First research of the contamination of the sediments from Kakhovka reservoir

Brief evaluation of chemical analyses of sediments from Dnipro river and soil samples from Zaporizhzhia region, Ukraine

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Content

Abbreviations

BDS - BioDetection Systems

BEQ - Bioanalytical Equivalent Quantity

BFRs - Brominated Flame Retardants

DBDPE - Decabromodiphenyl Ethane

DDD - Dichlorodiphenyldichloroethane

DDE - Dichlorodiphenyldichloroethylene

DDT - Dichlorodiphenyltrichloroethane

dl-PCBs - Dioxin-Like Polychlorinated Biphenyls

dm – dry matter

DMSO - Dimethyl Sulfoxide

DP - Dechlorane Plus

ECF: Electrochemical Fluorination

et al. - Et alia

Fig. - Figure

HBBz - Hexabromobenzene

HBCDs - Hexabromocyclododecanes

HCB - Hexachlorobenzene

HCBD - Hexachlorobutadiene

HCH - Hexachlorocyclohexane

IARC - International Agency for Research on Cancer

LOQ - Limit of Quantification

MCCPs - Medium-Chain Chlorinated Paraffins

MS - Mass Spectrometry

NBFRs - Novel Brominated Flame Retardants

NECs - Non-Polar Extractable Compounds

NGO - Non-Governmental Organization

OCPs - Organochlorine Pesticide Residues

PAHs - Polycyclic Aromatic Hydrocarbons

PBDEs - Polybrominated Diphenyl Ethers

PCBs - Polychlorinated Biphenyls

PCDD/Fs - Polychlorinated Dibenzo-p-dioxins and Dibenzofurans

PCNs - Polychlorinated Naphthalenes

PeCB - Pentachlorobenzene

PFASs - Per- and Polyfluoroalkyl Substances

PFHxS - Perfluorohexane Sulfonate

PFOA - Perfluorooctanic Acid

PFOS - Perfluorooctanesulfonic Acid

POPs - Persistent Organic Pollutants

SCCPs - Short-Chain Chlorinated Paraffins

TEQ - Toxic Equivalent Quantity

USEPA - United States Environmental Protection Agency

WHO - World Health Organization

1 Introduction

This report is part of a larger project, Clean Air for Ukraine (https://cleanair.org.ua/) which is an international long term programme established in 2017 in Ukraine by the Czech NGO Arnika in cooperation with the Ukrainian partner organisations Free Arduino (IvanoFrankivsk) and Green World (Dnipro). The programme has been focusing on and implementing in the main, activities related to industrial air pollution but since February 2022, also to the environmental damage caused by the war (Angurets et al. 2023; Skalsky et al. 2023). Since the very beginning of the war, Ukraine began to record the damage caused by the Russia. Preliminary monitoring of environmental impact shows substantial damage to urban and rural environments across a wide geographic area. Numerous incidents have caused serious pollution to air, water and soil and have seriously damaged many ecosystems. Extensive field assessment work is, and will be required, to evaluate the exact level of environmental damage and to define the recovery requirements. The remediation of the environmental consequences is crucial not only for the security of Ukrainian society but is also an essential part of the future post-war reconstruction.

One of the best-known, and most stirring examples, of environmental damage caused by the war is the destruction of the Kakhovka Dam. The Kakhovka dam was destroyed on June 6, 2023, causing widespread flooding which hit settlements and farmland across the region. The downstream flooding was accompanied by a rapid decrease in the water level in the Kakhovka reservoir (see Photo 1.1). At the end of June, the reservoir had almost completely disappeared and the original network of branches of the river re-emerged at the site of the former reservoir (Vyshnevskyi et al. 2023); nearly 90% of the reservoir drained, exposing 1870 square kilometres of former lakebed (Stone 2024). To indicate the level of risk caused by potential contamination of the sediments of the exposed river bottom, five samples were collected in cooperation with the Environmental Inspectorate of the Southern District in Zaporizhzhia. In addition, two more soil samples were taken from the craters after the impact of an S-300 missile, which will form part of further studies focused on the damage caused by military actions.

The team of the Clean Air for Ukraine focuses on mapping and analysing contamination of soils and sediments caused by the military actions as well as the historical industrial pollution. The Kakhovka Reservoir study is the first part of a long-term project which will be carried out till 2025 in the Dnipropetrovsk, Zaporizhzhian and Kharkiv regions.

In 2023, first stage of the sampling has started. Five sediment samples from the river Dnipro and two soil samples from craters after explosions of missiles were taken in Zaporizhzhia city and downstream up to Kakhovka reservoir (four sediment samples). One sediment sample from the Dnipro River was taken in the city of Kherson. Heavy metals, polycyclic aromatic hydrocarbons (PAHs), non-polar extractable compounds (NECs), hydrocarbons $C_{10} – C_{40}$, cyanides, polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), pentachlorobenzene (PeCB), hexachlorobutadiene (HCBD), organochlorine pesticide residues (OCPs), brominated flame retardants (BFRs), dechlorane plus (DP), polychlorinated naphthalenes (PCNs), poly- and perfluoroalkylated substances (PFASs), short and medium chain chlorinated paraffins (SCCPs and MCCPs) and dioxins (PCDD/Fs) and dioxin-like PCBs (dl PCBs) by DR CALUX bioassay were analysed in the samples.

Photo 1.1 Bottom of the Kakhovka dam. (Photo: Majda Slámová)

2 Sampling and Analyses

2.1 Description of Sampling Locations

Sampling locations are marked in maps at Figures 2.1 and 2.2, and their characteristics can be visible also at Photos 2.1 – 2.7 attached to descriptions below.

Figure 2.1: Map of the locations in Zaporizhzhia area.

2.1.1 Site L1 Zaporizhzhia Central city beach

The Central city beach is the largest recreation area in Zaporizhzhia and in the past was actively used by local residents during the summer season. Near the beach, after the water level dropped because of the explosion at the Kakhovka reservoir, three sewage pipes of the local water supply were exposed. Zaporizhzhia Regional Infectious Disease Hospital is also nearby. It is impossible to accurately determine all enterprises that discharge wastewater in this area because there is a strong suspicion of the illegal connection of enterprises to the local sewage systems.

Photo 2.1: Site L1 Zaporizhzhia - Central city beach (Photo: Olexiy Angurets)

2.1.2 Site L2 Zaporizhzhia Sukha Moskovka

The confluence of the Sukha Moskovka Creek with the Dnipro River. Nearby is the Peremohy City Park. The Sukha Moskovka Creek passes through the industrial districts of the city of Zaporizhzhia, adjacent to the Zaporizhzhia industrial enterprises "Zaporizhstal" and "Dniprospetsstal", who discharge their wastewater into the Creek. Due to this, the waters of Sukha Moskovka have an intensive red-brown colour and are highly mineralized.

2.1.3 Site L3 Zaporizhzhia Sailing school

This is a site on the Dnipro River located at the southern periphery of the city. There is an equipped recreation area with a sandy beach, potentially clean zone. Nearby is the city Sailing School and rowing canal. Recreation centres are concentrated nearby in the green zone. There is a serious risk of contamination by the wastewater released from the city of Zaporizhzhia.

Photos 2.2: Site L2 Zaporizhzhia - Sukha Moskovka (Photo: Olexiy Angurets)

Photo 2.3: Site L3 Zaporizhzhia Sailing school (Photo: Olexiy Angurets)

2.1.4 Site L4 Malokatyrynivka village

The site is in Malokaterynivka village, near the Kankrynivka railway station, which was closed as the result of the full-scale Russian invasion. The settlement of Malokaterinivka is located 20 km south of the city of Zaporizhzhia and 13 km north of the territory temporarily occupied by Russia, on the left bank of the Kakhovka Reservoir, near the confluence of the Konka River. The samples were taken from the bottom of the Kakhovka reservoir, drained after the explosion, approximately 100 m from the shore.

Photo 2.4: Site L4 Zaporizhzhia – Malokatyrynivka village (Photo: Olexiy Angurets)

2.1.5 Site K1 Crater near Orihivske road, Zaporizhzhia

A crater of caused by a C-300 missile fired by Russian forces, is in the South-eastern periphery of Zaporizhzhia, next to the M-18 Kharkiv-Simferopol highway and its intersection with the Orihiv highway. The rocket strike hit the territory of a local garden centre. Soil samples were taken from the bottom of the crater which was formed following the explosion. Missile debris was found in and near the crater. The approximate date of the missile's impact was 30.06.2023.

2.1.6 Site K2 Crater Dubovka park

A crater caused by a C-300 missile fired by Russian forces. It is in the central part of Zaporizhzhia City, next to the Dubovka Park in a green area in front of a 9-floor residential building. Nearby is the Skoda car centre, which was destroyed because of the shelling. Soil samples were taken from the bottom of the crater which was formed following the explosion. There were remains of construction material in and near the crater related to the explosion but also some household waste was noticed. The date of the missile's impact was 11.10.2022.

Photo 2.5: Site K1 Crater near Orihivske road (Photo: Pavel Mothejl)

Photo 2.6: Site K2 Crater Dubovka park (Photo: Olexiy Angurets)

2.1.7 Site CH Cherson, Antonivka

The site is in Kherson near Luhova street, Antonivka approximately 400 metres from the original bank of Dnipro River, near the beach Molodizhnyy plyazh. It is on the wider riverbed, covered with vegetation. The sampling site was under water during the flooding after the dam was destroyed.

Photo 2.7: Site CH in Kherson, Antonivka (Photo: Pavel Mothejl)

Figure 2.2: Map with marked location of sample CH in Kherson.

2.2 Sampling

The sampling took place on 14th July 2023 in Zaporizhzhia and 20th July 2023 in Kherson and was carried out in cooperation with the Czech company Dekonta. Five samples of sediments of the Dnipro River were taken as point samples. All sediment samples were collected using a stainless-steel shovel from a layer at a depth of 25 to 30 cm below the surface. Both soil samples from the craters were also collected using a stainless-steel shovel, this time from a depth of 15 to 20 cm below the surface. The samples were homogenized and transported in polyethylene Ziplock bags to the laboratory, where they were stored in a cool environment.

Photo 2.8: Sampling in July 2023. (Photo: Pavel Mothejl)

2.3 Analytical Methods

Chemical analyses were done in three specialized laboratories. Heavy metals, PAHs, NECs, cyanides, and some OCPs were analysed by the Czech company Dekonta in its accredited laboratory. Seven indicator PCB congeners, DDT and its metabolites, hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), pentachlorobenzene (PeCB) and hexachlorobutadiene (HCBD), BFRs, PCNs, PFASs, SCCPs and MCCPs were analysed in the laboratory at University of Chemistry and Technology, Prague, Faculty of Food and Biochemical Technology, Department of Food Analysis and Nutrition. DR CALUX dioxin-like activity in all seven samples was analysed by the BioDetection Systems (BDS) in Amsterdam, Netherlands.

Sixteen PAHs were determined in five sediment samples by the method of gas chromatography with the MS detection by the test method SOP no. 20, procedure B (according ČSN P CEN/TS 16181 and ČSN P CEN/TS 16645). NECs were analysed by EL – the spectrometric method by the test method SOP no. 18, procedure B (ČSN 757505:1998, ČSN 757506:2002).

