

OUTPUT TITLE:

**SEDIMENT QUALITY LABORATORY PROTOCOL FOR HSS
OUTPUT 4.2**

PROJECT TITLE:

**SEDIMENT-QUALITY INFORMATION, MONITORING AND
ASSESSMENT SYSTEM TO SUPPORT TRANSNATIONAL
COOPERATION FOR JOINT DANUBE BASIN WATER MANAGEMENT**

ACRONYM: SIMONA

PROJECT DURATION:

1ST JUNE 2018 TO 1ST MAY 2021, 36 MONTHS

DATE OF PREPARATION:

31/10/2019

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

SEDIMENT QUALITY LABORATORY PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

**PART OF THE SEDIMENT-QUALITY INFORMATION,
MONITORING AND ASSESSMENT SYSTEM (SIMONA)**

**THE MAIN AIM IS TO SUPPORT TRANSNATIONAL
COOPERATION FOR JOINT DANUBE BASIN WATER
MANAGEMENT**

31/10/2019

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



Authors: Ana Čaić Janković (HR-HGI-CGS), Ajka Šorša (HR-HGI-CGS)

Co-authors:

Lidija Galović (HR-HGI-CGS)	Stela Ginin (BG-ExEA)
Danijel Ivanišević (HR-HGI-CGS)	Prvoslav Marjanović (RS-JCI)
Ivan Mišur (HR-HGI-CGS)	Marko Marjanović (RS-JCI)
Jasmina Antolić (HR-CW-HV)	Dragica Vulić (RS-JCI)
Đorđa Medić (HR-CW-HV)	Tatjana Mitrović (RS-JCI)
Ines Đurđević (HR-CW-HV)	Igor Striček (SK-SGIDS)
Neven Bujas (HR-CW-HV)	Jozef Kordík (SK-SGIDS)
Jelena Vićanović (BA-JUVS)	Jarmila Nováková (SK-SGIDS)
Aleksandra Kovačević (BA-JUVS)	Ivana Lemak (SK-SGIDS)
Jasminka Alijagić (SI-GEOZS)	Zsófia Kovács (HU-OVF)
Robert Šajn (SI-GEOZS)	Zsolt Szakacs (RO-TUCN)
Győző Jordán (HU-SZIE)	Damian Gheorghe (RO-TUCN)
Péter Fodor (HU-SZIE)	Kristina Šarić (RS-UB-FMG)
Sebastian Pfeleiderer (AT-GBA)	Volodymyr Klos (UA-UGC)
Katalin Mária Dudás (HU-NARIC)	Mária Mörtl (HU-NARIC)
Atanas Hikov (BG-GI-BAS)	András Székács (HU-NARIC)
Zlatka Milakovska (GI-BAS)	Ivana Živadinović (RS-UB-FMG)
Milena Vetseva (BG-GI-BAS)	Veronica Alexe (RO-IGR)
Petyo Filipov (BG-GI-BAS)	Anca-Marina Vijdea (RO-IGR)
Irena Peytcheva (BG-GI-BAS)	Barbara Keri (HU-BME)

Responsible(s) for the output: Ajka Šorša (HGI-CGS)

Co-responsible(s) for the output: Győző Jordán (HU-SZIE)

Editing and preparation for printing: Katalin Mária Dudás (HU-NARIC)

Please cite this protocol as: Čaić Janković, A., Šorša, A., The SIMONA Project Team. 2019. Sediment quality laboratory protocol for HSs. EU Interreg Danube Transnational Programme. 37p.

Table of Contents

1. Introduction.....	5
2. Selected Substances	7
2.1. Anthracene.....	7
2.2. Brominated diphenylethers.....	8
2.3. Cadmium and its compounds.....	8
2.4. C10-13-chloroalkanes	9
2.5. Di (2-ethylhexyl) phthalate (DEHP)	9
2.6. Fluoranthene.....	10
2.7. Hexachlorobenzene.....	11
2.8. Hexachlorobutadiene	11
2.9. Hexachlorocyclohexane.....	11
2.10. Lead and its compounds.....	12
2.11. Mercury and compounds.....	12
2.12. Pentachlorobenzene.....	14
2.13. Polyaromatic Hydrocarbons (PAH)	14
2.14. Tributyltin compounds (Tributyltin-cation).....	15
2.15. Dicofol	15
2.16. Perfluorooctane sulfonic acid and its derivatives (PFOS)	16
2.17. Quinoxifen	16
2.18. Dioxins and dioxin-like compounds	17
2.19. Hexabromocyclododecane (HBCDD)	17
2.20. Heptachlor and heptachlor epoxide	18
2.21. Nickel and its compounds.....	18
2.22. Arsenic and its compounds	19
2.23. Zinc and its compounds	20
2.24. Chromium and its compounds.....	20
2.25. Copper and its compounds.....	21

3. Sieving and drying	23
4. Sample storage and archive	25
5. Normalization.....	27
5.1. Grain size correction	27
5.2. Quartz correction.....	27
5.3. Al- and Li-normalization.....	28
6. Quality Control.....	29
7. References	31

Appendix 1

An overview of the laboratory methods and procedures (norms) for analysis of priority substances (PSs) from agricultural activities in DTP countries

Appendix 2

An overview of the laboratory methods and procedures (norms) for analysis of priority substances (PSs) predominantly released from the industrial activities in DTP countries

Appendix 3

An overview of the laboratory methods and procedures (norms) for analysis of heavy metals and its compounds in DTP countries

Appendix 4

An overview of the laboratory Quality Control for analysis of priority substances (PSs) in DTP countries

**The appendixes are downloadable
from the SIMONA website:
<http://www.interreg-danube.eu/simona/>**



1. INTRODUCTION

The Danube river basin is under great pressure from a diverse range of human activities. River sediments have an important role in the monitoring of the environment as they are considered to be the final sink of most contaminants. Many aquatic species live in the sediment. Microbial processes cause regeneration of nutrients and functioning of nutrient cycles for the whole water body. Accordingly, a healthy river needs sediment as a source of life. One of the aims of this study is to investigate the spatial and temporal variation in heavy metals and organic compound concentrations in sediment for the risk assessment status in the Danube river, with a review to determine its ability to sustain aquatic life.

The most used method for determination of heavy metals is Inductively-coupled plasma mass spectrometry (ICP-MS), and for the organic substances, Liquid chromatography and/or gas chromatography, linked to mass spectrometry (LC-MS and GC-MS) are commonly used.

The generally used method should satisfy the criteria recommended by WFD for the priority HSSs: they should be determined according to the ISO norms, have a limit of quantification (LOQ) $\leq 30\%$ Environmental Quality Standard (EQS) (or \leq **Predicted No Effect Concentration (PNEC)** for those without established EQSs) and a measurement uncertainty $\leq 50\%$ (EC, 2018).

Organic compounds are selected in the sediment according to their physico-chemical propensity for the solid phase. The more hydrophobic (water repulsing) the compound is, the less soluble in water it becomes, and therefore more likely to be adsorbed onto sediment particles. The octanol-water partition coefficient (K_{ow}) is used as a measure of the hydrophobicity of the organic compound (EC, 2010).

Compounds with $\log K_{ow} > 5$ should be measured in sediment or suspended particulate matter (SPM) and compounds with $\log K_{ow} < 3$ should be measured in water. Compounds with a $\log K_{ow}$ between 3 and 5 will depend on the degree of contamination. If the degree of contamination for a hydrophobic compound is unknown or expected to be low, sediment should be an additional monitoring matrix (due to accumulation).

The overviews of the laboratory methods and procedures (norms) for analysis of priority hazardous substances (PHSs) from agricultural activities, organic pollutants predominantly released from the industrial activities, heavy metals and its compounds, and Quality Control (QC) in DTP countries are presented in Appendices 1, 2, 3 and 4 respectively.

2. SELECTED SUBSTANCES

Under the European Water Framework Directive (WFD), the Environmental Quality Standards Directive 2008/105/EC was developed which proposed hazardous substances for monitoring in sediment. The Directive 2013/39/EU amending the Directive 2008/105/EC has proposed new priority substances for monitoring and has changed the status of some existing PSs.

The ISO and/or EPA standards for chemical analytical methods for the priority substances are described in this protocol in paragraphs 2.1. to 2.25. For those substances with a lack of standards, literature where their analytical methods were described is given.

Additionally, 5 heavy metals (1 priority substance plus 4 Danube river basin specific pollutants) and their compounds from the List of Priority Substances for the Danube River Basin are included in this protocol in paragraphs 2.21. to 2.25. (ICPDR, 2003).

2.1. ANTHRACENE

Anthracene is a polycyclic aromatic hydrocarbon (PAH). It is primarily used as an intermediate in the production of dyes and smoke screens. In the environment, it has been found in surface and drinking water, air, exhaust emissions, cigarette smoke, in smoked foods and edible aquatic organisms. Exposure to anthracene could cause skin burning and itching, headaches, nausea and loss of appetite (Faust, 1991).

- ◆ EPA Method 8100:1986 Polynuclear Aromatic Hydrocarbons. US Government Printing Office, Washington, DC, USA.

