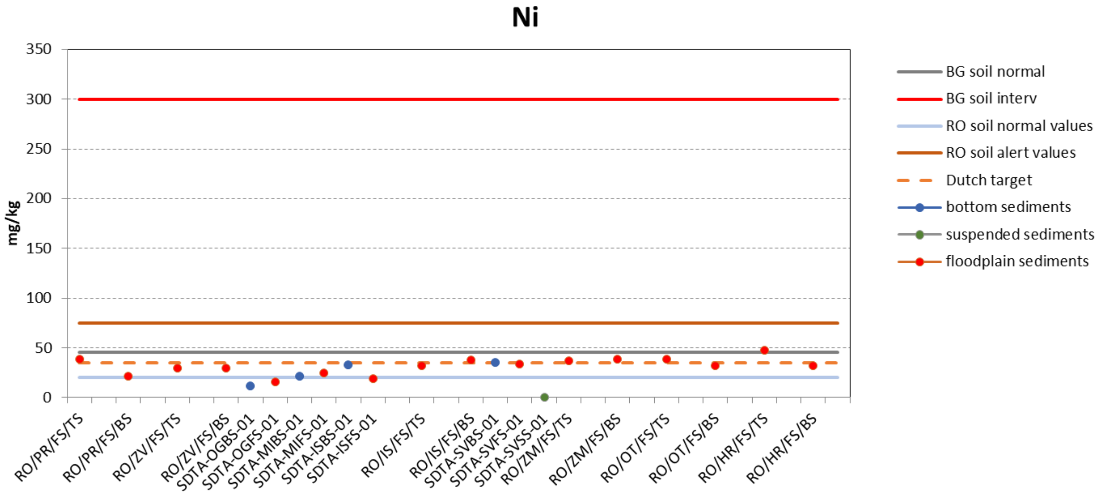


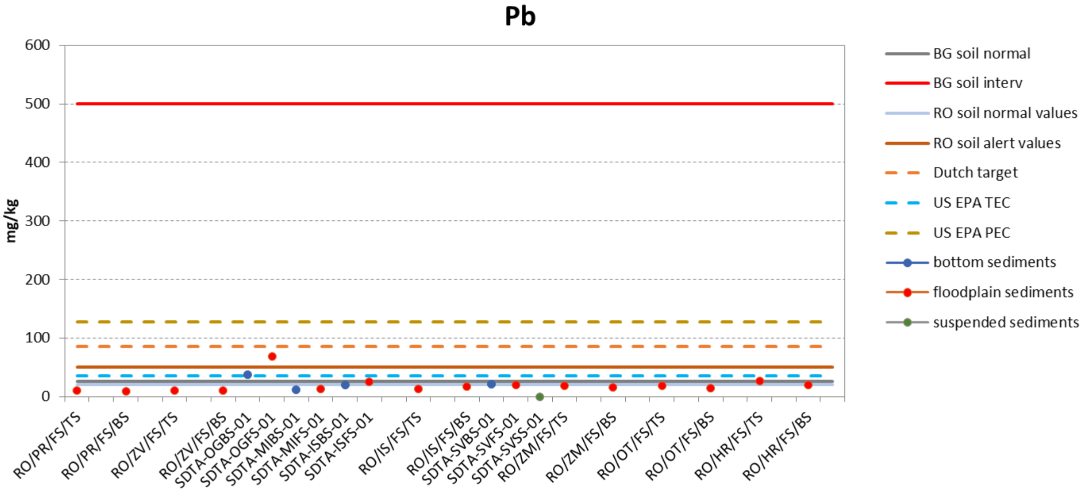

Cd
mg/kg
BG soil normal
BG soil interv
RO soil normal values
RO soil alert values
bottom sediments
floodplain sediments
suspended sediments
Dutch tareget
US EPA TEC
US EPA PEC