Three hexabromocyclododecane (HBCD) isomers[1,2] 16 polybrominated diphenyl ether (PBDE) congeners[3], and six novel BFRs[4] (nBFRs), DP, seven indicator PCB congeners, HCBD, 13 PCN congeners[5], PeCB, HCB, SCCPs and MCCPs were analysed in all samples. Additionally, all samples were also analysed by the DR CALUX® bioassay.

PBDEs were isolated from the samples by Soxhlet extraction followed by gel permeation chromatography (GPC) clean-up. The analysis was performed using gas chromatography coupled with mass spectrometry and negative chemical ionisation (GC-MS-NCI). HBCD isomers were isolated by acetonitrile and analysis was conducted by ultra-high-performance liquid chromatography coupled with tandem mass spectrometry with electrospray ionisation in negative mode (UHPLC-ESI-MS/MS). The same analytical method was used for analysis of PFASs. Selected PCB congeners, HCBD, PeCB, HCB, DP and PCNs were isolated from the samples by Soxhlet extraction followed by GPC clean-up. Analysis was conducted by gas chromatography coupled with tandem mass spectrometry and electron ionisation (GC-MS/MS-EI). All these analyses were conducted by the ISO/IEC 17025:2018 accredited Metrological and Testing Laboratory (University of Chemistry and Technology, Prague, Czech Republic). Gas chromatography coupled to high-resolution mass spectrometry with negative ion chemical ionization (GC-HRMS-NICI) was used for the analysis of selected chlorinated paraffins.

Photo 2.9: Sampling in July 2023. (Photo: Pavel Mothejl)

[1] An isomer is each of two or more compounds with the same formula but a different arrangement of atoms in the molecule and different properties.
[2] α-, β- and γ-HBCD
[3] PBDE 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207 and 209
[4] This group of chemicals is represented by the following chemicals: 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBBz), octabromo-1,3,3-trimethylpheny-1-indan (OBIND), 2,3,4,5,6-pentabromoethylbenzene (PBEB), and pentabromotoluene (PBT).
[5] PCN 4, 9, 18, 20, 41, 42, 52, 56, 66, 70, 73, 74 and 75.

The DR CALUX bioassay was conducted by the commercial laboratory of BioDetection Systems, Amsterdam, The Netherlands. For the sum parameter PCDD/Fs (separated TEQ), the method used is extraction with organic solvents; the extracts are cleaned on an acid silica column and separation is done with a florisil column. The cleaned extracts are dissolved in dimethyl sulfoxide (DMSO). The DR CALUX activity is determined (24h exposure) and benchmarked against 2,3,7,8-TCDD. The DR CALUX analysis is done according to the p-bds-051 in-house method. For the sum parameter dl-PCBs (separated TEQ), the sequence of operations is the same; however, separation is done with an alumina column.

For the method DR CALUX and the sum parameter PCDD/Fs expressed as bioanalytical equivalents (BEQ[6]; semi) and sum parameter PCDD/Fs and dl-PCBs (BEQ; semi), the method used is shake extraction with organic solvents (hexane); the extracts are cleaned on an acid silica column. The cleaned extracts are dissolved in DMSO. The DR CALUX activity is determined (24h exposure). The response of the sample is corrected for the background and subsequently corrected for the apparent bioassay recovery with a reference sample at the level of interest. The evaluation is done on the maximum levels for PCDD/Fs and for the sum of PCDD/Fs and dl-PCBs, from which cut off values have been established (2/3 of maximum levels). After the evaluation, an estimation is given of the samples in the form of BEQ outcomes.

[6] A bioanalytical equivalent (BEQ) is a unit of measure in the field of bioassays.

3 Results and Discussion

Results of the analyses for the chemicals specified in chapter 2.2 Analytical methods are summarized in Table 1 (see Chapter 3.1). More detailed results are in larger Table A2 in Annex 2 (marked as Chapter 5.2).

Highest levels of hydrocarbons C_{10} – C_{40}, arsenic, chromium, mercury, PAHs, PCBs (both seven indicator congeners and dioxin-like PCBs), and sum of DDT were measured in sediment sample from Zaporizhzhia public beach (marked as L1).

Highest level of 3 isomers of hexabromocyclododecane (HBCD) was measured in sample from one crater (K2). This brominated flame retardant was used mainly in polystyrene foams for insulation of buildings. Some polystyrene foams were observed at sampling site as well and are considered to be a major source of that contaminant. However measured levels are not so high to raise much concern. The same sample (K2) contained the highest concentration of HBBz, being the only one with this nBFR concentration above the level of quantification (LOQ). Levels for all PBDE congeners, DP as well as for 6 nBFRs, PCNs and HCBD were below LOQs in all sediment samples.[7]

While in sediment sample L1, the highest levels of POPs (Persistent Organic Pollutants) and mercury were found among the examined samples, in sediment L2, the highest concentrations of heavy metals (such as cadmium, chromium, lead, arsenic, nickel, copper, and tin) were observed along with HCB and PeCB.

The concentrations of PFASs in the five analysed sediment samples in this study were generally low, with only a few instances exceeding the limit of quantification (LOQs).[8]

The following chapters include a comparison of the measured values of individual pollutants in sediment samples from Zaporizhzhia and Kherson with limits for the remediation of contaminated sites (Chapter 3.1). Subsequently, there is a comparison with the concentrations measured in sediment samples from the Dnipro River and its tributaries in its upper course (in Belarus) in 2012 and from Dnipro and Boh Estuary (Chapter 3.2.1) and with other locations in Europe and elsewhere, including sites potentially or demonstrably contaminated with POPs (Chapters 3.2.2 – 3.2.4).

3.1 Comparison with Pollution Limits for Environmental Remediation

The results of the analyses of samples from Table 1 were evaluated in terms of the need to decontaminate sediments or soils. The sediments at the bottom of the damaged Kachovka reservoir is suspected to have accumulated toxic substances over the years of dam operation, either from the use of pesticides in the era of Soviet agriculture or from industry accumulated in Zaporizhia and its surroundings. For this purpose, we utilized indicative contamination levels from the Methodological Guidelines of the Czech Ministry of the Environment (MŽP ČR 2014), which are based on the Regional Screening Levels set by the USEPA for the rock environment (USEPA 2023). The comparison of measured values for individual pollutants with indicative contaminant levels is in Table 1.

[7] PBDEs, DP, PCNs and HCBD were below LOQ also in both soil samples from the craters.
[8] Levels above LOQ were measured for following PFASs: PFOA, PFDA, PFOS, and HFPO-DA.

Photo 3.1: Area where sample L3 in Zaporizhzhia, near the sailing school, was taken on 14-th of July, 2023. (Photo: Stanislav Krupař)

Photo 3.2: Area where sample L4, near the Malokaterynivka village, was taken on 14-th of July 2023. (Photo: Stanislav Krupař)

Table 1: Summary of the results of chemical analyses of seven samples from Zaporizhzhia and Kherson, along with their comparison to indicative levels for decontamination used in the Czech Republic (MŽP ČR 2014).

Chemicals	L1	L2	L3	L4	CH	K1	K2	Units	Indicative levels for decontam.
NEC	16 330	718	272	490	354	-	-	mg/kg dm	
Hydrocarbons C10-C40	20 705	2 350	<100	<100	<100	-	-	mg/kg dm	500
Cyanides	<0.02	<0.02	<0.02	<0.02	<0.02	-	-		22
Acenaphthene	200	0.337	<0.05	<0.05	<0.05	-	-	mg/kg dm	3400
Acenaphthylene	8.13	0.213	<0.05	<0.05	<0.05	-	-	mg/kg dm	
Anthracene	22.4	0.583	<0.05	<0.05	<0.05	-	-	mg/kg dm	17000
Benzo(a)anthracene	78.7	0.816	<0.05	<0.05	<0.05	-	-	mg/kg dm	0.15
Benzo(a)pyrene	35.6	0.456	<0.05	<0.05	<0.05	-	-	mg/kg dm	0.015
Benzo(b)fluoranthene	47.3	1.06	<0.05	<0.05	<0.05	-	-	mg/kg dm	0.15
Benzo(k)fluoranthene	36.8	1.33	<0.05	<0.05	<0.05	-	-	mg/kg dm	1.50
Dibenzo(a.h)anthracene	1.73	<0.05	<0.05	<0.05	<0.05	-	-	mg/kg dm	0.015
Fluorene	1.2	0.312	<0.05	<0.05	<0.05	-	-	mg/kg dm	2300
Fluoranthene	196	2.46	<0.05	<0.05	<0.05	-	-	mg/kg dm	2300
Chrysene	75.8	1.34	<0.05	<0.05	<0.05	-	-	mg/kg dm	210
Indeno(1.2.3cd)pyrene	5.98	0.162	<0.05	<0.05	<0.05	-	-	mg/kg dm	0.15
Naphthalene	5.65	<0.05	<0.05	<0.05	<0.05	-	-	mg/kg dm	3.60
Phenanthrene	45.5	0.746	<0.05	<0.05	<0.05	-	-	mg/kg dm	-
Pyrene	130	2.2	<0.05	<0.05	<0.05	-	-	mg/kg dm	1700
Benzo(g.h.i)perylen	4.45	0.151	<0.05	<0.05	<0.05				-
16 PAHs	895.24	12.166	0	0	0	-	-	mg/kg dm	-
Antimony	1.44	5.83	<0.611	1.92	3.82	-	-	mg/kg dm	31
Arsenic	7.41	24.5	<0.611	2.83	4.24	-	-	mg/kg dm	0.61
Baryum	101	90.9	17.7	74.5	144	-	-	mg/kg dm	15000
Berylium	0.744	<0.804	<0.611	<0.889	<0.515	-	-	mg/kg dm	160
Cadmium	0.299	10.5	0.484	1.31	0.113	-	-	mg/kg dm	70
Cobalt	6.15	6.75	0.793	3.8	3.48	-	-	mg/kg dm	23
Chromium	26.5	256	14.2	40.4	20.9	-	-	mg/kg dm	0.29
Copper	28.6	55.1	3.56	10	11.1	-	-	mg/kg dm	3100
Lead	23	171	8.73	14.4	12.8	-	-	mg/kg dm	400
Manganese	402	1 820	126	805	222	-	-	mg/kg dm	1800
Mercury	9.99	0.379	<0.050	0.082	<0.050	-	-	mg/kg dm	10
Nickel	11.5	81.9	4.58	9.08	10.8	-	-	mg/kg dm	1500
Selenium	0.521	2.55	<0.611	<0.889	<0.515	-	-	mg/kg dm	390
Silver	<1.33	<1.60	<1.22	<1.77	<1.03	-	-	mg/kg dm	390
Tin	5.4	10.5	2.16	5.64	2.79	-	-	mg/kg dm	47000
DDD	2 467	6.4	0.18	0.45	1.2	0.16	14.2	ng/g dm	2000