- ◆ ISO 18287:2006 Soil quality – Determination of polycyclic aromatic hydrocarbons (PAH) – Gas chromatographic method with mass spectrometric detection (GC-MS). International Organization for Standardization.
- ◆ EN 16181:2018 Soil, treated bio-waste and sludge – Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC). European Standardisation Organisation.

2.2. BROMINATED DIPHENYLETERS

Polybrominated diphenyl ethers or PBDEs are organobromine compounds used as a fire retardant. Humans are exposed to PBDEs by ingestion of food, by inhalation and in their homes from some common household items. PBDE bioaccumulates in blood, breast milk and adipose tissue. According to EPA (2017) there is an indication of the carcinogenic potential of decaBDE.

- ◆ ISO 22032:2006 Water quality – Determination of selected polybrominated diphenylethers (PBDE) in sediment and sewage sludge – Method using extraction and gas chromatography/mass spectrometry. International Organization for Standardization.
- ◆ EPA Method 1614:2007 Brominated Diphenyl Ethers in water soil, sediment and tissue by HRGC/HRMS. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.

2.3. CADMIUM AND ITS COMPOUNDS

Cadmium is a trace element and a transition metal. It is used in the manufacture of batteries, electrical conductors and metal plating. Cadmium is also a by-product of the mining and processing of iron, nickel and other metals. An increased level of cadmium has been observed in the environment due to contamination of the water supply from mining. Cadmium is suspected as one of the most eco-toxic heavy metals for humans, animals and plants. It could enter the body by inhalation or by ingesting food or drink (Alloway, 2013; Šorša and Halamić, 2014).

SEDIMENT QUALITY LABORATORY PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- ◆ ISO 11885:2007 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.

2.4. C₁₀₋₁₃-CHLOROALKANES

These compounds are also known as short-chain polychlorinated paraffins (SCCPs).

C₁₀₋₁₃ -chloroalkanes are compounds of unknown or variable composition. Substances with varying chlorine contents (up to about 70% by weight) and carbon chain lengths (between C₁₀ and C₁₃). C₁₀₋₁₃ -chloroalkanes have low water solubility and a strong tendency for adsorption to organic matter and soil. They are mainly released into the water during their production and use as a metal fluid, or by accidental discharges during transport and storage. People can be exposed to chlorinated paraffins via products and via the working environment. Exposure to C₁₀₋₁₃ -chloroalkanes could be harmful to the kidneys and liver and they may be carcinogenic (Danish EPA, 2013).

- ◆ ISO 22032:2006 Water quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge – Method using extraction and gas chromatography/mass spectrometry. International Organization for Standardization.

2.5. DI (2-ETHYLHEXYL) PHTHALATE (DEHP)

Di-2-ethylhexyl phthalate (DEHP) is a manufactured chemical used as an additive to Polyvinyl chloride plastics (PVC) to make them flexible in the production of medical devices. DEHP could leach from PVC medical devices into the environment. DEHP has low solubility in water and binds strongly to soil particles

or organic material. Humans exposed to DEHP or its metabolites can show effects in the liver, reproductive tract, kidneys, lungs, and heart (Tickner et al., 2001).

- ◆ ISO 13913:2014 Soil quality – Determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC/MS). International Organization for Standardization.

2.6. FLUORANTHENE

Fluoranthene is a polycyclic aromatic hydrocarbon (PAH). This PAH together with other PAHs could be found in combustion products. Fluoranthene is carcinogenic, toxic to reproduction, very persistent and bio-accumulative (Emsbo-Mattingly and Litman, 2016).

- ◆ ISO 13877:1998 Soil quality – Determination of polynuclear aromatic hydrocarbons -- Method using high performance liquid chromatography. International Organization for Standardization.
- ◆ ISO 17993:2002 Water quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction. International Organization for Standardization.
- ◆ ISO 15753:2006 Animal and vegetable fats and oils – Determination of polycyclic aromatic hydrocarbons. International Organization for Standardization.
- ◆ EPA Method 8100:1986 Polynuclear Aromatic Hydrocarbons. US Government Printing Office, Washington, DC, USA.
- ◆ ISO 18287:2006 Soil quality – Determination of polycyclic aromatic hydrocarbons (PAH) – Gas chromatographic method with mass spectrometric detection (GC-MS). International Organization for Standardization.
- ◆ EN 16181:2018 Soil, treated biowaste and sludge – Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC). European Standardisation Organisation.

2.7. HEXACHLOROBENZENE

Hexachlorobenzene is a persistent organic pollutant, insoluble in water and denser than water. It was used as a fungicide, in the production of dyes and rubber, and in wood preservation. Oral exposure to Hexachlorobenzene causes a liver disease with associated skin lesions (Barber et al., 2005).

- ◆ EPA Method 1625:1989 Semivolatile Organic Compounds by Isotope Dilution GCMS. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- ◆ ISO 10382:2002 Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection. International Organization for Standardization.

2.8. HEXACHLOROBUTADIENE

Hexachloro-1,3-butadiene is an organochlorine compound which is a colourless liquid with a mild odour. It is insoluble in water and denser than water. This substance is used as a solvent, then in gyroscopes, in the production of lubricants, as a heat transfer liquid, and as a hydraulic fluid. Hexachloro-1,3-butadiene may be toxic by ingestion or inhalation (Fatta et al., 2007).

- ◆ EN ISO 15009:2016 Soil quality – Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons – Purge-and-trap method with thermal desorption. Croatian Standards Institute.
- ◆ ISO 10382:2002 Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection. International Organization for Standardization.

2.9. HEXACHLOROCYCLOHEXANE

Hexachlorocyclohexane (HCH), formally known as benzene hexachloride (BHC), is a manufactured chemical form. One of its isomers was lindane (γ -HCH), used as an insecticide on fruit, vegetables, and forest crops. The HCHs have been found in soil, sediments, and surface waters near hazardous waste

sites. Hexachlorocyclohexane could accumulate in the fat of fish. It can cause liver cancer, blood disorders, dizziness and headaches (ATSDR, 2005; Macgregor et al., 2010).

- ◆ ISO 10382:2002 Soil quality — Determination of organochlorine pesticides and polychlorinated biphenyls — Gas-chromatographic method with electron capture detection. International Organization for Standardization.

2.10. LEAD AND ITS COMPOUNDS

Lead is a heavy metal, one of the most infamous environmental pollutants. It is widely used in the production of batteries and electrodes, paints, glass, ceramics, alloys, tyres, as a shield against radiation. Lead can enter the human body and accumulate from food, water, or by inhaling the dust. Lead is very toxic and causes neurological damage, diseases of the kidneys and liver, increased blood pressure, anaemia, cancer and problems with reproduction (Alloway, 2013; Šorša and Halamić, 2014).

- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- ◆ ISO 11885:2007 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.

2.11. MERCURY AND COMPOUNDS

Mercury is a silvery-white metal, liquid at room temperature. The use of Mercury is varied: in measuring techniques (thermostats, pumps etc.), in dental and medical equipment, in the production of insecticides and fungicides, in gold mines, and for the production of caustic soda and chlorine. It comes into the environment (water in particular) from chemical industry waste, by precipitation onto water and soil, through the waste mud, industrial and

SEDIMENT QUALITY LABORATORY PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

household wastes and the pesticides based on mercury. Mercury is highly toxic for humans, plants and animals. Mercury poisoning in people can provoke mutagenic, carcinogenic and teratogenic effects, damage to the immune system, blood vessels and central nervous system, deformation of DNA, reduced reproduction and interference with child growth and development (Alloway, 2013; Šorša and Halamić, 2014).

Mercury determination in soils and sediments is based on ISO 12846:2012 using flameless AAS.

- ◆ ISO 5666:1999 Water quality – Determination of mercury. International Organization for Standardization.
- ◆ ISO 16590:2000 Water quality – Determination of mercury – Methods involving enrichment by amalgamation. International Organization for Standardization.
- ◆ ISO 16772:2004 Soil quality – Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry. International Organization for Standardization.
- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 12846:2012 Water quality – Determination of mercury – Method using atomic absorption spectrometry (AAS) with and without enrichment. International Organization for Standardization.
- ◆ EPA Method 7473:1998 Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- ◆ EPA Method 245.5:1982 The Determination of Mercury in Soils, Sediments and Sludges by Cold Vapor Atomic Absorption Spectroscopy. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.

2.12. PENTACHLOROBENZENE

Pentachlorobenzene is benzene in which five of the hydrogens are replaced by chlorines. It is a persistent organic pollutant. Pentachlorobenzene could be found in the fluids with PCB transformers, in small amounts in the fungicide pentachloronitrobenzene (where it could be an impurity), herbicides, in wood treatment chemicals and by burning organic compounds. It is a persistent and bioaccumulative chemical substance that could have harmful effects on the environment and biological diversity. Assessment of the available data showed the potential carcinogenicity of pentachlorobenzene has not been identified (Giddings et al., 2008).

- ◆ ISO 10382:2002 Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection. International Organization for Standardization.