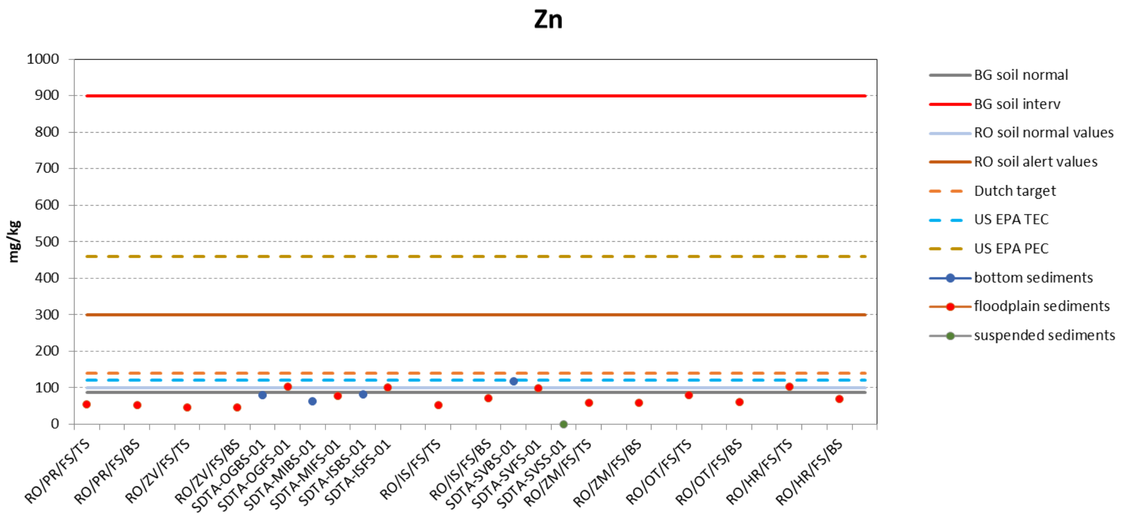

Cr
mg/kg
BG soil normal
BG soil interv
RO soil normal values
RO soil alert values
Dutch target
bottom sediments
floodplain sediments
suspended sediments


Cu
mg/kg
BG soil normal
BG soil interv
RO soil normal values
RO soil alert values
bottom sediments
floodplain sediments
suspended sediments
Dutch target
US EPA TEC
US EPA PEC

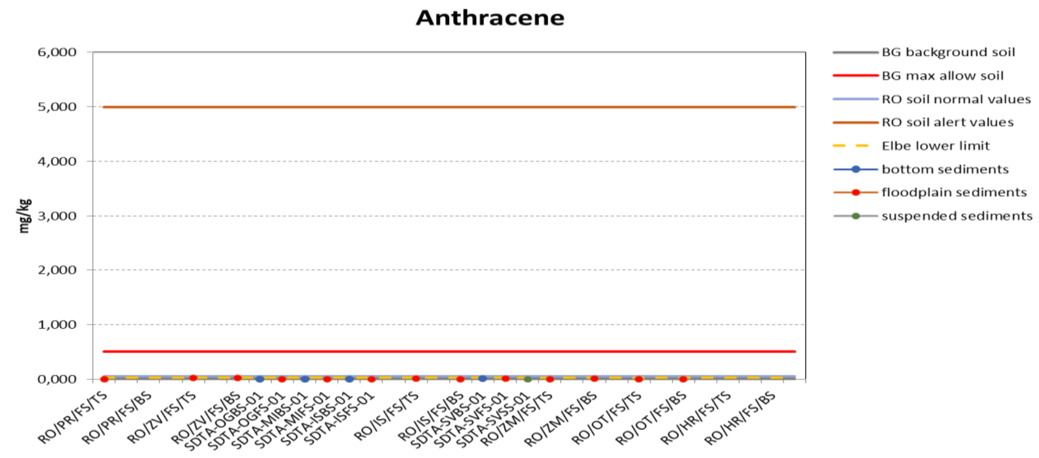

Hg
mg/kg
BG soil normal
BG soil interv
RO soil normal values
RO soil alert values
Dutch target
bottom sediments
floodplain sediments
suspended sediments