DDE	404	8.0	0.24	0.56	2.9	0.058	17.9	ng/g dm	1400
DDT	<0.02	1.4	<0.02	<0.02	0.15	<0.02	32.6	ng/g dm	1700
alfa-HCH	2.3	0.063	0.035	0.067	0.042	0.45	0.40	ng/g dm	77
beta-HCH	8.2	0.19	0.038	0.088	0.074	<0.02	0.98	ng/g dm	270
gama-HCH	9.1	0.041	0.031	0.039	<0.02	0.032	0.13	ng/g dm	520
PCB 28	<0.02	4.35	0.054	0.168	0.183	<0.02	0.036	ng/g dm	110
PCB 52	5.95	3.48	0.054	1.459	0.230	<0.02	0.092	ng/g dm	110
PCB 101	15.1	6.83	0.178	2.730	0.619	<0.02	0.213	ng/g dm	110
PCB 118	17.6	6.99	0.244	3.211	0.821	<0.02	0.269	ng/g dm	110
PCB 138	10.8	4.93	0.228	1.501	0.685	<0.02	0.339	ng/g dm	110
PCB 153	6.08	3.68	0.189	0.944	0.486	<0.02	0.217	ng/g dm	110
PCB 180	1.69	1.12	0.044	0.159	0.113	<0.02	0.122	ng/g dm	110
7 PCB congeners	57.2	31.4	1.0	10.2	3.1	<0.02	1.3	ng/g dm	220
Hexachlorobenzene (HCB)	2.29	10.8	0.172	0.188	0.059	<0.02	0.075	ng/g dm	300
Pentachlorobenzene (PeCB)	1.03	3.31	0.047	0.066	<0.02	<0.02	0.061	ng/g dm	49000
Hexachlorobutadiene (HCBD)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	ng/g dm	6200
PCDD/Fs – DR CALUX	6	10	3.6	1.4	1.1	<0.2	2.8	pg BEQ/g dm	4.5
Sum of PFASs	<LOQ	0.025	0.100	0.168	0.028	0.104	0.098	ng/g dm	-
Sum of PBDEs	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ng/g dm	-
Sum of HBCDs	<0.05	2.718	0.094	<0.05	4.339	0.000	51.98	ng/g dm	-
BTBPE	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	ng/g dm	-
DBDPE	<10	<10	<10	<10	<10	<10	<10	ng/g dm	-
HBBz	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.662	ng/g dm	-
OBIND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	ng/g dm	-
PBEB	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	ng/g dm	-
PBT	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	ng/g dm	-
DP	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	ng/g dm	-
Sum of PCNs	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ng/g dm	-
SCCP C10-C13	<5	<5	<5	<5	<5	57.0	12.2	ng/g dm	-
MCCP C14-C17	<10	191	<10	<10	<10	<10	290	ng/g dm	-

The sample that most frequently exceeded the indicative contamination levels for other soils in the Czech Republic is L1. The substances of concern were polyaromatic hydrocarbons (total concentration range <0.05 to 684 mg/kg dm), namely benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene, as well as benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene and naphthalene. For the first four, sample L2 was problematic for the same reason.

L1 exceeded the values for the other soils for benzo(a)anthracene (limit concentration 0.15 mg/kg dm) more than 500 times, for benzo(a)pyrene (limit concentration 0.015 mg/kg dm) more than 2300 times, for benzo(b)fluoranthene (limit concentration 0.15 mg/kg dm) more than 300 times, etc., in the case of sample L2 the exceedances are only a few times.

Samples L1 and L2 exceeded the indicator levels set for hydrocarbons $C_{10} – C_{40}$. They surpassed the contamination threshold, set at 500 mg/kg, by more than 41 and almost 5 times, respectively.

With respect to metals, arsenic was still of concern in more than half of the samples collected (L1, L2, L4 and CH). Apart from L3 (< 0.61 mg/kg dm) and samples K1 and K2 that were not analysed. The arsenic concentrations in the remaining samples ranged from 14.2 to 256 mg/kg, while the indicative level for decontamination was set at 0.61 mg/kg dm, i.e. sample L2 exceeded this limit by almost 900 times, the sample with the lowest (14.2 mg/kg dm) but exceeding concentration measured, L3, by almost 50 times.

In addition, an elevated manganese concentration of 1820 mg/kg dm was found in sample L2, while the indicative decontamination level is set at 1800 mg/kg dm. Sample L1 is also close to the same limit for mercury, with a measured concentration of 9.99 mg/kg dm approaching the limit of 10 mg/kg dm.

The indicative level for decontamination pro dioxins is established for the most toxic congener 2,3,7,8-TCDD at a level of 4.5 pg/g dm. However, we did not conduct a conventional analysis determining the concentrations of individual congeners. Instead, we performed a bioassay analysis, which assessed the biological equivalent of toxicity compared to the toxicity of the most toxic congener (2,3,7,8-TCDD). If we were to consider that these values are comparable, then the determined limit would exceed dioxins at levels of 6 and 10 pg BEQ/g dm in samples L1 and L2, respectively. In practice, this approach is not followed, but we present it as a certain comparison.

One of the DDT breakdown products, DDD, was detected at elevated concentrations in sample L1. The measured concentration of 2,467 ng/g dm exceeded the indicative decontamination level of 2 mg/kg dm.

Dioxin activity was measured in all samples using the DR CALUX test. In contrast to the TEQ, this provides information on how (much) substances with this activity in the samples affect mammalian cells, whereas the TEQ only provides information on the concentration of each congener (converted to the most toxic) without any conceivable effect. Ideally, it would be useful to have both values available.

Levels for DDT, some PAHs, arsenic, and mercury in this sample indicate the need for decontamination of area, based on indicative levels set by the Czech Ministry of Environment (MŽP ČR 2014). Levels of DDT, PAHs and hydrocarbons $C_{10} – C_{40}$ in sediment sample from Dnipro River in Zaporizhzhia also represent a major health concern among observed contamination in evaluated 7 samples.

3.2 Comparison of Contaminant Concentrations in Samples from the Dnipro River with Other Research on Sediments

3.2.1 Comparison with Sediments from Dnipro and Tributaries in its Upper Stream and Estuary

In the following section, we compare a summary of sediment samples collected in the Zaporizhzhia and Kherson regions with samples collected in the estuary of Dnipro and Boh in 2006–2008 (Burgess et al. 2011), and from Belarus in 2011 and 2012 from the upper stream of the Dnipro River and its tributaries—specifically, samples from Mogilev, Zhlobyn, Gatovo, and Berezinsky (see Photo 3.

(Nezhyba et al. 2012).[9] It is essential to consider the over ten years' difference between samples from Belarus (2011-2012), the Dnipro and Boh Estuary (2006-2008), and our samples from Ukraine (2023). The results of chemical analyses for the compared sediment samples from both countries are summarized in Table 2.

The highest level of NEC was found in Zaporizhzhia (16,330 mg/kg dm). NECs were also measured in Kherson (354 mg/kg dm), with values slightly higher than those near the Gatovo car shredder (<LOQ to 636 mg/kg dm) (Nezhyba et al. 2012).

For metals, the levels detected in Zaporizhzhia are higher for arsenic (up to 24.5 mg/kg dm) and cadmium (up to 10.5 mg/kg dm) than at the Druzhnyi reference site (up to 0.23 mg/kg dm for As; 0.18 mg/kg dm for Cd). For mercury, the concentration is higher in Zaporizhzhia (up to 9.99 mg/kg dm) than in the reference site (up to 0.023 mg/kg dm in Druzhnyi). For Cd, higher concentrations were found in Kherson (0.113 mg/kg dm) than at the Berezinsky reference site (<LOQ); (Nezhyba et al. 2012).

The highest concentrations of arsenic were found in Zaporizhzhia (up to 24.5 mg/kg dm), comparable to the highest concentrations in Gatovo-Svislach (up to 31.7 mg/kg dm) or Mogilev (up to 25.8 mg/kg dm). Concentrations in Kherson (4.24 mg/kg dm) were also higher than in the two reference sites, Berezinskyi (<LOQ), and Druzhnyi (0.23 mg/kg dm); (Nezhyba et al. 2012).

Even the lowest concentration of cadmium in Zaporizhzhia (0.299 mg/kg dm) was higher than in the reference sites (between <LOQ and 0.18 mg/kg dm). The highest concentration measured in Zaporizhzhia (10.5 mg/kg dm) was like the highest Cd concentration measured in Gatovo (8.6 mg/kg dm); (Nezhyba et al. 2012).

The highest copper concentration in Zaporizhzhia (28.6 mg/kg dm) was comparable to the highest concentration in Mogilev – sewage plant (27.2 mg/kg dm) or Mogilev (29.8 mg/kg dm), but concentrations as high as 1,120 mg/kg dm were detected in samples from Svislach River in Gatovo (Nezhyba et al. 2012).

The presence of lead above the LOQ was detected at all sampled sites in Ukraine and Belarus where it was analysed. The highest concentration was found in samples from Zaporizhzhia (up to 171 mg/kg dm), about half of the highest concentration found in Gatovo (81 mg/kg dm). In all cases, the highest concentration detected was higher than at the Berezinskyi reference site (5.5 mg/kg dm); (Nezhyba et al. 2012).

The sample with the highest measured concentration of mercury (Hg) was found in Zaporizhzhia (9.99 mg/kg dm), which was also two orders of magnitude higher than both the Berezinskyi (up to 0.011 mg/kg dm) and Druzhnyi (0.023 mg/kg dm) reference sites (Nezhyba et al. 2012). Similarly to Zaporizhzhia, the maximum concentration of mercury in the sediments of the Dnipro and Boh Estuary (Burgess et al. 2011) was relatively high compared to the other sites under examination.

[9] Samples from Mogilev were divided into two groups: samples collected from Dnipro as it flows throughout the city and samples taken at the outlet of the canal leading from the local sewage treatment plant. Zhlobyn is located near a metallurgical plant where scrap metal is processed, and Gatovo is a location with a car shredder plant. Two reference sites were chosen: Berezinsky, which is situated in the upper course of a stream or at the outlet of a lake with peat bogs, and Druzhnyi, which is characterized by wetlands.

Table 2: Comparison of chemical substance concentrations in sediments from the Dnipro River basin in Ukraine and Belarus.