2.13. POLYAROMATIC HYDROCARBONS (PAH)

Polycyclic aromatic hydrocarbons (PAHs, also *polyaromatic hydrocarbons*) are compounds consisting of multiple aromatic rings of carbon and hydrogen. PAHs occur naturally in coal, crude oil, and gasoline. They are also emitted by burning fossil fuels, waste, and in forest fires. These compounds are poorly soluble in water; they therefore predominantly occur in the solid state, bound to particulate air pollution, soils, or sediments.

Human health effects from environmental exposure to low levels of PAHs are unknown. Large amounts of naphthalene in air can irritate the eyes and respiratory tract. Several of the PAHs are considered to be cancer-causing chemicals (Abdel-Shafy and Mansour, 2016).

- ◆ ISO 13877:1998 Soil quality – Determination of polynuclear aromatic hydrocarbons -- Method using high performance liquid chromatography. International Organization for Standardization.
- ◆ ISO 17993:2002 Water quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction. International Organization for Standardization.
- ◆ EPA Method 8100:1986 Polynuclear Aromatic Hydrocarbons. US Government Printing Office, Washington, DC, USA.

- ◆ ISO 18287:2006 Soil quality – Determination of polycyclic aromatic hydrocarbons (PAH) – Gas chromatographic method with mass spectrometric detection (GC-MS). International Organization for Standardization.
- ◆ EN 16181:2018 Soil, treated biowaste and sludge – Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC). European Standardisation Organisation.

2.14. TRIBUTYLTIN COMPOUNDS (TRIBUTYLTIN-CATION)

Tributyltin (TBT) is a toxic, persistent and bio-accumulative pollutant. This chemical was used as a biocide in boat paint, as slime control in paper mills, disinfection of circulating industrial cooling waters, antifouling agents, and the preservation of wood. Tributyltin is a very important pesticide in marine and freshwaters in Europe. Exposure to humans through dietary intake could affect the blood and liver (Hamwijk et al.; 2005; Antizar-Ladislao, 2008; Lee et al., 2011).

- ◆ EN ISO 23161:2018 Soil quality – Determination of selected organotin compounds. Gas-chromatographic method. International Organization for Standardization.

2.15. DICOFOL

Dicofol is an organochlorine pesticide chemically related to DDT. It is persistent and highly toxic in an aquatic environment (Zhong, 2012). Assessment of dispersion in the environment should take into account the potential of dicofol for long-range transport. Dicofol is used for controlling mites that damage cotton, fruit trees and vegetables. Dicofol exposure to humans could cause neurotoxicity, immune and reproductive effects, and it is possibly carcinogenic (e.g. prostate cancer, leukaemia).

- ◆ DIN 38407-2:1993 German standard methods for the determination of water, waste water and sludge; jointly determinable substances (group F); determination of low volatile halogenated hydrocarbons by gas chromatography. German Institute for Standardisation.

- ◆ ISO 10382:2002 Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection (DIN ISO 10392: 2003-05). International Organization for Standardization.

2.16. PERFLUOROCTANE SULFONIC ACID AND ITS DERIVATIVES (PFOS)

Perfluorooctane sulfonic acid and its derivatives (PFOS) are persistent, resistant to environmental degradation and bio-accumulative organic pollutants. PFOS are used in fire-fighting foams, galvanic baths, in the photochemical industry, as a waterproofing chemical for textile and leather, treatment agents for paper, furniture and carpets. Exposure to PFOS is a human health hazard. The studies report associations between PFOS exposure and high cholesterol and cancers including those of the bladder, colon and prostate (EPA, 2016).

- ◆ DIN 38407-42:2011-03 German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 42: Determination of selected polyfluorinated compounds (PFC) in water – Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction. German Institute for Standardisation.

2.17. QUINOXYFEN

Quinoxifen is protectant fungicide used for the prevention and control of powdery mildew diseases on a variety of crops (Vermeirssen et al., 2017). It is toxic to aquatic life, with long term effects. Exposure to quinoxifen concentrate may cause irritation to the eyes and allergic skin reactions such as rashes and burns. It is advisable not to enter into soil and waterways which contain Quinoxifen.

- ◆ DIN 38407-35:2010-10 German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 35: Determination of selected phenoxyalkyl carbonic acids and further acid plant treatment agents – Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) (F35). German Institute for Standardisation.

2.18. DIOXINS AND DIOXIN-LIKE COMPOUNDS

Dioxins and dioxin-like compounds comprise Polychlorinated dibenzo-p-dioxins (PCDDs), Polychlorinated dibenzofurans (PCDFs), Polychlorinated biphenyls (PCBs) (twelve of them have "dioxin-like" properties). These compounds are extremely persistent. Dioxins occur as by-products in the production of some organochlorines, in the incineration of chlorine-containing substances such as PVC, burning waste, household trash, wood, coal or oil, in the chlorine bleaching of paper, smoking, and from natural sources such as volcanoes and forest fires.

Dioxins can get into the environment by emissions from combustion and by discharged wastewaters from chemical factories. Dioxins are highly toxic and can cause cancer, as well as reproductive, developmental, immune system and hormonal disorders (EPA, 2006).

- ◆ EPA Method 1613:1994 Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- ◆ DIN 38414-24:2000-10 German standard method for the examination of water, waste water and sludge – Sludge and sediments (group 5) – Part 24: Determination of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (S 24). German Institute for Standardisation.
- ◆ ISO 10382:2002 Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection. International Organization for Standardization.

2.19. HEXABROMOCYCLODODECANE (HBCDD)

Hexabromocyclododecane (HBCDD) is a persistent organic pollutant (POP). HBCDD is a high production volume chemical used as a flame retardant, mainly within the polymer and textile industries. HBCDD may influence the developmental and reproductive health of humans. It is potentially dangerous for aquatic organisms.

LC-MS methods are most commonly used, including those where other polluting flame retardants are determined simultaneously (Morris et al., 2006).

- ◆ ISO 22032:2006 Water quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge – Method using extraction and gas-chromatography/mass spectrometry. International Organization for Standardization.

2.20. HEPTACHLOR AND HEPTACHLOR EPOXIDE

Heptachlor was an insecticide used for soil and seed treatment to protect corn and grains from pests. The products with heptachlor are still permitted for fire ant control in power transformers and termite control. Heptachlor could be found in the air as a result of product use, then in food (fish, shellfish and meat) and drinking water. Humans may be affected by inhalation or ingestion which can cause problems with the nervous and gastrointestinal systems and an increased risk of cancer (Thomas et al.; 2012; Zhou et al., 2006).

- ◆ EPA Method 1699:2007 Pesticides in water, soil, sediment, biosolids, and tissue by HRGC/HRMS. EPA-821-R-08-001. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- ◆ ISO 10382:2002 Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection. International Organization for Standardization.

2.21. NICKEL AND ITS COMPOUNDS

Nickel is a trace element with siderophile and chalcophile properties. Nickel and its compounds are broadly used in metallurgy, in the production of magnets, alloys, Ni-Cd batteries, instruments, as a catalyst in hydrogenation and oxidation processes, as paints in the ceramic and glass industries. Anthropogenic input of this metal into the environment is through industrial dust, industrial waste and waste water, as well as by the combustion of fossil fuels. Increased concentrations of nickel in humans may cause genotoxic, neurologic, reproductive and carcinogenic effects. The use of drinking water containing higher amounts of nickel can trigger stomach pains and can damage the kidneys. On the other hand, Nickel deficiency provokes retardation in an animal's growth and in humans disturbances in metabolism (Alloway, 2013).

SEDIMENT QUALITY LABORATORY PROTOCOL FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS

- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma – atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- ◆ ISO 11885. 2007. Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.
- ◆ ISO 18227:2014 Soil quality – Determination of elemental composition by X-ray fluorescence. International Organization for Standardization.
- ◆ ISO 13196:2013 Soil quality – Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument. International Organization for Standardization.

2.22. ARSENIC AND ITS COMPOUNDS

Arsenic is a chalcophile trace element. It is common in association with mercury, antimony and bismuth. This element is used as a component of lead alloys, in leather and fur processing, in pharmaceuticals, the glass industry, for wood protection, the production of photoelectric devices, Pb-acid batteries, and pesticides. Arsenic can impact the environment through mining (for copper, zinc, lead and silver), metallurgical production, by the combustion of coal and use of pesticides in agriculture. Arsenic accumulates in the hair and fingernails and causes changes in the skin, lungs, kidneys, liver, and bladder (cancer) (Alloway, 2013).

- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- ◆ ISO 11885:2007 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.

2.23. ZINC AND ITS COMPOUNDS

Zinc is an oxychalcophile trace element. The main contributors to the total zinc content in stream sediments and soils are the rock parent material and agricultural input (use of zinc-containing fertilisers and agrochemicals). The environmental pollution through atmospheric deposition is caused by mining, zinc and metal production facilities, corrosion of galvanised structures, coal and fuel combustion, waste disposal and incineration. Zinc is an essential trace element in all living systems from bacteria to humans. It is present in metal enzymes and proteins. Generally, toxicity of zinc and most zinc-containing compounds is small. Deficiency of zinc in the soil can cause many diseases, including degenerative diseases, such as neurodegeneration (Alzheimer disease, stroke), diabetes, cancer, and wound healing. Zinc is toxic to humans at high concentrations (Alloway, 2013).

- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- ◆ ISO 11885:2007 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.
- ◆ ISO 18227:2014 Soil quality – Determination of elemental composition by X-ray fluorescence. International Organization for Standardization.
- ◆ ISO 13196:2013 Soil quality – Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument. International Organization for Standardization.

2.24. CHROMIUM AND ITS COMPOUNDS

Chromium is a lithophile trace to minor element. It is mostly used for; steel enabling, production of high temperature materials, galvanization, production of pigments, chemicals and some fertilizers. The environment is affected by chromium pollution from industrial waste waters (diverse paints and methods

of leather processing), degradation of alloys, processes in thermal power plants, and combustion of waste. Chromium is an essential micronutrient for the efficient metabolism of vegetable, animal and human diets. Toxicity of chromium depends on its state (Cr^{3+} is relatively safe while Cr^{2+} and Cr^{6+} are highly toxic). Humans could be exposed to chromium by breathing, consumption food and drink and by skin contact. Health effects include irritation of the nose and stomach, anaemia, breathing difficulties and skin allergies. Longer inhalation of chromium (Cr^{6+}) can cause lung cancer (Shekhawat et al., 2015).

- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- ◆ ISO 11885:2007 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.
- ◆ ISO 18227:2014 Soil quality – Determination of elemental composition by X-ray fluorescence. International Organization for Standardization.
- ◆ ISO 13196:2013 Soil quality – Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument. International Organization for Standardization.

2.25. COPPER AND ITS COMPOUNDS

Copper is a chalcophile trace element associated with other transition elements such as chromium, iron, nickel, cobalt and arsenic. Copper is widely used for the production of water-pipe, copper wires, electromagnets, roof plates, statues, coins, etc. then in agriculture (mineral fertilizers and pesticides) and as a food supplement for poultry and cattle. Emissions in the environment are various, through the processes of melting, industrial dust, fungicides in agriculture, combustion of fossil fuels, cement factories and waste mud. Health problems are expressed by dermal contact as soiling of skin, by eye contact as eye-redness, by inhalation of copper dust as an irritation of the upper respiratory tract and metal fume fever and by ingestion which may cause metallic taste and gastrointestinal irritation (Alloway, 2013).

- ◆ EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- ◆ ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- ◆ ISO 11885:2007 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.
- ◆ ISO 18227:2014 Soil quality – Determination of elemental composition by X-ray fluorescence. International Organization for Standardization.
- ◆ ISO 13196:2013 Soil quality – Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument. International Organization for Standardization.

3. SIEVING AND DRYING

A wet-sieving should be done in the field or if not possible in the reference laboratory. Once the sample is submitted to the laboratory, it must be dried at max. temperature 25-30°C (some compounds need freeze drying). Homogenization of a dried and sieved sample is very important and a homogeneity test must be performed during homogenization. The reference laboratory divides the homogenized sample into three parts: one part remains in the reference laboratory for analysis, the other part is sent to the national analysis laboratory while the third part is archived.

Air-drying here not recommended because of the high risk of pollution. The samples should be dried in an oven at 25-30°C until more or less constant weight. At temperatures >30°C mercury escapes.

For a wet sieved sample fraction <63 µm (wet sieving in the field) and for a subsequent analysis of organic compounds, the freeze-drying of samples is recommended.

Different types of sediments may require different preparation (drying, sieving and homogenization) as described in ISO standards:

- ◆ ISO 5667-15:2009 Water quality – Sampling – Part 15: Guidance on the preservation and handling of sludge and sediment samples (reviewed and confirmed in 2015). International Organization for Standardization.
- ◆ ISO 5667-13:2011 Water quality – Sampling – Part 13: Guidance on sampling of sludges. International Organization for Standardization.

According to recommendation Guidance No. 25 (EC, 2010), all samples must be sieved over 2mm mesh as soon as possible after collection to remove large detritus and benthic organisms. Otherwise, during subsequent sample

handling and processing, biotic material will deteriorate and become part of the sediment sample. Sieving should take place in the laboratory under controlled conditions. Wet sieving is best performed with ambient water. The same water should be reused to prevent changing the equilibrium. The silt and clay could be separated by sieving over a 63µm mesh sieve (fraction <63µm).

Sieves are traditionally made of corrosion-resistant brass (rim and mesh). Stainless steel is preferred for organic analyses. These must not be used for the analysis of trace metals. For trace metals, polymer sieves are recommended (PVC or acrylic rim, with e.g. nylon or polyester mesh) (recommendation Guidance No. 25).

4. SAMPLE STORAGE AND ARCHIVE

The samples are placed in plastic and dark glass bottles and stored in a cool place (usually at 2°C to 8°C). For storage for short periods (up to 24h), cooling at 2°C to 8°C in laboratory refrigerators is acceptable. For sample storage over longer periods (more than a month) it is recommended freezing samples at -20°C (HRN ISO 5667-12:2001, ISO 5667-12:2017, ISO 5667-15:2009 (reviewed and confirmed in 2015)).

All storage methods will affect the sample to some extent, and the choice of preservation technique depends mainly on the objective of the sample collection.

According to recommendation Guidance No. 25 (EC, 2010), some methods for the various analyses may interfere with each other. To avoid this problem, the collected sample volume should be large enough for all analyses and archiving material to be undertaken. Samples can be stored at 4°C for about a week and up to 3 months when frozen at -20°C, if this is allowed according to the specific analytical methods. It is recommended that freezing be avoided since it could change the grain size distribution in the sediment.

5. NORMALIZATION

Numerous impacts on bulk sediment composition, such as particle size fraction, the dilution of contaminants by materials such as quartz or carbonates, the organic matter content and parent material (natural geochemical background) influence the reliable interpretation of the laboratory results. Normalizing could include grain size correction, quartz correction, common normalizers are Al and Li, with some limitations Fe, then organic carbon and trace elements (Cs, Eu, Rb, Sc, Sm, and Th, etc.).

5.1. GRAIN SIZE CORRECTION

Coarser grain fractions dilute the pollution. The fine fraction, especially the clay-silt fraction (<63µm) is suitable for analysis. The first step is sieving to isolate the fine fraction. Some minerals could remain in the fine fraction and it is necessary to make corrections for them. Silica minerals and carbonates naturally contain negligible amounts of heavy metals and therefore dilute the pollution in sediments.

5.2. QUARTZ CORRECTION

The high concentration of the quartz fraction in the sample produces a dilution of the existing contaminants which is known as a „matrix effect“. According to Thomas (1972) the quartz correction could be calculated by the formula: $C_c = (C_o \times 100) / (100 - q_z)$, where C_c is the quartz corrected concentration, C_o is the trace metal observed concentration and q_z is the % of quartz content. The

quartz content could be determined by X-ray diffraction (Till and Spears, 1969) or by the gravimetric determination of total quartz plus feldspar (Trostell and Wynne, 1940).

5.3. AL- AND LI-NORMALIZATION

The content of Al and Li has a significant correlation with heavy metals. Aluminium is one of the most abundant naturally-occurring metals which could be found in the aluminosilicate mineral fraction. It is immobile and has negligible anthropogenic impact. Lithium is a better normalizer for sediment enriched in phyllosilicates.

6. QUALITY CONTROL

The field quality assurance involves a series of steps, procedures, and practise. The quality of data generated in a laboratory depends, to a large degree, on the integrity of the samples that arrive there. Consequently, the field investigator must take the necessary precautions to protect the samples from contamination and deterioration.

There are many sources of contamination; the following are some basic precautions to consider:

- ◆ Sample containers must be cleaned according to recognised methods and certified by the issuing laboratory as ‘contamination free’.
- ◆ Only the recommended type of sample container for each analysis should be used.
- ◆ The inner portion of the sample container and caps must not be touched by anything other than the sample itself.
- ◆ Sample containers must be kept in a clean environment, away from dust, dirt, flames and grime. Containers must be capped at all times and possibly stored in coolers before and after sampling.
- ◆ Petroleum products (e.g., gasoline, oil, exhaust fumes) are prime sources of contamination. Exhaust fumes and cigarette smoke can contaminate samples with lead and other trace elements.
- ◆ Samples must never be permitted to get warm. They should be stored in a cool place, coolers packed with ice packs are recommended.

In addition to the standardised field procedure, field quality control requires the submission of replicate and reference samples. Replicate samples detect heterogeneity, allow the precision of the measurement process to be

estimated, and provide a check that the sample is reproducible. Reference samples are used primarily to document the bias of the analytical (laboratory) process. The frequency of replicate and reference samples should be established in the project design. Reference samples should be submitted to the analysing laboratory with the samples collected in the field.

The laboratory should check during the reception of samples that all the relevant information according to preservation and transport conditions of the sample is provided (ISO 5667-15:2009 -reviewed and confirmed in 2015).