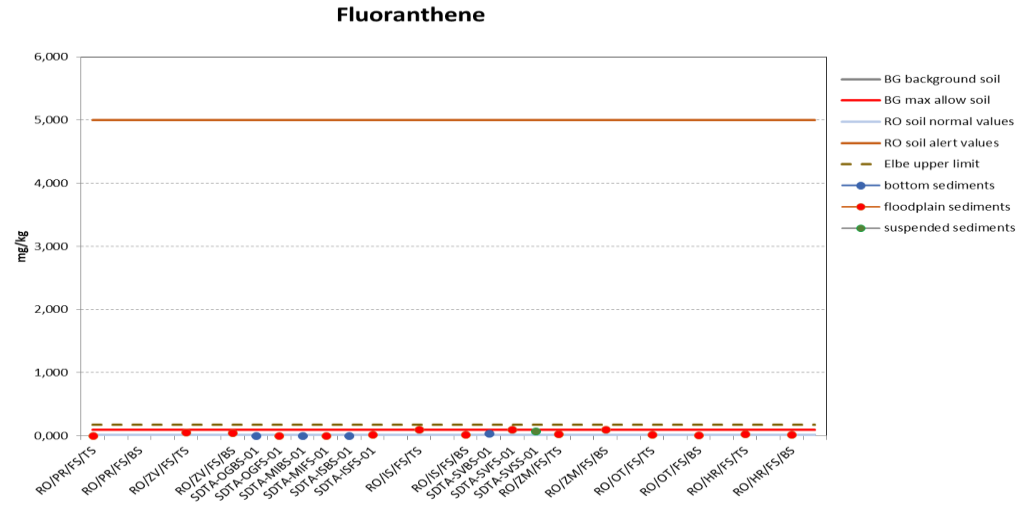

Ni
mg/kg
BG soil normal
BG soil interv
RO soil normal values
RO soil alert values
Dutch target
bottom sediments
suspended sediments
floodplain sediments

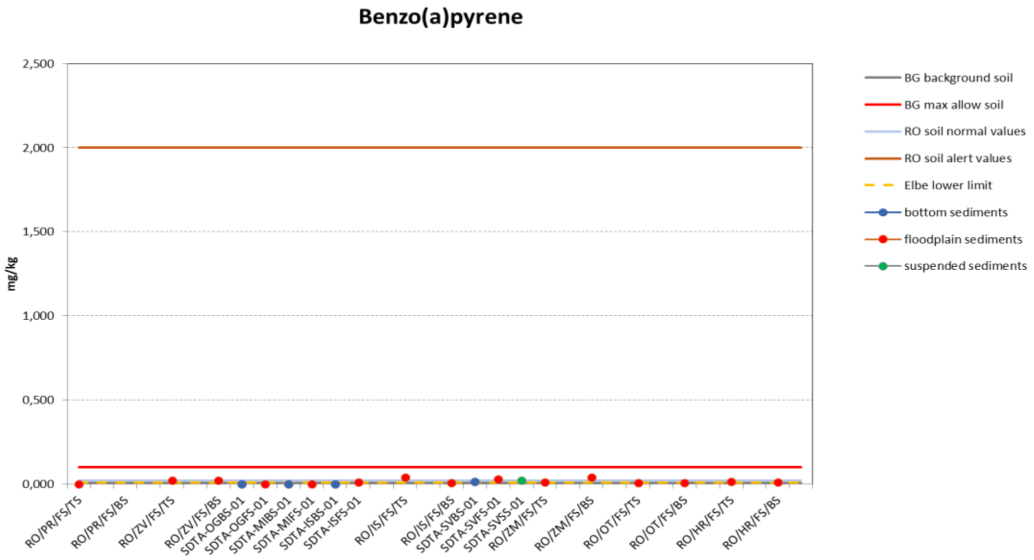

Pb
mg/kg
BG soil normal
BG soil interv
RO soil normal values
RO soil alert values
Dutch target
US EPA TEC
US EPA PEC
bottom sediments
floodplain sediments
suspended sediments