River	Units	Dnipro River						Svislach	Reference sites	
Chemicals		Zaporizhzhia	Kherson	Dnipro / Boh Estuary	Mogilev	Mogilev - sewage plant	Zhlobyn - Dobysna and Dnipro	Gatovo - Svislach	Berezinsky	Druzhnyi
NEC	mg/kg dm	272 – 16330	354	NA	<LOQ - 211	77		<LOQ - 636		
Arsenic	mg/kg dm	<0.611 - 24.5	4.24	NA	<LOQ - 25.8	<LOQ	0.36 - 0.69	<LOQ - 31.7	<LOQ	0.23
Cadmium	mg/kg dm	0.299 - 10.5	0.113	NA	<LOQ - 1.8	<LOQ	0.36 - 0.39	<LOQ - 8.6	<LOQ	0.18
Chromium	mg/kg dm	14.2 – 256	20.9	<LOQ - 380	<LOQ - 119	87.9			<LOQ	
Copper	mg/kg dm	3.56 - 28.6	11.1	NA	<LOQ - 29.8	27.2		<LOQ - 1120	2.7 - 3.3	
Lead	mg/kg dm	8.73 – 171	12.8	NA	<LOQ - 70	6.6	7.78 - 15.5	4.6 - 81	5.1 - 5.5	
Mercury	mg/kg dm	<0.050 - 9.99	<0.050	0.04 – 6.90	<LOQ - 0.41	0.03	0.047 - 0.053	0.012 - 0.177	<LOQ - 0.011	0.023
Sum of DDT	ng/g dm	0.42 – 2872	4.24	2.0 – 342	<LOQ	<LOQ	0.52-2.26	<LOQ - 7.73	<LOQ	1.68
Sum HCH	ng/g dm	0.10 - 19.6	0.12	NA				<0.70		<0.70
7 PCB cong.	ng/g dm	0.992 – 57	3.14	0.30 – 264	<0.01 - 0.899	149	1.07 - 5.38	4.12 - 8.8	<0.01 - 0.112	0.910
Hexachlorobenzene (HCB)	ng/g dm	0.172 - 10.8	0.059	NA	NA	NA	NA	0.31	NA	0.59
Sum of OCPs	ng/g dm	0.742 - 2895	4.417	NA	na	na	na	<LOQ - 8.0	na	2.27
Sum of PBDEs	ng/g dm	<LOQ	<LOQ	NA	0.591 - 2.25	15.6	0.85 - 19.1	<LOQ - 179	<LOQ - 0.014	0.27
Sum of HBCD	ng/g dm	<0.05 - 2.72	4.34	NA	<0.75	1.64	<0.75	<0.75	<0.75	<0.75
PCDD/Fs + dl PCBs – DR CALUX	pg BEQ/g dm	1.83 - 35	1.69	NA	0.4 - 10	LOQ (0.18)	0.82 - 1.2	1.1 - 47	2.5	2.4
Sum of PFASs	ng/g dm	<0.04 - 0.168	0.028	NA	<LOQ	20.6	<LOQ	<LOQ - 0.23	<LOQ <0.30	<0.75

LOQ – level of quantification; NA – not analysed; na – not applicable

Photo 3.3: Berezinsky reference site in upper part of Dnipro basin in Belarus, where sediment sample was taken on 20-th of August 2012. (Photo: Jindřich Petrlík)

Photo 3.4: Discharge of wastewater from local sewage system to Dnipro River in Zaporizhzhia - near the site L1 Central beach. (Photo: Majda Slámová)

When it comes to POPs, for seven PCB congeners, even the lowest measured values in Zaporizhzhia (from 0.992 ng/g dm) and Kherson (3.137 ng/g dm) were higher than those in both reference sites, Berezinskyi (up to 0.112 ng/g dm), and Druzhnyi (up to 0.910 ng/g dm). However, it is worth noting that the highest PCB value (264 ng/g dm) was found in sediment from the Dnipro and Boh Estuary (Burgess et al. 2011), followed by the effluent channel of the wastewater treatment plant in Mogilev (179 ng/g dm); (Nezhyba et al. 2012).

Photo 3.5: Sampling on Dnipro riverbank near Bilenke village in 2023. (Photo: Majda Slámová)

For hexachlorobenzene (HCB), the measured concentration at Zaporizhzhia (up to 10.8 ng/g dm) was about 20 times higher than at the Druzhnyi reference site (0.59 ng/g dm); (Nezhyba et al. 2012). In contrast, the concentration measured in Kherson (0.059 ng/g dm) was 10 times lower than that found in Druzhnyi.

For the sum of OCPs, concentrations more than 1000 times higher were found in Zaporizhzhia (up to 2,895 ng/g dm) than at the reference site, while in Kherson and in all other cases of Belarusian samples, higher concentrations were found than at the Druzhnyi reference site (2.27 ng/g dm); (Nezhyba et al. 2012). The highest contribution to this difference comes from the concentration of DDT included in the total sum of OCPs.

Concentrations of DDT in both Zaporizhzhia (up to 2,872 ng/g dm) and Kherson (4.24 ng/g dm) samples are higher than in comparable samples from Belarus, except for sample from Svislach River in Gatovo (up to 7.73 ng/g dm); (Nezhyba et al. 2012), which is higher than the level in sediment from Kherson, but three orders of magnitude lower in the case of the L1 sample from Zaporizhzhia. The concentration in the L2 sample is an order of magnitude higher than in the sample from the Druzhnyi reference site (1.68 ng/g dm); (Nezhyba et al. 2012), while the concentrations of DDT in the other two samples, L3 and L4, are lower compared to the Druzhnyi reference site.

In the case of the sum of hexachlorocyclohexanes (HCH), higher concentrations were measured in Zaporizhzhia (up to 19.64 ng/g dm) than in the Druzhnyi reference site (<0.70 ng/g dm); (Nezhyba et al. 2012).

For the sum of polybrominated diphenyl ethers (PBDEs), concentrations at both sites in Ukraine were below the limit of quantification (LOQ), while in samples from Gatovo (up to 178.56 ng/g dm), Zhlobyn (up to 19.1 ng/g dm), Mogilev (2.25 ng/g dm), and Mogilev - sewage plant (15.6 ng/g dm), higher values were reached (Nezhyba et al. 2012). Sampling of the sediments from Dnipro River by the Mogilev sewage plant is on Photo 3.6.

For the sum of HBCDs, higher concentrations were found in both Zaporizhzhia (up to 2.72 ng/g dm) and Kherson (up to 4.34 ng/g dm) than in all sediment samples from Belarus (Nezhyba et al. 2012), including the reference samples (<0.75 ng/g dm), but the concentration in the L3 sample was below the LOQ (<0.05 ng/g dm).

For PCDD/Fs + dl PCBs - DR CALUX, the lowest values found in Zaporizhzhia (1.83 pg BEQ/g dm) and in Kherson (1.69 pg BEQ/g dm) were comparable to the reference values in Berezinsky (2.5 pg BEQ/g dm) and Druzhnyi (2.4 pg BEQ/g dm). However, the highest value, 35 pg BEQ/g dm, found in Zaporizhzhia was more than 10 times higher than the reference values and comparable to the 47 pg BEQ/g dm found in Gatovo (Nezhyba et al. 2012).

The concentrations of PFASs detected (up to 0.168 ng/g dm for Zaporizhzhia) were not as high as those found at the Mogilev wastewater treatment plant (20.6 ng/g dm), but higher than those found at the reference sites of Berezinsky (<0.30 ng/g dm) and Druzhnyi (<0.75 ng/g dm); (Nezhyba et al. 2012).

Photo 3.6: Sampling by discharge outflow from water purification plant into Dnipro River by Mogilev, Belarus, on 19-th of August, 2012. (Photo: Jindřich Petrlík)

3.2.2 Comparison with Other Riverine Sediments

Highest level of DDT in the sample from Zaporizhzhia (L1) is comparable to the highest levels observed in contaminated sediments from Ukraine, Czech Republic, or Poland (Burgess et al. 2011; Holoubek and Růžičková 2007; Ivanova et al. 2021). Situation is serious, considering that the sample was taken from the area dedicated for public use, not industrialized area.

Results of chemical analyses for PAHs, the sum of OCPs including the total of DDT and its metabolites, three isomers of HCH, and hexachlorobenzene (HCB), seven PCB congeners, mercury, lead, and arsenic were compared with multiple studies focusing on these substances in river and similar sediments. Where studies allowed, we outlined specific ranges of values for these frequently measured substances and compared them with sediments from the Dnipro River in our study. For others, we had to settle for describing the basic research findings. We aimed to select primarily more recent studies reflecting a situation not older than 10 years. In our comparison, we also included four studies by Arnika focused on sediments from 1) the Nura River in central Kazakhstan (Petrlik et al. 2015), 2) rivers in the Western Balkan countries (Montenegro, Serbia, and Bosnia and Herzegovina), mostly from the vicinity of large coal power plants and coal mines (Šír et al. 2015), 3) Czech rivers Labe (Elbe), Odra and their tributaries (Mach 2015; Mach and Petrlík 2016), and 4) rivers and watercourses in Thailand from the vicinity of industrial operations (Tha Tum and Map Ta Phut) and a gold mine in Loei (Bystriansky et al. 2018; Mach et al. 2018). Basic information about the studies and the comparison is included in Annex 3, which also features Table A3, serving as the basis for the text below.

The maximum measured PAH value in sediment L1 from Zaporizhzhia is comparable to the maximum value from the Thai location Tha Tum (Bystriansky et al. 2018; Mach et al. 2018), and the concentration in sediment L2 is nearly nine times lower than the concentration found in the Černý Stream near the Ostrava steelworks, which is a tributary of the Odra River, in 2015 (Mach and Petrlík 2016). In all other compared locations, PAH concentrations were lower. However, it should be noted that in two sediments from Zaporizhzhia and one from Cherson, PAH concentrations were below the limit of quantification (LOQ), i.e., less than 0.05 mg/kg dm, which is lower than in most cases from comparative studies.

The overall concentration of OCPs in sediment L1 is significantly higher than in most sediments from the compared studies in Table A3 (Annex 3), due to the previously mentioned high concentration of DDT. The OCP concentration in sample L2 exceeds the maxima from studies in the Huveaune River (France), Durance River and Berre Lagoon (France), or Thai sediments from the 2018 Arnika study but is lower than the maxima found in the Nura (Kazakhstan) or Somesu Mic River (Romania); (Barhoumi et al. 2019; Bystriansky et al. 2018; Kanzari et al. 2015; Kanzari et al. 2014; Petrlik et al. 2015).

The maximum concentration of seven PCB congeners found in sediment L1 (57 ng/g dm) is nearly eight times, more than six times, or more than four times lower than that observed in sediments from studies of the Huveaune River in France (435 ng/g dm); (Kanzari et al. 2014), the Labe River and its tributaries in the Czech Republic (361 ng/g dm); (Mach and Petrlík 2016), or the Somesu Mic River in Romania (253 ng/g dm); (Barhoumi et al. 2019). Simultaneously, it is a value comparable to the maximum (61.5 ng/g dm) found in a Czech study in a stream within the area of concentration of metallurgical industry (Mach and Petrlík 2016). However, it is several times higher than the highest concentrations in sediments from Durance and Berre Lagoon in Belgium. It is also more than 612 times lower than the highest sum of six PCB congeners measured in the Nura River sediment in Kazakhstan in the 2015 Arnika study (Petrlik et al. 2015). This indicates that PCB concentrations are not exceptionally high compared to European and non-European river locations.

Photo 3.7: Metallurgical industry influences the environment of Nura River basin in Kazakhstan as the photo taken in Temirtau in August 2013 shows. (Photo: Ondřej Petrlík)

Photo 3.8: Sampling of sediments from Nura River in Kazakhstan in August 2013. (Photo: Ondřej Petrlík)

Sediments from the Nura River in Kazakhstan (see Photos 3.7 and 3.8) also had more than seventeen times higher mercury concentration compared to the maximum concentration from Zaporizhzhia in this study. This is likely due to Nura being contaminated with mercury and PCBs from old industrial operations (Petrlik et al. 2015). Nevertheless, the maximum concentration of almost 10 mg/kg in sediment L1 from Zaporizhzhia is seven to twenty times higher than the maximum values found in sediments from the western Balkans or Thailand, including sites affected by coal power plants (Mach et al. 2018; Saetang et al. 2013; Šír et al. 2015). However, for arsenic, even the maximum value from sediment L2 from Zaporizhzhia is lower than those from Balkan or Thai locations affected by coal or chemical industries, or mining. This is not the case for lead, which reached a higher value in sediment L2 than the maxima measured in studies from the Balkans, Thailand, or France. However, it is lower than the maximum lead value measured in sediments from the Nura River in central Kazakhstan.