Quality control should be properly ensured in the laboratory using the following recommendations:

- ◆ Proper quality assurance / quality control of method validation by analytical laboratories, routine Internal QC procedures, and independent external QC procedures;
- ◆ The validation of an analytical method, including the determination of measurement reliability, bias, etc., requires the use of certified reference materials;
- ◆ In CIS Guidance No. 19 (EC, 2009), Annex III gives a complete list of sediment certified reference materials (CRM) available for the determination of metals, PAHs and chlorinated pesticides in sediment (no CRM developed for other substances);
- ◆ Internal QC procedures should routinely monitor the performance of analytical methods for example by including duplicate samples or (laboratory) reference materials in analytical batches. The results are evaluated using standard statistical methods, such as Shewhart charts, to ensure that the methods remain under statistical control;
- ◆ The laboratory should regularly participate in external inter-laboratory comparisons.

It is recommended that quality control is carried out in accordance with ISO/IEC 17025:2017. The analytical laboratories had to prove a valid accreditation for the required parameters and analytical methods as well as conforming to ISO/IEC 17025:2017.

- ◆ ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories. International Organization for Standardization and International Electrotechnical Commission.

7. REFERENCES

- Abdel-Shafy, H.I., Mansour, M.S. 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum* 25, 107-123.
- ATSDR 2005. Toxicological Profile for Alpha-, Beta-, Gamma-, and Delta-Hexachlorocyclohexane (Update). Department of Public Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA, U.S, 325p.
- Alloway, B.J. (Ed.) 2013. *Heavy Metals in Soils Trace Metals and Metalloids in Soils and their Bioavailability*. Springer Netherlands, 613p.
- Antizar-Ladislao, B. 2008. Environmental levels, toxicity and human exposure to tributyltin (TBT)-contaminated marine environment. A review. *Environment International* 34, 292-308.
- Barber, J.L., Sweetman, A.J., Van Wijk, D., Jones, K.C. 2005. Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. *Science of the Total Environment* 349, 1-44.
- Danish EPA 2013. Evaluation of health hazards by exposure to Chlorinated paraffins and proposal of a health-based quality criterion for ambient air. Ed. Elsa Nielsen, Ole Ladefoged
- DIN 38407-2:1993 German standard methods for the determination of water, waste water and sludge; jointly determinable substances (group F); determination of low volatile halogenated hydrocarbons by gas chromatography. German Institute for Standardisation.
- DIN 38407-35:2010-10 German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 35: Determination of selected phenoxyalkyl carbonic acids and further acid plant treatment agents – Method using high performance liquid chromatography and mass spectrometric detection (HPLC-MS/MS) (F35). German Institute for Standardisation.

- DIN 38407-42:2011-03 German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 42: Determination of selected polyfluorinated compounds (PFC) in water – Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42). German Institute for Standardisation.
- DIN 38414-24:2000-10 German standard method for the examination of water, waste water and sludge – Sludge and sediments (group 5) – Part 24: Determination of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans 8PCDF) (S 24). German Institute for Standardisation.
- EC 2009. Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document No. 19 Guidance on Surface Water Chemical Monitoring under The Water Framework Directive Luxembourg: Office for Official Publications of the European Communities.
- EC 2010 Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Guidance Document No. 25 Guidance on chemical monitoring of sediment and biota under the Water Framework Directive Luxembourg: Office for Official Publications of the European Communities.
- EC 2018 Common Implementation Strategy for the Water Framework Directive (2000/60/EC): Technical Guidance for deriving Environmental Quality Standards, Guidance Document No. 27 Updated version 2018.
- Emsbo-Mattingly, S.D., Litman, E. 2016. Polycyclic aromatic hydrocarbon homolog and isomer fingerprinting. In: Stout, S.A., Wang, Z. (Eds.). Standard Handbook Oil Spill Environmental Forensics. Elsevier, 255-312.
- EN ISO 15009:2016 Soil quality – Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons – Purge-and-trap method with thermal desorption. European Standardisation Organisation and International Organization for Standardization.
- EN ISO 23161:2018 Soil quality – Determination of selected organotin compounds. Gas-chromatographic method. European Standardisation Organisation and International Organization for Standardization.
- EN 16171:2016 Sludge, treated bio-waste and soil. Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). European Standardisation Organisation.
- EN 16181:2018 Soil, treated biowaste and sludge – Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC). European Standardisation Organisation.
- EPA. 2006. An Inventory Of Sources And Environmental Releases Of Dioxin-Like Compounds In The U.S. For The Years 1987, 1995, And 2000 (Final,

**SEDIMENT QUALITY LABORATORY PROTOCOL
FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS**

- Nov 2006). U.S. Environmental Protection Agency, Washington, DC, EPA/600/P-03/002F.
- EPA 2016. Health Effects Support Document for Perfluorooctane Sulfonate (PFOS). U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA, 245p.
- EPA 2017 Technical Fact Sheet – Polybrominated Diphenyl Ethers (PBDEs). U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA, 5p.
- EPA Method 1613:1994 Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- EPA Method 1614:2007 Brominated Diphenyl Ethers in water soil, sediment and tissue by HRGC/HRMS. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- EPA Method 1625:1989 Semivolatile Organic Compounds by Isotope Dilution GCMS. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- EPA Method 1699:2007 Pesticides in water, soil, sediment, biosolids, and tissue by HRGC/HRMS. EPA-821-R-08-001. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- EPA Method 7473:1998 Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry. U.S. Environmental Protection Agency, Office of Water, Washington, DC, USA.
- EPA Method 8100:1986 Polynuclear Aromatic Hydrocarbons. US Government Printing Office, Washington, DC, USA.
- Fatta, D., Michael, C., Canna-Michaelidou, St., Christodoulidou, M., Kythreotou, N., Vasquez, M. 2007. Pesticides, volatile and semivolatile organic compounds in the inland surface waters of Cyprus. *Desalination* 215, 223-236.
- Faust, R.A., 1991. Toxicity Summary for Anthracene. Oak Ridge National Laboratory, Chemical Hazard Evaluation Group. Oak Ridge.
- Giddings, M., Meek, M.E., Gomes, R. 2008. Pentachlorobenzene: Evaluation of risks to health from environmental exposure in Canada. *Journal of Environmental Science and Health, Part C, Environmental Carcinogenesis and Ecotoxicology Reviews*. 12 (2), 435-441.
- Hamwijk, C., Schouten, A., Foekema, E.M., Ravensberg, J.C., Collombon, M.T., Schmidt, K., Kugler, M. 2005. Monitoring of the booster biocide dichlofluanid in water and marine sediment of Greek marinas. *Chemosphere* 60, 1316-1324.
- HRN ISO 5667-12:2001 Water quality – Sampling – Part 12: Guidance for bottom sediment sampling (ISO 5667-12:1995). Croatian Standards Institute.

- ICPDR 2003. List of Priority Substances for the Danube River Basin. International Commission for the Protection of the Danube River, 4p.
- ISO/IEC 17025:2017 General requirements for the competence of testing and calibration laboratories. International Organization for Standardization and International Electrotechnical Commission.
- ISO 5666:1999 Water quality – Determination of mercury. International Organization for Standardization.
- ISO 5667-12:2017 Water quality – Sampling – Part 12: Guidance on sampling of bottom sediments from rivers, lakes and estuarine areas. International Organization for Standardization.
- ISO 5667-13:2011 Water quality – Sampling – Part 13: Guidance on sampling of sludges. International Organization for Standardization.
- ISO 5667-15:2009 Water quality – Sampling – Part 15: Guidance on the preservation and handling of sludge and sediment samples (reviewed and confirmed in 2015). International Organization for Standardization.
- ISO 10382:2002 Soil quality – Determination of organochlorine pesticides and polychlorinated biphenyls – Gas-chromatographic method with electron capture detection. International Organization for Standardization.
- ISO 11885:2007 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). International Organization for Standardization.
- ISO 12846:2012 Water quality – Determination of mercury – Method using atomic absorption spectrometry (AAS) with and without enrichment. International Organization for Standardization.
- ISO 13196:2013 Soil quality – Screening soils for selected elements by energy-dispersive X-ray fluorescence spectrometry using a handheld or portable instrument. International Organization for Standardization.
- ISO 13877:1998 Soil quality – Determination of polynuclear aromatic hydrocarbons -- Method using high performance liquid chromatography. International Organization for Standardization.
- ISO 13913:2014 Soil quality – Determination of selected phthalates using capillary gas chromatography with mass spectrometric detection (GC/MS). International Organization for Standardization.
- ISO 15753:2006 Animal and vegetable fats and oils – Determination of polycyclic aromatic hydrocarbons. International Organization for Standardization.
- ISO 16590:2000 Water quality – Determination of mercury – Methods involving enrichment by amalgamation. International Organization for Standardization.