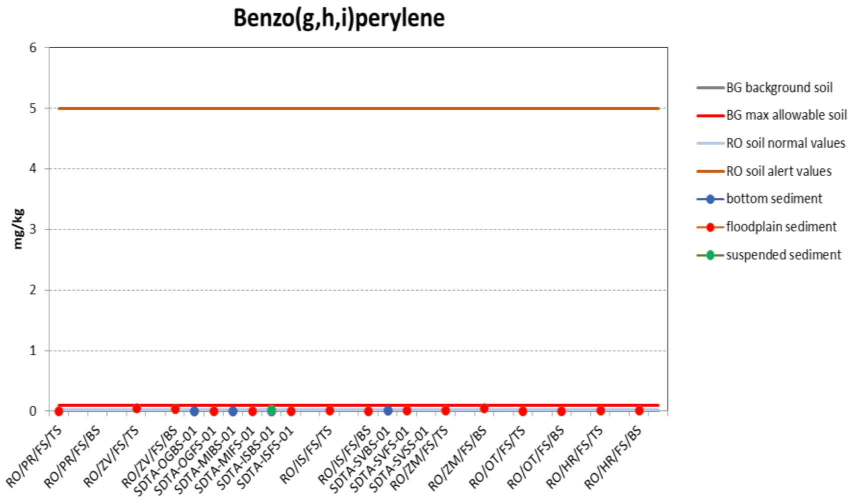

Zn
mg/kg
1000
900
800
700
600
500
400
300
200
100
0
RO/PR/FS/TS
RO/PR/FS/BS
RO/ZV/FS/TS
RO/ZV/FS/BS
SDTA-OGBS-01
SDTA-OGFS-01
SDTA-MIBS-01
SDTA-MIFS-01
SDTA-ISBS-01
SDTA-ISFS-01
RO/IS/FS/TS
RO/IS/FS/BS
SDTA-SVBS-01
SDTA-SVFS-01
SDTA-SVSS-01
RO/ZM/FS/TS
RO/ZM/FS/BS
RO/OT/FS/TS
RO/OT/FS/BS
RO/HR/FS/TS
RO/HR/FS/BS
BG soil normal
BG soil interv
RO soil normal values
RO soil alert values
Dutch target
US EPA TEC
US EPA PEC
bottom sediments
floodplain sediments
suspended sediments

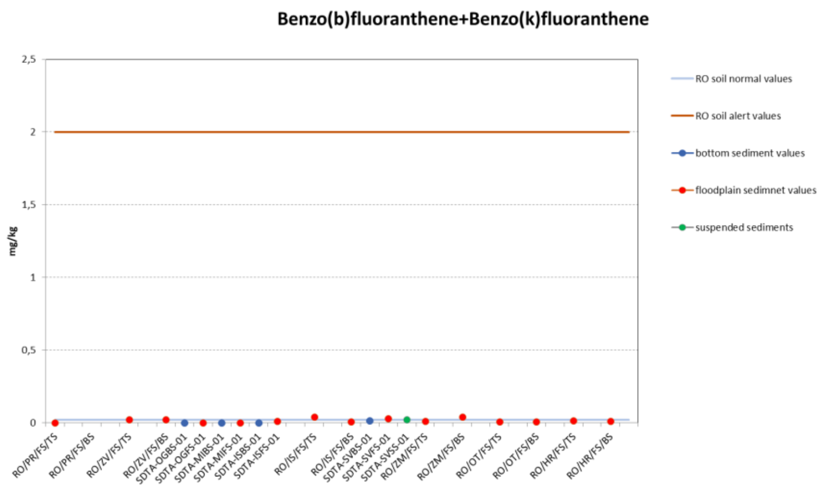
PAHs:

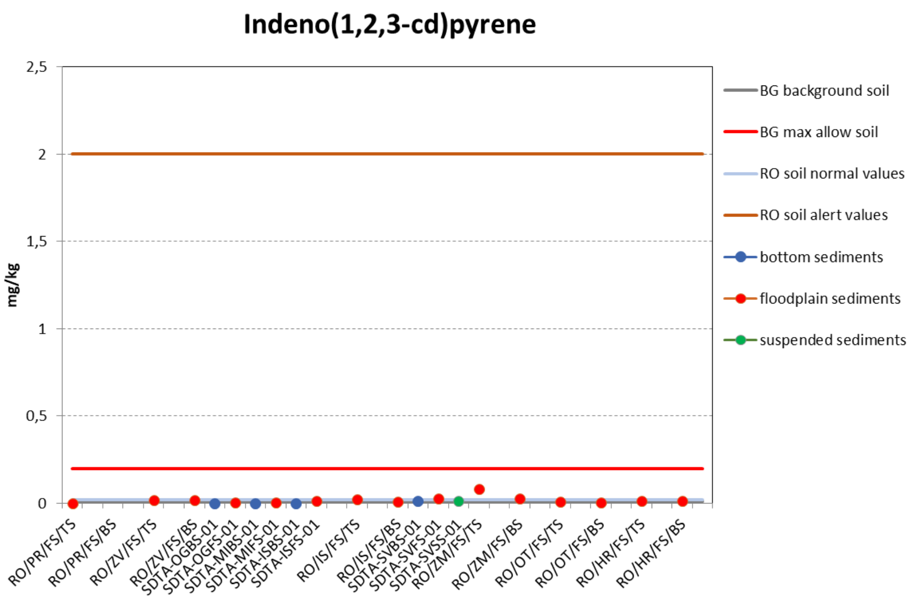

Anthracene
6,000
5,000
4,000
3,000
2,000
1,000
0,000
mg/kg
RO/PR/FS/TS
RO/PR/FS/BS
RO/ZV/FS/TS
RO/ZV/FS/BS
SDTA-OGBS-01
SDTA-OGFS-01
SDTA-MIBS-01
SDTA-MIFS-01
SDTA-ISBS-01
SDTA-ISFS-01
RO/IS/FS/TS
RO/IS/FS/BS
SDTA-SVBS-01
SDTA-SVFS-01
SDTA-SVSS-01
RO/ZM/FS/TS
RO/ZM/FS/BS
RO/OT/FS/TS
RO/OT/FS/BS
RO/HR/FS/TS
RO/HR/FS/BS
BG background soil
BG max allow soil
RO soil normal values
RO soil alert values
Elbe lower limit
bottom sediments
floodplain sediments
suspended sediments


Fluoranthene
6,000
5,000
4,000
3,000
2,000
1,000
0,000
mg/kg
RO/PR/FS/TS
RO/PR/FS/BS
RO/ZV/FS/TS
RO/ZV/FS/BS
SDTA-OGBS-01
SDTA-OGFS-01
SDTA-MIBS-01
SDTA-MIFS-01
SDTA-ISBS-01
SDTA-ISFS-01
RO/IS/FS/TS
RO/IS/FS/BS
SDTA-SVBS-01
SDTA-SVFS-01
SDTA-SVSS-01
RO/ZM/FS/TS
RO/ZM/FS/BS
RO/OT/FS/TS
RO/OT/FS/BS
RO/HR/FS/TS
RO/HR/FS/BS
BG background soil
BG max allow soil
RO soil normal values
RO soil alert values
Elbe upper limit
bottom sediments
floodplain sediments
suspended sediments


Benzo(a)pyrene
2,500
2,000
1,500
1,000
0,500
0,000
mg/kg
RO/PR/FS/TS
RO/PR/FS/BS
RO/ZV/FS/TS
RO/ZV/FS/BS
SDTA-OGBS-01
SDTA-OGFS-01
SDTA-MIBS-01
SDTA-MIFS-01
SDTA-ISBS-01
SDTA-ISFS-01
RO/IS/FS/TS
RO/IS/FS/BS
SDTA-SVBS-01
SDTA-SVFS-01
SDTA-SVSS-01
RO/ZM/FS/TS
RO/ZM/FS/BS
RO/OT/FS/TS
RO/OT/FS/BS
RO/HR/FS/TS
RO/HR/FS/BS
BG background soil
BG max allow soil
RO soil normal values
RO soil alert values
Elbe lower limit
bottom sediments
floodplain sediments
suspended sediments







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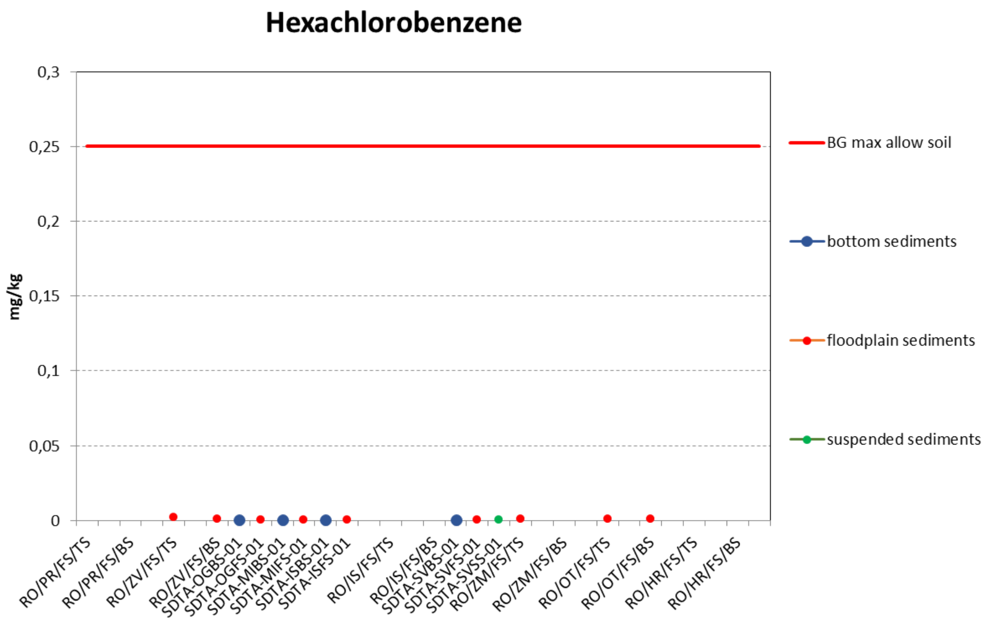