The highest concentration of PAHs found in sediment L1 is more than eighty times higher than the highest concentration found in the Chinese Liangtan River and over a hundred times higher than in the German Ammer River (Liu et al. 2013). However, the concentration in sediment L2 is comparable to the maximum level of 11 mg/kg dm found in sediment from the Liangtan River (Liu et al. 2013). In the Portuguese Sado Estuary (Ribeiro et al. 2016), the maximum concentration of PAHs in sediment (over 7 mg/kg dm) was similar to that in the Ammer River (8 mg/kg dm); (Liu et al. 2013), thus lower than in sediments L1 and L2 from Zaporizhzhia.

In sediments from the port of Prahovo on the Danube in Serbia (Radomirović et al. 2023), PAH concentrations were orders of magnitude lower compared to concentrations in sediments L1 and L2. The values for arsenic and lead in samples L2 and L1 were higher than the maximum value from the Prahovo port. However, copper concentrations (38.3 mg/kg dm) were comparable or lower with them (Radomirović et al. 2023).

A study focused on Czech rivers in 2015, among other things, also measured PFASs in sediments, finding concentrations ranging from below the limit of quantification (LOQ) to 1.40 ng/g dm (Mach and Petrlík 2016). This is one order of magnitude higher compared to samples from the Dnipro River in Zaporizhzhia and Kherson (see Table 1). The discovery of low concentrations of PFASs in sediments from the Dnipro River in this study aligns with findings from other studies. For instance, a study conducted in Malaysia concluded that PFASs concentrations in sediments were generally below the limit of quantification (LOQ), and when detected, PFASs concentrations were generally lower than those measured in water and biota (Mohamad et al. 2022).

3.2.3 Comparison with Mining Localities in Armenia

In comparison with the sediment samples collected in Armenia in 2022 and 2023 from the sites affected by mining, it can be noted that the arsenic concentration in sample L2 (24.5 mg/kg dm) was higher than the average of the three samples collected at the Surenavan site and similar to the average arsenic concentration in samples from Melikgyugh - 26 mg/kg dm (7 samples) and Karaberd - 28.3 mg/kg dm (7 samples); (Matoušková et al. 2023).

In the case of chromium, the average concentration in the same sites in Armenia ranged from 14.5 to 77 mg/kg dm (Matoušková et al. 2023), while in the samples (L1-L4 and CH) the concentrations ranged from 14.2 to 256 mg/kg dm.

On average, mercury concentrations at the Armenian sites ranged from 0.0182 mg/kg dm to 0.1492 mg/kg dm (Matoušková et al. 2023), while concentrations <0.05 to 9.99 mg/kg dm were found in samples from L1 to L4 and CH.

3.2.4 Comparison with Sediments from Sites Contaminated with POPs

In the sediments of a stream near a location contaminated with OCPs in the Klatovy – Luby area in the Czech Republic, the study from 2007 measured their total sum to be between 22.4 and 48.1 ng/g dm, while for HCB, the sum of DDT, and HCH, it was 1.9–3.6, 19.3–44.5 ng/g, and 1.2–1.6 ng/g, respectively (Dvorská et al. 2007). The highest concentrations for OCPs, sum of DDT, and HCH in sediment L1 exceeded these values, particularly for the sum of DDT, surpassing it by two orders of magnitude. The HCB value is comparable, but its concentration in sediment L2 (10.8 ng/g dm) triples that of Klatovy – Luby. In sediments L3, L4, and CH, the concentrations of all OCPs are much lower than those found in the vicinity of the OCP-contaminated site in the Czech Republic.

Additional data from sites contaminated with POPs in the Czech Republic were gathered by the updated National POPs Inventory based on research by VÚV TGM conducted in 2005-2006 (Fuksa and Kužílek 2007). It revealed DDT concentrations in the following locations: Labe – Černínovsko 6,170 ng/g dm, Libišská strouha 310 ng/g dm, Labe – Obříství 195 ng/g dm, and in sediments from Czech rivers from other locations, 2.8–678 ng/g dm. For the sum of HCH, concentrations were: Labe - Černínovsko 216 ng/g, Libišská strouha 19 ng/g dm, Labe – Obříství 171 ng/g dm, and in other general river locations, 0.2–4.1 ng/g dm (Fuksa and Kužílek 2007). The Černínovsko, Libišská strouha, and Obříství locations are near one of the largest Czech chlorine chemical plants that previously worked with DDT and produced HCH. Until recently, it was one of the most contaminated POPs sites in the Czech Republic. While the concentration of the sum of DDT in sediment L1 from Zaporizhzhia is more than twice lower than in sediment Labe – Černínovsko, it is on the same order of magnitude, whereas in sediment L2, the DDT concentration is substantially lower compared to the highest value in Czech rivers from 2005–2006. The concentration of the sum of HCH in sediment L1 is at a level found in Libišská strouha but lower than in more contaminated locations such as Černínovsko and Obříství. In other Ukrainian sediments in this study, HCH levels are at the lower limit of what was measured in Czech rivers.

The relatively high concentration of HCB (10.8 in sediment L2) was twice lower than at the Nong Bua electronic waste landfill in Thailand (Dvorska et al. 2023) or in sediment from the Bílina River (see Photo 3.9) in 2003 near a chemical factory in Ústí nad Labem (Kuncová et al. 2006). However, it was significantly higher than in sediment from a pond near the Nong Bua waste landfill. A similar comparison holds for the sum of 7 PCBs in sediments L1 and L2 with sediments from the Thai location. Conversely, all investigated BFRs in sediments from the Thai location showed much higher concentrations (Dvorska et al. 2023), attributed to the concentration of electronic waste at the Thai site.

Soils from industrial areas, waste lagoons, and landfills in the Czech Republic, according to the National POPs Inventory, exhibited PAH values of 0.448–611.5 mg/kg. The highest level of PAHs is from the Synthesia Pardubice lagoon, while other riverine sediments in the Czech Republic ranged from 0.805 to 23.75 mg/kg (Fuksa and Kužílek 2007). The highest PAH value from Dnipro River in sediment L1 is higher than the maximum from contaminated sites in the Czech Republic, while the second highest in sediment L2 (12.17 mg/kg dm) is lower than the maximum from Czech rivers in 2005–2006.

Photo 3.9: Bílina river mouth into Labe (Elbe) river in year 2015. This river is counted as most polluted one in the Czech Republic, because of chemical industry. (Photo: Jindřich Petrlík)

3.3 Discussion about Potential Sources of Contamination

The concentrations of DDT and HCH in sediment L1 indicate the proximity of a site heavily contaminated with these obsolete pesticides. If this site is not yet documented as an obsolete pesticide stockpile, then the contamination hotspot should be identified.

There were 224 and 100 obsolete pesticides stockpiles in Zaporizhzhia and Kherson oblast respectively registered in 2007 (MEPU 2007). Obsolete pesticides stored in the stockpiles in Zaporizhzhia oblast included DDT as well. „According to the data of MAPU, 8,470.6 tons of products of the POPs group were used in 1967 and 1968 in Ukraine," from which majority was DDT (MEPU 2007).

The high concentrations of other substances in sediments suggest that the source could be heavy industry, whether metallurgical or engineering. Elevated concentrations of arsenic may be related to coal combustion or the use of materials with a high arsenic content. Further research in Zaporizhzhia should also focus on these sources.

Photo 3.10: Dnipro river near Bilinke village. (Photo: Majda Slámová)

4 Conclusions

Highest levels of hydrocarbons C_{10} – C_{40}, arsenic, chromium, mercury, PAHs, PCBs (both seven indicator congeners and dioxin-like PCBs), and the sum of DDT were measured in sediment sample from Zaporizhzhia public beach (marked as L1). Levels of DDT, some PAHs, arsenic, and mercury in this sample indicate the need for decontamination of the area. The highest level of DDT in that sample is comparable to the highest levels observed in contaminated river sediments from Ukraine, the Czech Republic, or Poland and is comparable to sediments from locations contaminated by DDT production or preparation. It is accompanied by a relatively high concentration of the sum of HCH. The situation is serious, considering that the sample was taken from an area dedicated for public use, not an industrialized area.

In sediment L2, some heavy metals (especially arsenic, manganese, and chromium) pose a greater problem than POPs. The concentration of PCDD/Fs measured by bioassay analysis is also alarming. All of this suggests that the accumulation here is more associated with industrial influence than contamination related to obsolete pesticides, which differs from the situation in sediment L1.

The highest level of the three isomers of hexabromocyclododecane (HBCD) was measured in a sample from one crater. This brominated flame retardant was mainly used in polystyrene foams for building insulation. Some polystyrene foams were observed at the sampling site and are considered a major source of that contaminant. However, measured levels are not high enough to raise significant concerns.

Levels of DDT, 16 PAHs, and hydrocarbons C_{10} – C_{40} in the sediment sample from the Dnipro River in Zaporizhzhia represent a major health concern among the observed contamination in the evaluated seven samples.

5 Annexes

5.1 Annex 1: A Brief Characterization of Harmful Substances Monitored in This Study

C_{10}-C_{40} hydrocarbons: The determination of the concentration of C_{10}-C_{40} hydrocarbons results in the amount of non-polar extractable compounds (NEC) of both petroleum and non-petroleum origin present in the matrix (MŽP ČR 2008). Chemically, these are mainly fats, oils, and petroleum products (Kuráň et al. 2011). The European standard EN 14039 is used for the determination of C10-C40 hydrocarbons. According to this standard, all hydrocarbons with a boiling point between 175 °C and 525 °C, e.g. alkanes from $C_{10}H_{22}$ to $C_{40}H_{82}$, isoalkanes, cycloalkanes, alkylbenzenes, alkylnaphthalenes and polycyclic aromatic hydrocarbons, are determined by gas chromatography unless they are adsorbed on a Florisil column during purification. It does not apply to the quantitative determination of volatile hydrocarbons (ČSN EN 2005). The chromatographic method determines a narrower range of compounds in the range of hydrocarbons C_{10} - C_{40} than the method used for the determination of NEC.

Non-polar extractable compounds (NEC): Extractable compounds are divided into two chemically distinct groups: polar and non-polar. Nonpolar extractable compounds (NEC) are aliphatic, alicyclic, aromatic and alkylaromatic hydrocarbons with long or branched chains. They were previously referred to as because they are the predominant constituents of petroleum and its products. These are substances that are difficult to biodegrade and have been monitored mainly in water bodies that are discharged with wastewater, but also because of various emergency situations (Maidlová 2010). This indicator, which is in decline due to the toxicity and harmfulness of the solvents used for determination and is being replaced by the sum of C_{10}-C_{40} hydrocarbons (Kuráň et al. 2011), was defined as the mass concentration of organic compounds that can be extracted from a water sample with trichlorotrifluoroethane and determined spectrometrically in the infrared part of the spectrum after removal of polar compounds.