**SEDIMENT QUALITY LABORATORY PROTOCOL
FOR HAZARDOUS SUBSTANCES IN SURFACE WATERS**

- ISO 16772:2004 Soil quality – Determination of mercury in *aqua regia* soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry. International Organization for Standardization.
- ISO 17993:2002 Water quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction. International Organization for Standardization.
- ISO 18227:2014 Soil quality – Determination of elemental composition by X-ray fluorescence. International Organization for Standardization.
- ISO 18287:2006 Soil quality – Determination of polycyclic aromatic hydrocarbons (PAH) – Gas chromatographic method with mass spectrometric detection (GC-MS). International Organization for Standardization.
- ISO 22032:2006 Water quality – Determination of selected polybrominated diphenyl ethers in sediment and sewage sludge – Method using extraction and gas chromatography/mass spectrometry. International Organization for Standardization.
- ISO 22036:2008 Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma – atomic emission spectrometry (ICP-AES). International Organization for Standardization.
- Lee, S., Chung, J., Won, H., Lee, D., Lee, Y.-W. 2011. Analysis of antifouling agents after regulation of tributyltin compounds in Korea. *Journal of Hazardous Materials* 185, 1318-1325.
- Macgregor, K., Oliver, I.W., Harris, L., Ridgway, I.M. 2010. Persistent organic pollutants (PCB, DDT, HCH, HCB & BDE) in eels (*Anguilla anguilla*) in Scotland: Current levels and temporal trends. *Environmental Pollution* 158, 2402-2411.
- Morris, S., Bersuder, P., Allchin, C.R., Zegers, B. 2006. Determination of the brominated flame retardant, hexabromocyclododecane, in sediments and biota by liquid chromatography-electrospray ionisation mass spectrometry. *Trends in Analytical Chemistry* 25, 343-349.
- Shekhawat, K., Chatterjee, S., Joshi, B. 2015. Chromium Toxicity and its Health Hazards. *International Journal of Advanced Research*. 3 (7), 167-172.
- Šorša, A., Halamić, J. 2014. *Geochemical Atlas of Sisak*. Public Library Vlado Gotovac Sisak, City Museum Sisak and Croatian Geological Survey, Sisak-Zagreb, 200p, (In Croatian and in English).
- Thomas, M., Lazartigues, A., Banas, D., Brun-Bellut, J., Feidt, C. 2012. Organochlorine pesticides and polychlorinated biphenyls in sediments and fish from fresh water cultured fish ponds in different agricultural contexts in north-eastern France. *Ecotoxicology and Environmental Safety* 77, 35-44.
- Thomas, R.L. 1972. The distribution of mercury in the sediments of Lake Ontario. *Canadian Journal of Earth Sciences* 9 (6), 636-651.

- Tickner, J.A., Schettler, T., Guidotti, T., McCally, M., Rossi, M. 2001. Health risks posed by use of Di-2-ethylhexyl phthalate (DEHP) in PVC medical devices: A critical review. *American Journal of industrial medicine* 39 (1), 100-111.
- Till, R., Spears, D.A. 1969. The determination of quartz in sedimentary rocks using an X-ray diffraction method. *Clays and Clay Minerals* 17, 323-327.
- Trostell, L.J., Wynne, D.J. 1940. Determination of quartz (free silica) in refractory clays. *Journal of the American Ceramic Society* 23, 18-22.
- Vermeirssen, E., Kase, R., Werner, I. 2017. The occurrence of 12 EU priority substances in Swiss surface waters and biota – a review of monitoring data. Ecotox Centre, Swiss Centre for Applied Ecotoxicology Eawag-EPFL. 44 p.
- Zhou, R., Zhu, L., Yang, K., Chen, Y. 2006. Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. *Journal of Hazardous Materials* 137, 68-75.

CONTACT DETAILS

Contact to project leader partner:

Geological Survey of Slovenia, Department for Mineral
Resources and Environmental Geochemistry
Dimiceva ulica 14, SI-1000 Ljubljana
Tel: +386 (0)1 2809 764 | Fax: +386 (0)1 2809 753
www.geo-zs.si

Project manager: Jasminka Alijagic, SI-GEOZS
Mob: +386 51 208 693 | jasminka.alijagic@geo-zs.si

Scientific coordinator: Gyozo Jordan, HU-SZIE
Mob: +36 30 728 4060 | gyozojordan@gmail.com

Contact to authors: Ajka Šorša, HR-HGI-CGS
Tel: +385 1 6160 739 ajka.sorsa@hgi-cgs.hr
Ana Čaić Janković, HR-HGI-CGS
Tel: +385 1 6160 732 acaic@hgi-cgs.hr

OTHER INFORMATION

Project title:

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

Partnership of the project SIMONA:

The SIMONA partnership has 17 full partners (11 ERDF, 4 IPA
and 2 ENI) and 12 associated partners (ASPs) from 13 Coun-
tries, which is a balanced and strong representation of almost
the whole Danube River Basin.

Project duration:

01/06/2018 - 31/05/2021

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

For further information on the project, partnership and
the Danube Transnational Programme:
www.interreg-danube.eu/simona



FIND SIMONA PROTOCOLS ON THE WEBSITE!



Country	Austria		Bulgaria		Croatia		Federation BH		Hungary		Moldova		Montenegro		Republic of Srpska (B&H)		Romania		Slovakia		Slovenia		Ukraina	
	HSS from agricultural activities	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	
1. Alachlor				VIM 1015/2010 (w)					EPA 8270D:2007	GC/MSD (SIM)					EPA 525.2:1994		ISO 10382:2002	GC_ECD						
2. Atrazine				VIM 1015/2010(w)					EPA 8141 A:1994						EPA 525.2:1994		ISO 10382:2002	GC_ECD						
3. Chlorfenvinphos									MSZ EN ISO 10695:2000	GC-MS					EPA 525.2:1994		ISO 10382:2002	GC_ECD						
4. Chlorpyrifos (Chlorpyrifos-ethyl)									EPA 8270D:2007	GC/MSD (SIM)					EPA 525.2:1994		ISO 10382:2002	GC_ECD						
5. Cyclo-diene pesticides									EPA 8141 A:1994															
6. Total DDT				VIM 4006/2010 (1,2,3,5) (s)					EPA 8270D:2007	GC/MSD (SIM)					EPA 525.2:1994		ISO 10382:2002	GC_ECD						
7. Diuron				Not analyzed					MSZ EN ISO 6468:1998	GC/MSD (SIM)					EPA 508.1:1994		ISO 10382:2002	GC_ECD						
8. Endosulfan				VIM 1014/2010 (w)					EPA 8270D:2007						BAS EN ISO 11369:2002									
9. Hexachlorobenzene				VIM 1014/2010 (w)					EPA 8270D:2007	GC/MSD (SIM)					EPA 508.1:1994									
10. Hexachlorociklohexene				VIM 4006/2010 (1,2,3,5) (s)					MSZ EN ISO 10695:2000	GC-MS					EPA 525.2:1994		ISO 15009:2016	PT						
11. Isoproturon				VIM 1014/2010 (w)					MSZ EN ISO 10695:2000	GC-MS														
12. Pentachlorophenol				Not analyzed					EPA 8270D:2007	GC/MSD (SIM)														
13. Simazine				VIM 1015/2010 (w)					EPA 8151 A:1996	GC/MSD (SIM)														
14. Trifluralin				VIM 1015/2010 (w)					MSZ EN ISO 10695:2000	GC-MS														
15. Dicofof									MSZ EN ISO 10695:2000	GC-MS														
16. Quinoxifen																								
17. Aclonifen																								
18. Bifenox																								
19. Cybutryne																								
20. Cypermethrin																								
21. Dichlorvos																								
22. Heptachlor and heptachlor epoxide									MSZ EN ISO 6468:1998	GC/MSD (SIM)														
23. Terbutryn									EPA 8270D:2007	GC/MSD (SIM)														
24. Perfluorooctane sulfonic acid and its derivatives																								
25. Anthracene				ISO 18287 (s)																				
26. Benzene				BSS EN ISO 15680 (w)																				
27. Fluoranthene				VIM 1016/2010 (w)					MSZ EN ISO 6468:1998	GC-MSD (SIM)														
28. Hexachloro-butadiene				ISO 18287 (s)					EPA 8270D:2007															
29. Naphthalene				BSS EN ISO 15680 (w)					MSZ 1484-6:2003 (w)	GC-MS														
30. Pentachlorobenzene				VIM 1016/2010 (w)					MSZ 21470-84:2002 (s)	GC-MS														
31. Benzo(a)pyrene				ISO 18287 (s)					MSZ 1484-6:2003 (w)	GC-MS														
32. Benzo(b)fluoranthene				VIM 1014/2010 (w)					MSZ 21470-84:2002 (s)	GC-MS														
33. Benzo(k)fluoranthene				VIM 1016/2010 (w)					MSZ 1484-6:2003 (w)	GC-MS														
34. Benzo(g,h,i)-perylene				ISO 18287 (s)					MSZ 21470-84:2002 (s)	GC-MS														
35. Indeno(1,2,3-cd)-pyrene				VIM 1016/2010 (w)					MSZ 1484-6:2003 (w)	GC-MS														
36. Tributyltin compounds (Tributyltin-cation)				ISO 18287 (s)					MSZ 21470-84:2002 (s)	GC-MS														
37. Dioxins and dioxin-like compounds				Not analyzed																				
38. PCB (total)				VIM 1016/2010 (w)					MSZ 1484-6:2003 (w)	GC-MS														
39. PAH (total)				ISO 18287 (s)					MSZ 21470-84:2002 (s)	GC-MSD (SIM)														

Hydrochemical analyses are standardized by Austrian norms: ÖNORM M 6616, DIN 38404, DIN EN ISO 17294, DIN EN ISO 10304

GC-MS

All compounds are mentioned, but there are no norms for particular compound.