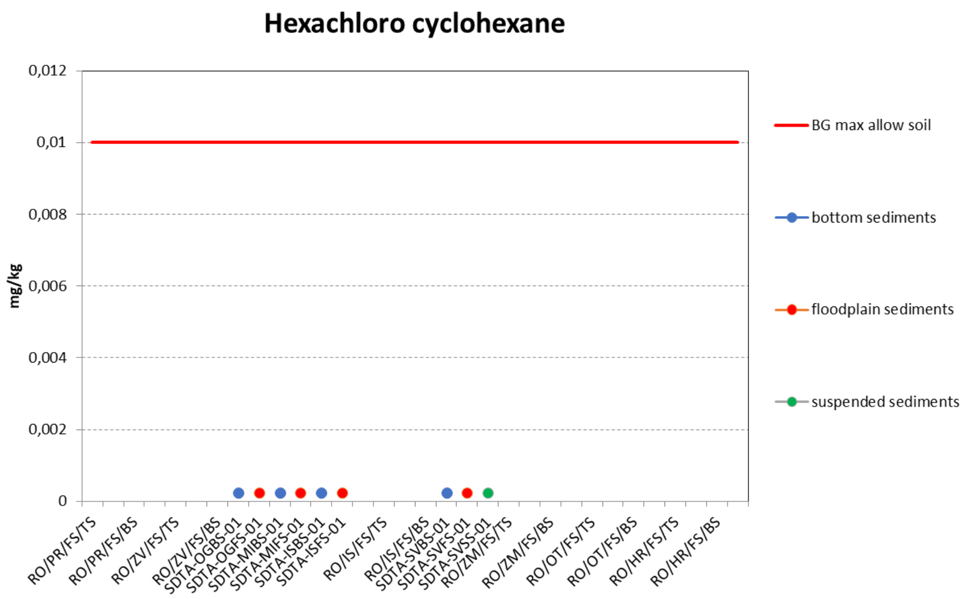

Project co-funded by the European Union (ERDF, IPA and ENI)

REFERENCES

Bird G., Brewer P., Macklin M., Nikolova M., Kotsev Ts., Mollov M., Swain C. Dispersal of Contaminant Metals in the Mining-Affected Danube and Maritsa Drainage Basins, Bulgaria,Eastern Europe. Water Air Soil Pollut (2010) 206:105–127

Cholakova Z.2006. Landscape-Geochemical Approach for Evaluation of the Iskar River Basin State in the Western Balkan Mountain (Bulgaria) – In: Proceedings of BALWOIS Conference on Water Observation and Information System for Decision Support, Ohrid, 23–26 May, FYR Macedonia.

Cholakova Z.2004. GEOCHEMICAL PECULIARITIES OF MIGRATION AND CONCENTRATION of some heavy metals in the ISKAR RIVER BASIN IN STARA PLANINA MOUNTAIN. In: Proceedings of First International Conference "Human Dimensions of Global Change in Bulgaria", 22-24 April, Sofia, Bulgaria

Basin Directorate Danube Region. National water management plan 2016-2021.

Basin Directorate Danube Region – Status and assessment reports for the Danube region.

Ministry of the Environment and Water, Executive Environmental Agency. 2017. Национален доклад за състоянието и опазването на околната среда (National report for ecological status of the Environment).

"АКВА-ENV" Consortium. 2017. Report „Проучване и оценка на химичното състояние на повърхностните води" ("Survey and assessment of surface water chemical status")

Fodor D., G. Baican, 2001, Impactul industriei miniere asupra mediului, Editura Infomin, Deva.

Lăcătuşu R., A.R. Lăcătuşu, M. Lungu, I.G. Breaban, 2008, Macro- and microelements abundance in some urban soils from Romania , Carpathian Journal of Earth and Environmental Sciences, Vol. 3, no. 1

Oros V., 2008, Ecotoxicologie – Note de curs, Universitatea de Nord Baia Mare [10]

*** Ordin nr. 756/1997 pentru aprobarea Reglementării privind evaluarea poluării mediului

U.S. EPA. 1998. "Method 7473 (SW-846): Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry," Revision 0. Washington, DC.

Project co-funded by the European Union (ERDF, IPA and ENI)