Cyanides are white crystalline substances containing carbon and nitrogen in the molecule. A variety of elements such as sodium, potassium, and others may be present as cations. Cyanides may also contain toxic metals as cations. These can include cadmium, lead, and many other metals. Sodium cyanide and potassium cyanide are the most common compounds in this group. Cyanides are soluble in both water and alcohol. Cyanides are used in metallurgy, the chemical and photographic industries, and in the production of plastics (nylon). They can also be found in the manufacture of rubber, explosives, and fuel. Sodium and potassium cyanide are important agents in the electrochemical plating and hardening of steel. Cyanides can also be used in the mining industry to extract gold and silver from minerals. Cyanides are produced in combustion processes and are used in several industries (Botz 2001; MŽP 2021a). Cyanides are not stable when they enter water or soil, so bioaccumulation in aquatic organisms is unlikely. They can evaporate rapidly from water and soil into the air as hydrogen cyanide, especially at low pH. They are subject to microbial degradation. Cyanides do not bind to soil particles and may leach into groundwater. Cyanides are highly toxic to fish and other aquatic life. All cyanides are toxic to aerobic organisms including human by interfering with oxygen fixation by respiratory enzymes (MŽP 2021a). The presence of cyanide ions in food and their use in the industry are dangerous to people's health and safety. Compounds containing cyanide ions are rapidly acting poison, which mainly interferes with the process of cellular respiration, that results in several ailments and illnesses and even death (Jaszczak et al. 2017). Cyanides are a frequent source of fish poisoning in surface waters of long reaches of rivers (Arnika 2020; Cunningham 2005; Svobodová and Sehonová 2021).

Toxic metals: Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure (Tchounwou et al. 2012).

Arsenic (As), occurring naturally and via mining, metallurgy, and coal burning (Bencko 1984; Bhattacharya et al. 2007; Rasheed et al. 2016), poses acute inhalation risks (gastrointestinal and nervous system effects) (Rahman et al. 2011; Rodriguez et al. 2003). Chronic exposure leads to skin irritation, neurological issues (Chen et al. 2013; Tsai et al. 2003; Tseng et al. 2003). IARC designates arsenic and arsenic trioxide as a human carcinogen, strongly linked to lung and bladder cancer; evidence for other cancers is partial (IARC 2012). Non-carcinogenic risks include foetal development, children's neurodevelopment, nervous system impact, and heart/vessel diseases (EFSA CONTAM 2009).

Cadmium (Cd), a highly toxic element found naturally in soil, is prevalent in the environment due to human activities (Genchi et al. 2020b; Kubier et al. 2019; Musilova et al. 2017). Its primary route of human exposure is through the ingestion of contaminated foods (Hellstrom et al. 2007; Hosseini et al. 2013; Perez and Anderson 2009) and water (Genchi et al. 2020b). Prolonged exposure leads to cadmium accumulation in the kidneys, causing kidney disease, fragile bones, and lung damage. Chronic exposure is associated with hypertension, arthritis, anaemia, cardiovascular disease, diabetes, hypoglycaemia, headaches, osteoporosis, and an elevated risk of cancer (Nordberg et al. 2022). Furthermore, cadmium adversely affects the female reproductive system (Chen et al. 2015; Ju et al. 2012; Lin et al. 2015). Mitigating sources of cadmium exposure is crucial for safeguarding human health and preventing associated detrimental effects. Cadmium is frequently detected in urine samples from communities affected by mining (Suta et al. 2020) or metallurgy, and it is also observed in sediments in those areas (Grechko et al. 2021; Matoušková et al. 2023). IARC classifies cadmium and its compounds as carcinogenic to humans (Group 1); (IARC 2023).

Chromium (Cr) exists naturally in minerals and is widely used in manufacturing, including metallurgy, textiles, papermaking, and various products like dyes and fertilizers. Its environmental presence stems from landfill leaching, ore extraction, and petroleum/coal combustion (Dellantonio et al. 2008; Jin et al. 2014). Chromium (VI) causes skin issues, respiratory problems, weakened immunity, and kidney/liver damage, inducing oxidative stress and DNA/protein damage (Guertin et al. 2004; Song et al. 2012). Inhalation of its compounds leads to nasal membrane ulcers, throat irritation, bronchitis, wheezing, and respiratory distress. Classified as group 1 by IARC. Remarkably, chromium (III) is vital for human nutrition, found naturally in vegetables, fruits, meats, yeasts, and grains (Anderson 1997; Pechova and Pavlata 2007).

Lead (Pb), a major global environmental health hazard, poses serious risks, particularly to young children, with approximately 80–90% of daily exposure occurring through food consumption (Krejpcio et al. 2005; Liu et al. 2010). Elevated blood lead levels are associated with neurodevelopmental issues in children, including attention-deficit disorders and learning disabilities (Flora et al. 2006). Chronic lead exposure disrupts various body functions, causing neurological, cardiovascular, hematologic, and reproductive issues, including central nervous system dysfunction and encephalopathy (Debnath et al. 2019; Pal et al. 2015; Rao et al. 2014). Lead exposure during pregnancy is linked to miscarriage, while prolonged exposure reduces male fertility (Amadi et al. 2017; Vigeh et al. 2011). Environmental impacts include lead binding to airborne dust particles, settling on vegetation, and its presence in soil and water (Nieder et al. 2018). Lead is cumulative and has a long half-life in bones, posing ongoing risks, especially during physiological changes. Lead is classified as a human carcinogen 2B (IARC 2023).

Mercury (Hg) occurs naturally in various forms, spread through erosion (MŽP 2021b), weathering, and anthropogenic sources like combustion processes, coal burning, and mining (Sundseth et al. 2017). Inhaling mercury vapor poses significant risks to the nervous, immune, digestive, respiratory, and renal systems, with symptoms ranging from neurological disorders to potential fatality (Basu 2023; Tchounwou et al. 2003). In aquatic settings, inorganic mercury transforms into highly toxic methylmercury (MeHg), accumulating in fish and shellfish and posing serious health risks upon consumption (Evers et al. 2013; Harris et al. 2003). MeHg adversely affects the nervous, cardiovascular, liver, kidney systems, and disrupts hormones, impacting developing fetuses and inhibiting plant growth (Kumari et al. 2020; Trasande et al. 2016). IARC classifies methylmercury compounds as possibly carcinogenic to humans (Group 2B); (IARC 2023).

Nickel (Ni), a transition element prevalent in the environment from both natural sources and human activities, poses risks to human health and the environment. Human exposure to nickel can result in various health issues, including allergies, cardiovascular and kidney diseases, lung fibrosis, and cancers of the lungs and nasal passages (Genchi et al. 2020a). Nickel compounds, classified as Group 1 human carcinogens by the International Agency for Cancer Research (IARC) in 1990 and reaffirmed in 2012 (IARC 2023), exhibit genotoxic and epigenotoxic effects. Chronic exposure to nickel, even over weeks, leads to sufficient nickel uptake with persistent effects observed after exposure cessation (Klein and Costa 2022). The toxicity of nickel is associated with mitochondrial dysfunctions and oxidative stress. Additionally, nickel-induced epigenetic alterations have been identified, contributing to genome perturbations (Klein and Costa 2022). Nickel poses dangers to aquatic organisms, leading to stricter limits in surface waters compared to drinking water (Fernandez-Luqueno et al. 2013; MŽP 2021b).

Copper (Cu) is a vital element for the human body, crucial for functions such as hormone secretion, nerve conduction, electron transfer, bone and connective tissue growth, and red blood cell synthesis. Despite its small quantity (50–120 mg) in the body, copper plays a critical role in various biochemical processes and its deficiency in adults can lead to blood and nervous system disorders (Ackah et al. 2014; Medeiros et al. 2012; Saracoglu et al. 2009). However, excessive copper intake can lead to health issues such as inflammation in the brain tissues, fatigue, hair loss, allergies, and even serious conditions like kidney dysfunction and cancer (Sobhanardakani et al. 2018). Environmental impacts highlight that copper, while essential for animals and plants, can become toxic to aquatic organisms in higher concentrations (Hossain and Rakkibu 1999).

Tin (Sn) exists in both inorganic and organic forms, with inorganic tin naturally occurring in the environment and organic tin compounds being anthropogenic pollutants (Ostrakhovitch 2022). While inorganic tin compounds have low toxicity, methylation reactions can convert them into more harmful methyltin forms. Organotins, used in economic development, have resulted in environmental pollution, particularly in aquatic ecosystems. Despite bans, organotins persist in the environment, posing risks to human health through endocrine disruption, immunotoxicity, neurotoxicity, hepatotoxicity, and genotoxicity (Ostrakhovitch 2022).

Manganese (Mn), essential for humans, faces anthropogenic enrichment, particularly in occupational settings like mining and alloy production, and environmental exposure from industrial emissions and contaminated water (Lucchini et al. 2015). Mn overload, impacting the central nervous system, can result in motor and cognitive impairment, with neurological disorders like manganism observed in occupational inhalation exposures. O'Neal and Zheng (2015) underscores evolving research, linking Mn exposure to Parkinson's-like symptoms in various environmental contexts.

Other metals that were found in the samples included antimony, barium, beryllium, cobalt, selenium, and silver. Information about their effects on environment and human health can be found elsewhere (Mayfield et al. 2014; van et al. 2005; Winder 2004).

Polycyclic aromatic hydrocarbons (PAHs) represent a very broad range of different substances characterized by the fact that they contain condensed aromatic nuclei in their molecule and do not carry any heteroatoms or substituents. Pure compounds are white or yellowish crystalline solids. They are sparingly soluble in water but readily soluble in fats and oils. A summary of the PAHs monitored by the US EPA is given in Table xx.

PAHs are among the most common pollutants formed during the combustion of any carbonaceous material unless the combustion is perfect. This includes the combustion of almost all types of carbonaceous fuels. PAHs are toxic to a wide range of living organisms. Their primary hazards are carcinogenicity, mutagenicity, and teratogenicity. Some PAHs that are not carcinogenic can have mutually reinforcing effects. Their effects on whole populations of organisms are therefore serious. The most problematic property of PAHs is their persistence, i.e. their ability to resist natural degradation processes and to bioaccumulate (especially in fats). When emitted during combustion processes, they are capable of long-range transport through the atmosphere (in the form of adsorbed soot grains and dust particles). Traces of these substances have been found even in the most remote parts of the world. PAHs are strongly adsorbed to sediments in water bodies, which therefore act as reservoirs for these substances. A major risk is the accumulation of benzo(a)pyrene in aquatic organisms, to which is benzo(a)pyrene highly toxic. This compound is most dangerous PAH in terms of human health effects, for which the mechanism by which it directly damages the genetic information of cells has been elucidated (ATSDR 1995; MŽP 2021c; Smejkal 2013)[6, 7], it is also considered as carcinogenic to human (1) according to IARC (2023).

From the point of view of water and hygiene, the most toxic PAHs (benzo[ghi]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene and fluoranthene) have been identified by Decision No 2455/2001/EC as priority substances of very high concern for the aquatic environment under the Directive.

Table A1: Polycyclic Aromatic Hydrocarbons monitored by US EPA (Smejkal 2013).