GC-MS, GC-MS/MS and LC-MS/MS.

No data.

No data.

Hazardous substances are analyzed in external laboratories as follows:
 1. Institute of Hydro-meteorology and seismology of Montenegro, <http://www.meteo.co.me/ekologija/Akreditacija.pdf>
 2. Institute for Public Health from Podgorica,
 3. Center for Eco-Toxicology Research from Podgorica, - http://eng.cet.me/?page_id=3610

Almost all compounds are mentioned, but there are no norms for particular compound.

GC-ECD, HPLC-UV, GC-MS

For the analysis of water, sediment and biota samples, standardized analysis methods are validated and documented in accordance with ISO / IEC 17025 and meet the minimum efficiency criteria for the analytical methods set out in Article 16 of the Surface Water Surveillance Regulation.

DSTU ISO 6468-2002

DSTU ISO 17993: 2008

PT: Purge-and-trap method with thermal desorption



Country	Austria		Bulgaria		Croatia		Federation BH		Hungary		Moldova		Montenegro		Republic of Srpska (B&H)		Romania		Slovakia		Slovenia		Ukraina			
	HSSs from industrial activities	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods			
1. Brominated diphenylether	Hydrochemical analyses are standardized by Austrian norms: ÖNORM M 6616, DIN 38404, DIN EN ISO 17294, DIN 38409, DIN EN ISO 10304			Not analyzed	All compounds are mentioned, but there are no norms for particular compound.								Hazardous substances are analyzed in external laboratories as follows: 1. Institute of Hydrometeorology and seismology of Montenegro, http://www.meteo.me/ekologija/Akreditacija.pdf 2. Institute for Public Health from Podgorica, http://eng.cet.me/?page_id=3610 3. Center for Eco-Toxicology Research from Podgorica, http://eng.cet.me/?page_id=3610													
2. Carbon-tetrachloride				BSS EN ISO 15680						MSZ 1484-7:2009 MSZ 1484-4:1998 (visszavont)	GC-FID	EPA Method 524.3		GC-MS					ISO 15009:2016	PT						
3. C10-13 Chloroalkanes				Not analyzed						MSZ 1484-7:2009 MSZ 1484-4:1998 (visszavont)	GC-FID									ISO 16558-1:2015	gas chromatography (static headspace method) GC-FID					
4. 1,2-Dichloroethane				BSS EN ISO 15680						MSZ 1484-5:1998 3.2. szakasz	HS-GC-ECD HS-GC/MSD (SIM)	EPA Method 524.3		GC-MS		StaticHeadspace/GC/ Theory &Practice				ISO 15009:2016	PT					
5. Dichloromethane				BSS EN ISO 15680						MSZ 1484-5:1998 3.2. szakasz	HS-GC-ECD	EPA Method 524.3		GC-MS		StaticHeadspace/GC/ Theory &Practice				ISO 15009:2016	PT					
6. Di(2-ethylhexyl)-phthalate (DEHP)				Not analyzed												EPA 525.2:1994				ISO 13913:2014	GC-MS					
7. Nonylphenol (4-Nonylphenol)				BSS EN ISO 18857-1		GC-MS						ISO/TS 13907:2012 ISO 14154:2005 ISO/DTS 17182		GC-MS GC-ECD GC-MS		EPA 8040				ISO/TS 13907:2012	GC-MS					
8. Octylphenol ((4-(1,1',3,3'-tetramethylbutyl)-phenol))				BSS EN ISO 18857-1								ISO/TS 13907:2012 ISO 14154:2005 ISO/DTS 17182		GC-MS GC-ECD GC-MS		EPA 8040				ISO/TS 13907:2012	GC-MS					
9. Tetrachloro-ethylene				BSS EN ISO 15680						MSZ 1484-5:1998 3.2. szakasz	HS-GC-ECD	EPA Method 524.3		GC-MS						ISO 15009:2016	PT					
10. Trichloro-ethylene				BSS EN ISO 15680						MSZ 1484-5:1998 3.2. szakasz	HS-GC-ECD	EPA Method 524.3		GC-MS						ISO 15009:2016	PT					
11. Trichloro-benzenes				BSS EN ISO 15680								EPA Method 8015C		GC						ISO 6468:1996	Gas chromatographic method after liquid-liquid extraction					
12. Trichloro-methane				BSS EN ISO 15680						MSZ 1484-5:1998 3.2. szakasz	HS-GC/ECD	EPA Method 524.3		GC-MS		StaticHeadspace/GC/ Theory &Practice				ISO 15009:2016	PT					
13. Hexabromocyclododecane (HBCDD)																										

PT: Purge-and-trap method with thermal desorption



Country / Heavy metals	Cadmium (Cd) and its compounds		Lead (Pb) and its compounds		Mercury (Hg) and its compounds		Nickel (Ni) and its compounds		Arsenic (As) and its compounds		Zinc (Zn) and its compounds		Chromium (Cr) and its compounds		Copper (Cu) and its compounds	
	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods	Procedures (norms)	Methods
1. Austria	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF	DIN EN ISO 17294-2	ICP-MS 7500 (Agilent) XRF
2. Bulgaria	BSS EN ISO 17294/2004	ICP-MS (water)	BSS EN ISO 17294/2004	ICP-MS (water)	VIM 1012/2010 (1 2.3.4)	ICP-MS (water)	BSS EN ISO 17294/2004	Flame AAS (water)	BSS EN ISO 17294/2004	ICP-MS (water)	BSS EN ISO 17294/2004	ICP-MS (water)	Cr _{total} BSS EN ISO 17294/2004; BSS 17.1.4.17 (1,2,3)	ICP-MS (water)	BSS EN ISO 17294/2004	ICP-MS (water)
	BSS EN ISO 17294/2004	Flame AAS (water)	BSS EN ISO 17294/2004	Flame AAS (water)	VIM 1012/2010 (1 2.3.4)	ICP-MS (water)	BSS EN ISO 17294/2004	Flame AAS (water)	BSS EN ISO 17294/2004	Flame AAS (water)	BSS EN ISO 17294/2004	Flame AAS (water)	BSS EN ISO 17294/2004; BSS 17.1.4.17 (1,2,3)	Flame AAS (water)	BSS EN ISO 17294/2004	Flame AAS (water)
In soils/ sediments: Hg, As, Cd, Cr, Cu, Ni, Pb, Zn, Co according to ISO 11047																
3. Croatia		ICP-MS (water)		ICP-MS (water)	EPA Method 245.7- Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry	Atomic Fluorescence Spectrometry		ICP-MS (water)		ICP-MS (water)		ICP-MS (water)		ICP-MS (water)		ICP-MS (water)
		ICP-MS (sediment)		ICP-MS (sediment)				ICP-MS (sediment)		ICP-MS (sediment)		ICP-MS (sediment)		ICP-MS (sediment)		ICP-MS (sediment)
4. Federation BH (B&H)					Water: USEPA-Method 245.1. Sediments: EPA Method 7473 -U.S. EPA Method 245.5(CVAAS) -ASTM D6722 -thermal decomposition * -ASTM D6414-99 (wet digestion)											
5. Hungary	Sediment: MSZ 21470-50:2006 4.2. szakasz 4.1. szakasz	Sediment: AAS ETA ICP-OES	Sediment: MSZ 21470-50:2006 4.2. szakasz 4.1. szakasz	Sediment: AAS láng ICP-OES	Sediment: MSZ 21470-50:2006 4.2.4.4. szakasz	Sediment: AAS	Sediment: MSZ 21470-50:2006 4.2. szakasz 4.1. szakasz	Sediment: AAS láng ICP-OES	Sediment: MSZ 21470-50:2006 4.2. szakasz 4.1. szakasz	Sediment: AAS ETA ICP-OES	Sediment: MSZ 21470-50:2006 4.2. szakasz 4.1. szakasz	Sediment: AAS láng ICP-OES	MSZ EN ISO 18412: 2007 Sediment: MSZ 21470-50:2006 4.2. szakasz 4.1. szakasz	photometric method Sediment: AAS láng ICP-OES	Sediment: MSZ 21470-50:2006 4.2. szakasz 4.1. szakasz	Sediment: AAS láng ICP-OES
6. Moldova	SM SR ISO 11047:2006	THGA-AAS (soil, sediments) Flame AAS (soil, sediments)	SM SR ISO 11047:2006	THGA-AAS (soil, sediments) Flame AAS (soil, sediments)			SM SR ISO 11047:2006	THGA-AAS (soil, sediments) Flame AAS (soil, sediments)	SM GOST R 51309:2006 SR EN ISO 5961:2002 ISO 20280:2007 (solid samples)	THGA-AAS (water)	SM SR ISO 11047:2006	Flame AAS (soil, sediments)	SM SR ISO 11047:2006	THGA-AAS (soil, sediments) Flame AAS (soil, sediments)	SM SR ISO 11047:2006	THGA-AAS (soil, sediments) Flame AAS (soil, sediments)
	SM GOST R 51309:2006 SR EN ISO 5961:2002 SM SR ISO 8288:2006 SR EN 1233:2003 SR ISO 9174-98	THGA-AAS (water) Flame AAS (water)	SM GOST R 51309:2006 SR EN ISO 5961:2002 SM SR ISO 8288:2006 SR EN 1233:2003 SR ISO 9174-98	THGA-AAS (water) Flame AAS (water)				SM GOST R 51309:2006 SR EN ISO 5961:2002 SM SR ISO 8288:2006 SR EN 1233:2003 SR ISO 9174-98	THGA-AAS (water) Flame AAS (water)		THGA-AAS (water)	SM SR ISO 11047:2006	Flame AAS (water)	SM GOST R 51309:2006 SR EN ISO 5961:2002 SM SR ISO 8288:2006 SR EN 1233:2003 SR ISO 9174-98	THGA-AAS (water) Flame AAS (water)	SM GOST R 51309:2006 SR EN ISO 5961:2002 SM SR ISO 8288:2006 SR EN 1233:2003 SR ISO 9174-98
7. Montenegro					National: EPA7473 (water/sediments) International (water): USEPA-Method 245.1. Sediments: EPA Method 7473 -U.S. EPA Method 245.5(CVAAS) -ASTM D6722 -thermal decomposition * -ASTM D6414-99 (wet digestion)	direct mercury analyzer DMA										
All water quality measurements are carried out in the Water Quality Laboratory, which is accredited for sampling and chemical analysis in accordance with MEST EN ISO / IEC 17025: 2011 (Institute for Hydrometeorology and Seismology of Montenegro). Dangerous substances are analyzed in external laboratories as follows: 1. Institute of Hydrometeorology and Seismology of Montenegro, http://www.meteo.co.me/ekologija/Akreditacija.pdf 2. Institute for Public Health from Podgorica, 3. Center for Eco-Toxicology Research from Podgorica, - http://en.ceti.me/?page_id=3610																
8. Republic of Srpska (B&H)	Standard Methods 3113-B, issued by APHA-AWWA-WEF 2005	Shimadzu FAAS AA6300	Standard Methods 3113-B, issued by APHA-AWWA-WEF 2005	Shimadzu FAAS AA6300	AMA 254, Advanced Mercury Analyser, Operating Manual	AMA 254	Standard Methods 3113-B, issued by APHA-AWWA-WEF 2005	Shimadzu FAAS AA6300	Standard Methods 3113-B, APHA-AWWA-WEF 2005	Shimadzu FAAS AA6300	Standard Methods 3113-B, APHA-AWWA-WEF 2005	Shimadzu FAAS AA6300	BAS ISO 9174	Shimadzu FAAS AA6300	Standard Methods 3113-B, APHA-AWWA-WEF 2005	Shimadzu FAAS AA6300
9. Romania	Solid (S): ISO 11047:1998	Flame and electrothermal atomic absorption spectrometric methods	S: ISO 11047:1998	Flame and electrothermal atomic absorption spectrometric methods	S: ISO/TS 16727:2013 ISO 16772:2004	Flame and electrothermal atomic absorption spectrometric methods	S: ISO 11047:1998	Flame and electrothermal atomic absorption spectrometric methods	S: ISO 20280:2007	Flame and electrothermal atomic absorption spectrometric	S: ISO 11047:1998	Flame and electrothermal atomic absorption spectrometric methods	S: ISO 11047:1998 ISO 15192:2010 (Cr VI) ISO/TR 18105:2014 (Cr VI)	Flame and electrothermal atomic absorption spectrometric methods	S: ISO 11047:1998	Flame and electrothermal atomic absorption spectrometric methods
	Water (W): ISO 5961:1994 ISO 8288:1986		W: ISO 8288:1986		W: ISO 12846:2012 ISO 17852:2006		W: ISO 8288:1986		W: ISO 17378-1:2014 ISO 17378-2:2014 ISO/TS 19620:2018 (HPL-ICP-MS or HG-AFS)	HPL-ICP-MS or HG-AFS	W: ISO 8288:1986		W: ISO 9174:1998 ISO 11083:1994 (Cr VI) ISO 18412:2005 (Cr VI)		W: ISO 8288:1986	
10. Slovakia		Water: ICP-OES Agilent ICP-MS Agilent/ Brucker		Water: ICP-OES Agilent ICP-MS Agilent/ Brucker		Water: AAS AMA- 254		Water: ICP-OES Agilent ICP-MS Agilent/ Brucker		Water: ICP-OES Agilent/ Brucker		Water: ICP-OES Agilent ICP-MS Agilent/ Brucker		Water: Cr ICP-OES Agilent ICP-MS Agilent/ Brucker Cr ⁶⁺ spectrophotometric method		Water: ICP-OES Agilent ICP-MS Agilent/ Brucker
		Solid: XRF ICP-MS Agilent/ Brucker		Solid: XRF ICP-MS Agilent/ Brucker		Solid: AAS AMA- 254		Solid: XRF ICP-MS Agilent/ Brucker		Solid: ICP-MS Agilent/ Brucker XRF		Solid: XRF		Solid: Cr XRF ICP-MS Agilent/ Brucker Cr ⁶⁺ ICP-OES Agilent		Solid: XRF ICP-MS Agilent/ Brucker
11. Slovenia	For the analysis of water, sediment and biota samples, standardized analysis methods are validated and documented in accordance with ISO / IEC 17025 and meet the minimum efficiency criteria for the analytical methods set out in Article 16 of the Surface Water Surveillance Regulation.															
12. Ukraina	DSTU ISO 15586: 2012; ISO 15586: 2003, IDT	AAS-ETA; AAS-Flame, Spectrophotometric	DSTU ISO 15586: 2012; ISO 15586: 2003, IDT	AAS-ETA; AAS-Flame, Spectrophotometric	DSTU ISO016772: 2005 (ISO 16772: 2004, IDT)	AAS Coldvapors	DSTU ISO 15586: 2012; ISO 15586: 2003, IDT	AAS-ETA; AAS-Flame, Spectrophotometric	DSTU ISO 15586: 2012; ISO 15586: 2003, IDT	AAS-ETA; AAS-Flame, Spectrophotometric	DSTU ISO 15586: 2012; ISO 15586: 2003, IDT	AAS-ETA; AAS-Flame, Spectrophotometric	DSTU ISO 15586: 2012; ISO 15586: 2003, IDT	AAS-ETA; AAS-Flame, Spectrophotometric	DSTU ISO 15586: 2012; ISO 15586: 2003, IDT	AAS-ETA; AAS-Flame, Spectrophotometric



An overview of the laboratory Quality Control for analysis of priority substances (PSs) in DTP countries
Appendix 4 of the SIMONA Sediment quality Laboratory protocol

Author: Ana Čaić Janković, Croatian Geological Survey

	Country	Quality Assurance/Quality Control (accuracy and precision check...)
1.	Austria	No data.
2.	Bulgaria	BS EN ISO/IEC 17025-General requirements for competence in testing and calibration from EA BAS. - http://eea.government.bg/en/nsmos/index.html
3.	Croatia	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. ISO / IEC 17025 (It could be consolidate all quality with this norm.)
4.	Federation BH (B&H)	No data.
5.	Hungary	ISO / IEC 17025
6.	Moldova	1. SM SR ISO 5725:1-2002. Exactitatea (justețea și fidelitatea) metodelor de măsurare și a rezultatelor măsurărilor. Partea 1. Principii generale și definiții 2. ISO 8466:1990 Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics. 3. ISO 8466:2001 Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second order calibration functions. 4. ISO 11843-2:2000 Capability of detection — Part 2: Methodology in the linear calibration case 5. EURACHEM. Quantifying Uncertainty in Analytical Measurement. LGC, 1995. ISBN 0-948926-08-2. 6. Mandel J., The statistical analysis of experimental data, Interscience Publ., J. Wiley & Sons,(1964), New York 7. 2007 ALACC Guide "How to meet ISO 17025 requirements for method verification" 8. Test methodic validation. CTB 1436-2004. Gosstandard, Minsk, 2004 (in Russian). 9. K. Doerfeli. The statistics in analytical chemistry. "Mir", 1969 (in Russian). 10. A.G. Orlov. Calculation methods in quantitative spectral analysis."Nedra", 1977 (in Russian).
7.	Montenegro	No data.
8.	Republic of Srpska (B&H)	ISO / IEC 1702
9.	Romania	No data.
10.	Slovakia	Accuracy was expressed by average yield for individual analytes of ten repeated measurements of two calibration points. Accuracy represents the average yield calculated from the individual measurements by comparing the average of the measured values with the reference value. Precision of the calibration points for each analyte was expressed by the standard deviation under the repeatability conditions, respectively relative standard deviation of repeatability.
11.	Slovenia	ISO / IEC 17025
12.	Ukraine	JMA 73.1-41-08.00.01: 2004