Name	CAS	name	CAS
naphthalene	91-20-3	benzo[ghi]perylene	191-24-2
acenaphthene	83-32-9	benz[a]anthracene	56-55-3
acenaphtylene	208-96-8	chrysene	218-01-9
Fluorene	86-73-7	benzo[b]fluoranthene	205-99-2
phenanthrene	85-01-8	benzo[k]fluoranthene	207-08-9
anthracene	120-12-7	benzo[a]pyrene	50-32-8
fluoranthene	206-44-0	dibenz[ah]anthracene	53-70-3
Pyrene	129-00-0	indeno[1,2,3-cd]pyrene	193-39-5

Benz(a)anthracene is a solid. There is no commercial production of this compound. Benz(a)anthracene is possibly carcinogenic to humans (2B); (IARC 2023). It is very toxic to aquatic organisms. It may cause long-term effects in the aquatic environment. The chemical may

bioaccumulate in aquatic organisms. It is strongly recommended that this chemical not be released into the environment (National Center for Biotechnology Information 2024d).

Benzo[a]pyrene is a liquid. Poses a threat to the environment. Easily penetrates soil and contaminates groundwater or nearby waterways. Benzo[a]pyrene (along with other PAHs) is released into the atmosphere as a component of smoke from forest fires, industrial processes, vehicle exhaust, cigarettes, and the combustion of fuels (such as wood, coal, and petroleum products). This substance is used for research purposes only. Benzo[a]pyrene is reasonably anticipated to be a human carcinogen and is a potent mutagen. It is of public health concern because of its possible effects on industrial workers, as an environmental contaminant, and as a component of tobacco smoke. It is very toxic to aquatic organisms. Bioaccumulation of this chemical may occur in fish, plants, and molluscs. The substance may cause long-term effects in the aquatic environment. It is strongly recommended that this chemical not be released into the environment (National Center for Biotechnology Information 2024b). Benzo[a]pyrene is classified as a human carcinogen (Group 1) by the IARC (2023).

Benzo(b)**fl**uoranthene is a solid. Benzo(b)fluoranthene is a component of coal tar pitch, which is used in industry as a binder for electrodes. It is also a component of creosote, which is used to preserve wood. B(b)F has some use as a research chemical. Benzo[b]fluoranthene is a probable human carcinogen (2B), based on no human data and sufficient data from animal bioassays (IARC 2023). This substance may be environmentally hazardous. Particular attention should be paid to air and water quality (National Center for Biotechnology Information 2024f).

Benzo[k]**fl**uoranthene is a probable human carcinogen (2B), based on no human data and sufficient data from animal bioassays (IARC 2023). This substance may be environmentally hazardous. Particular attention should be paid to air and water quality. Bioaccumulation of this chemical may occur in crustaceans and fish (National Center for Biotechnology Information 2024g).

Indeno(1,2,3-cd)pyrene forms yellow plates or needles with greenish-yellow fluorescence. There is no known use for this compound other than research. Indeno(1,2,3-cd)pyrene is possibly carcinogenic to humans (2B); (IARC 2023). This substance may be hazardous to the environment. Particular attention should be paid to air and water quality. Bioaccumulation of this chemical may occur in fish (National Center for Biotechnology Information 2024e).

Dibenz[ah]anthracene is a probable human carcinogen (2A); (IARC 2023). It is very toxic to aquatic organisms. The substance may cause long-term effects in the aquatic environment. Bioaccumulation of this chemical may occur along the food chain. It is strongly recommended that this chemical not be released into the environment (National Center for Biotechnology Information 2024c).

Naphthalene is possibly carcinogenic to humans (2B); (IARC 2023). It is toxic to aquatic organisms. The substance may cause long-term effects in the aquatic environment. Bioaccumulation of this chemical may occur along the food chain, e.g. in fish (National Center for Biotechnology Information 2024a).

Organochlorine pesticides (OCPs) in our study represent substances such as DDT, HCH (including lindane), and HCB. All of them were used in large quantities, and many places are still contaminated by them today. These are substances that individually affect human health, but it is also not possible to exclude their synergistic effect. For example, one study has reported OCP to trigger anti-androgenic effects in men and estrogenic effects in women (Freire et al. 2014). *„According to the data of MAPU, 8,470.6 tons of products of the POPs group were used in 1967 and 1968 in Ukraine,"* from which majority was DDT (MEPU 2007).

Dichlorodiphenyltrichloroethane (DDT), a globally recognized organochlorine insecticide in use since 1945, has played a significant role in agriculture and the control of vector-borne diseases, particularly malaria since 1955. Its inclusion in the initial list of Persistent Organic Pollutants (POPs) regulated by the Stockholm Convention led to restrictions on its use, with the World Health Organization permitting its reintroduction solely for vector-borne disease control in select tropical countries in 2006. The physicochemical properties of DDT, coupled with its remarkable persistence—characterized by a half-life of up to 30 years—contribute to its association with various health and societal problems. These issues stem from DDT's accumulation in the environment and its biomagnification in living organisms, as highlighted by Mansouri et al. (2017). The Stockholm Convention, listing DDT in Annex B, strictly regulates its production and use (Stockholm Convention 2010).

The term DDT generally refers to the commercial pesticide formulation that includes several related compounds. Consequently, the usage of DDT implies the release of at least six derivatives in the following relative amounts: p,p=-DDT> o,p=-DDT> p,p=-DDE> o,p=-DDE> p,p=-DDD> o,p=-DDD (Haller et al. 1945). Each para, para p,p=-substituted isomer is more abundant than the corresponding ortho, para o,p=-substituted one. The three major components, p,p=-DDT, p,p=-DDE, and p,p=-DDD are generally referred to in the literature as DDT, DDE, and DDD, respectively, and as isomers (or metabolites, although not always correct or the case); (Hellou et al. 2013).[10] Our use of DDT, DDE, and DDD without a prefix relates to both p,p=isomers and o,p=isomers.

Initially employed during World War II to safeguard soldiers and civilians from malaria and other insect-borne diseases, DDT continued post-war for disease control and agricultural purposes, notably on crops such as cotton. While its application against mosquitoes persists in certain countries to control malaria, DDT's stability and pervasive use have resulted in residues being found globally. Up to 50% of applied DDT can persist in the soil for 10-15 years, with traces even detected in the Arctic (Stockholm Convention 2019).

One of the most well-known toxic effects of DDT is eggshell thinning in birds, particularly birds of prey, as documented in Rachel Carson's influential work, "Silent Spring" (Carson 1962). This impact led to bans on DDT in numerous countries during the 1970s.[11] Despite these bans, DDT continues to be detected in food globally. Although residues in domestic animals have diminished, food-borne DDT remains a primary exposure source for the general population. Long-term exposure to DDT has

[10] The chemical nomenclature for these three prevalent structures is 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane for p,p DDT, 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene for p,p DDE, and 1,1-dichloro-2,2-bis (p-chlorophenyl)ethane for p,p DDD

[11] Environmental research on organochlorine contaminants (OCs) has been ongoing since the 1940s. One book, Silent Spring by Rachel Carson (1962), is unanimously cited as raising awareness of the dual role of synthetic chemicals, "the good and the bad sides". The book describes the eggshell thinning discovered in birds when the spraying of dichlorodiphenyltrichloroethane (DDT) was initiated to eradicate disease, especially malaria. This book played a major role in generating environmental awareness in the population at large, including scientists, because it was written in an accessible style.

been associated with chronic health effects, including its detection in breast milk, raising concerns about infant health (Stockholm Convention 2019). The findings of Carson are echoed in environmental literature such as "Our Stolen Future" (Colborn et al. 1997), emphasizing reproductive effects linked to DDT exposure (Hellou et al. 2013).

DDT exposure poses significant risks to human health, manifesting in neurological effects, liver effects, reproductive effects, and immunological effects, including neurodevelopmental impacts (ATSDR 2022; Dallaire et al. 2004). Additionally, DDT and its derivatives are recognized as endocrine-disrupting chemicals (Turusov et al. 2002). Compounds like DDE and DDD, proposed to be more persistent than the parent compound (Teeyapant et al. 2014), exhibit higher toxicity and ecotoxicity (Johnson and Finley 1980; Mansouri et al. 2017). DDT is a probable human carcinogen (2A); (IARC 2023).

Notably, high levels of DDT have been found in free-range chicken eggs, particularly in the vicinity of DDT production sites, obsolete pesticide stockpiles, and waste incinerators and dumpsites where DDT-containing waste was disposed (Dvorska et al. 2009; Dvorská et al. 2007; Hlebarov et al. 2005; Jayakumar et al. 2005; Khwaja et al. 2005; Mng'anya et al. 2005; Petrlik et al. 2022; Skalsky et al. 2006). Higher concentrations of DDT were found in free-range eggs from sites in post-Soviet countries in general, including Ukraine (Petrlik et al. 2016; Petrlik et al. 2018)

POPs, including DDT, exhibit a tendency to bind to small particles in the soil, starting to accumulate in sediments shortly after application (Barnhoorn et al. 2009). The fate and transport of DDT in sediment–water systems depend on various site-specific characteristics, environmental conditions, and geo-technical factors, encompassing topography, geology, tidal influences, and sediment composition. DDT in sediments can undergo transformation or partial degradation under suitable environmental conditions. Unfortunately, the resultant degradation products remain as toxic and persistent as the original pesticides. The half-life of DDT in sediments varies between 2 and 25 years (Augustijn-Beckers et al. 1994; Chattopadhyay and Chattopadhyay 2015).

High levels of DDT in sediments have been observed in the vicinity of contaminated sites, legacy production areas, and obsolete pesticide stockpiles (Jayakumar et al. 2005; Kohušová et al. 2010; Petrlik et al. 2006). This observation underscores the persistent environmental impact of DDT, necessitating ongoing monitoring and management efforts.

Hexachlorocyclohexanes (HCHs): Lindane (the gamma isomer of HCH) has been used as a broad-spectrum insecticide for seed and soil treatment, foliar applications, tree and wood treatment, and against ectoparasites in both veterinary and human applications (POP RC 2006b). Lindane is persistent, easily bioaccumulates in the food chain, and bioconcentrates rapidly. There is evidence of long-range transport and toxic effects (immunotoxic, reproductive, and developmental effects) in laboratory animals and aquatic organisms. Lindane is classified as human carcinogen (Group 1) by IARC (2023).

High levels of lindane and other HCH isomers were found in free range chicken eggs, from the vicinity of lindane production sites, obsolete pesticide stockpiles, and/or waste incinerators and dumpsites where the waste containing HCHs was disposed of (Agarwal et al. 2005; Blake 2005; Kleger et al. 2006). An extremely high concentrations were found, for example, in the vicinity of the Tintareni landfill in Moldova and abandoned lindane production site in Porto Romano, Albania (Kleger et al. 2006; Petrlik et al. 2022).

Alpha- and Beta-HCH are highly persistent in water in colder regions and may bioaccumulate and biomagnify in biota and Arctic food webs. These chemicals are subject to long-range transport, classified as probable human carcinogens (2B) to humans (IARC 2023), and have adverse effects on wildlife and human health in contaminated regions (UNEP 2020). Lindane is highly toxic to wildlife, including fish, bees, birds, and mammals (US EPA 2002). The half-life of lindane in humans is less than a day, while the half-life of its major metabolite (beta-HCH) is seven years. Therefore, it is more reliable to measure the latter.

Prenatal exposure to β-HCH has been correlated with altered thyroid hormone levels, which could affect brain development. Studies have shown that all isomers of HCH might reasonably be anticipated to cause cancer in humans (US EPA 2002). Cox et al. (2007) linked β-HCH to increase prevalence of diabetes.

Lindane is listed in Annex A to the Stockholm Convention with specific exemptions for the use of lindane as a human health pharmaceutical for the control of head lice and scabies as a second-line treatment (decision SC-4/15). Alpha- and beta-HCH are listed in Annex A to the Stockholm Convention without specific exemptions (decisions SC-4/10, SC-4/11) (UNEP 2020).

Polychlorinated biphenyls (PCBs) were produced until the 1980s in large volumes and they were used in industry as heat exchange fluids, in electric transformers and capacitors, and as additives in paint, carbonless copy paper, and plastics (Stockholm Convention 2019). Approximately 1.3 to 2 million tonnes of PCB were industrially produced in various countries from 1929 to the 1980s (Breivik et al. 2002; Weber et al. 2018). Twelve PCB congeners are considered as dioxin-like PCBs because of their effects and similar properties to PCDD/Fs (European Commission 2012; van den Berg et al. 2006). These congeners are listed as unintentionally produced POPs in Annex C to the Stockholm Convention (Stockholm Convention 2010). Technical mixtures of PCBs are characterised by six,[12] sometimes seven[13] indicator PCB congeners. Maximum levels in food are set for six indicator PCB congeners in food in the EU (European Commission 2012; European Commission 2016).

Polychlorinated naphthalenes (PCNs) were produced for similar uses to PCBs, so they are their predecessors in some way. PCNs make effective insulating coatings for electrical wires. Others have been used as wood preservatives, as rubber and plastic additives, for capacitor dielectrics, and in lubricants. To date, intentional production of PCN is assumed to have ended (Stockholm Convention 2017). They are also unintentionally generated during high-temperature processes in the presence of chlorine, similarly to PCDD/Fs and dl PCBs.

The following PCN congeners were measured in the samples for this study: PCN 4, PCN 9, PCN 18, PCN 20, PCN 41, PCN 42, PCN 52, PCN 56, PCN 66, PCN 70, PCN 73, PCN 74, and PCN 75. None of them exceeded LOQ level in measured samples.

Short-chain chlorinated paraffins (SCCPs) are a group of POPs added by governments to the Stockholm Convention for global elimination in 2017. Chlorinated paraffins (CPs) are complex mixtures of certain organic compounds containing chloride: polychlorinated n-alkanes. SCCPs can be used as a plasticiser in rubber, paints, adhesives, and flame retardants for plastics as well as an extreme-pressure lubricant in metal-working fluids (Stockholm Convention 2017). SCCPs are toxic to aquatic organisms at low levels, disrupt endocrine function, and are suspected to cause cancer in humans (POP RC 2015). SCCPs are other additives in plastics that might also be expected in waste

[12] PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180.
[13] PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180.

imported to and/or produced in Thailand. They were often used in the manufacture of wires and cables (POP RC 2009).

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants (BFRs) that include substances listed in the Stockholm Convention for global elimination, such as PentaBDE (2009), OctaBDE (2009), and DecaBDE (2017). PBDEs are additives mixed into plastic polymers that are not chemically bound to the material and therefore leach into the environment. They have already been identified in samples from other localities in Thailand (Bystriansky et al. 2018; Petrlik et al. 2017).

PBDEs have adverse effects on reproductive health as well as developmental and neurotoxic effects (POP RC 2006a; POP RC 2007a; POP RC 2014). DecaBDE and/or its degradation products may also act as endocrine disruptors (POP RC 2014).

PentaBDE has been used in polyurethane foam for car and furniture upholstery, and Octa- and DecaBDE have mainly been used in plastic casings for electronics. OctaBDE formed 10%-18% of the weight (Stockholm Convention 2016) of CRT television and computer casings and other office electronics made of acrylonitrile butadiene styrene (ABS) plastic. DecaBDE forms 7%-20% of the weight (POP RC 2014) of many different plastic materials, including high-impact polystyrene (HIPS), polyvinylchloride (PVC), and polypropylene (PP), used in electronic appliances. As this study examines samples from sites affected by the presence of electronic waste and/or by its incineration, all the above-mentioned PBDEs were part of the main focus of our investigation.

Hexabromocyclododecane (HBCD) is a brominated flame retardant primarily used in polystyrene building insulation. HBCD is an additive mixed into plastic polymers that is not chemically bound to the material and therefore may leach into the environment. HBCD is highly toxic to aquatic organisms and has negative effects on reproduction, development, and behaviour in mammals, including transgenerational effects (POP RC 2010). HBCD is also found in packaging materials, video cassette recorder housings, and electric equipment.

HBCD was listed in Annex A of the Stockholm Convention for global elimination with a five-year specific exemption for use in building insulation that expired for most Parties in 2019 (Stockholm Convention 2013).

Novel brominated flame retardants (nBFRs) are a group of chemicals that in many cases replaced the already restricted BFRs. A group of six novel BFRs was chosen for the analyses in environmental samples from the localities included in this study. Different sources list different chemicals among this group, but only a few of them are measured in the environment. Recent studies also show that nBFRs are becoming widespread in the environment, including in food, particularly in some Asian countries (Shi et al. 2016). A review of the levels of BFRs in soil concluded that: *"Although further research is required to gain baseline data on NBFRs in soil, the current state of scientific literature suggests that NBFRs pose a similar risk to land contamination as PBDEs"* (McGrath et al. 2017).

The scientific panel of the EFSA evaluated 17 "emerging"[14] and 10 "novel"[15] BFRs in 2012 and suggested that: *"There is convincing evidence that tris(2,3-dibromopropyl) phosphate (TDBPP) and dibromoneopentyl glycol (DBNPG) are genotoxic and carcinogenic, warranting further surveillance of their occurrence in the environment and in food. Based on the limited experimental data on environmental behaviour, 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and hexabromobenzene (HBB) were identified as compounds that could raise a concern for bioaccumulation"* (EFSA CONTAM 2012). EFSA's panel also stated that for most of the BFRs that were evaluated, there was not sufficient data about their presence in the environment for meaningful conclusions to be drawn.

Decabromodiphenyl ethane (DBDPE) was introduced in the early 1990s as an alternative to DecaBDE in plastic and textile applications (Ricklund et al. 2010). It was used mainly in wire coatings and polystyrene, in both cases as a replacement for DecaBDE. This widespread contaminant is a highly hydrophobic compound (with a log Kow of 11.1); (Covaci et al. 2011). DBDPE has been identified in sewage sludge (De la Torre et al. 2012), indoor dust (Ali et al. 2011; Julander et al. 2005) outdoor dust (Anh et al. 2018; Muenhor et al. 2010), chicken eggs (Tlustos et al. 2010), and food in general (Shi et al. 2016; Tlustos et al. 2010).

BTBPE was first produced in the 1970s and is used as a replacement for OctaBDEs (Hoh et al. 2005). It has been identified in various abiotic media (dust, the atmosphere, sediment, water) and biotic media (zooplankton, mussels, fish, aquatic birds' eggs, honey, chicken eggs, or food in general) (Ali et al. 2011; Anh et al. 2018; Hoh et al. 2005; Julander et al. 2005; Mohr et al. 2014; Petrlik 2016; Petrlik et al. 2017; Poma et al. 2014; Wu et al. 2011).

This compound has the ability to bioaccumulate and to biomagnify in aquatic food webs (Law et al. 2006; Wu et al. 2011). Similarly, to DecaBDE, a commercial mixture of BTBPE was found to contain brominated dioxins (PBDD/Fs) and/or to support their formation during the treatment of ABS plastic (Ren et al. 2017; Tlustos et al. 2010; Zhan et al. 2019). BTBPE has been measured in increased concentrations in Indonesia during passive air sampling conducted in 2005–2006 (Lee et al. 2016).

[14] The group of emerging BFRs included: BEH-TEBP – Bis(2-ethylhexyl) tetrabromophthalate, BTBPE – 1,2-Bis(2,4,6-tribromophenoxy)ethane, DBDPE – Decabromodiphenyl ethane, DBE-DBCH – 4-(1,2-Dibromoethyl)-1,2-dibromocyclohexane, DBHCTD – 5,6-Dibromo-1,10,11,12,13,13-hexachloro-11-tricyclo[8.2.1.02,9]tridecene, EH-TBB – 2-Ethylhexyl 2,3,4,5-tetrabromobenzoate, HBB – 1,2,3,4,5,6-Hexabromobenzene, HCTBPH – 1,2,3,4,7,7-Hexachloro-5-(2,3,4,5-tetra-bromophenyl)- bicyclo[2.2.1]hept-2-ene, OBTMPI – Octabromotrimethylphenyl indane (OBIND in this study), PBB-Acr – Pentabromobenzyl acrylate, PBEB – Pentabromoethylbenzene, PBT – Pentabromotoluene, TBNPA – Tribromoneopentyl alcohol, TDBP-TAZTO – 1,3,5-Tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-trione, TBCO – 1,2,5,6-Tetrabromocyclooctane, TBX – 1,2,4,5-Tetrabromo-3,6-dimethylbenzene, and TDBPP – Tris(2,3-dibromopropyl) phosphate.

[15] The group of novel BFRs included: BDBP-TAZTO – 1,3-Bis(2,3-dibromopropyl)-5-allyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, DBNPG – Dibromoneopentyl glycol, DBP-TAZTO – 1-(2,3-Dibromopropyl)-3,5-diallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, DBS – Dibromostyrene, EBTEBPI – N,N'-Ethylenebis(tetrabromophthalimide), HBCYD – Hexabromocyclododecane (HBCD or HBCDD are more of the abbreviations used for this chemical, already listed in Annex A to the Stockholm Convention), HEEHP-TEBP – 2-(2-Hydroxyethoxy)ethyl 2-hydroxypropyl 3,4,5,6-tetrabromophthalate, 4'-PeBPO-BDE208 – Tetradecabromo-1,4-diphenoxybenzene, TTBNPP – Tris(tribromoneopentyl) phosphate, and TTBP-TAZ – Tris(2,4,6-tribromophenoxy)-s-triazine.

HBB has commonly been used for the manufacture of paper, wood, textiles, plastics, and electronic goods (Watanabe and Sakai 2003; Yamaguchi et al. 1988) and it is *"likely widely distributed, as verified both by chemical analysis and estimated properties"* (Arp et al. 2011).

The laboratory at the Department of Food Chemistry and Analysis of the University of Chemistry and Technology, Prague, routinely measures six nBFRs in environmental samples, including the egg samples for this study: 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBB), octabromo-1,3,3-trimethylpheny-1-indane (OBIND), 2,3,4,5,6-pentabromoethylbenzene (PBEB), and pentabromotoluene (PBT).

Out of this group, BTBPE, DBDPE, and HBB are monitored more often in environmental samples (Mohr et al. 2014; Munschy et al. 2011; Poma et al. 2014; Vorkamp et al. 2015).

Dechlorane Plus (DP), a flame retardant in use since the 1960s, is prevalent in electrical coatings, plastic roofing, and polymeric systems. Its release during production, use, and recycling increased post the global elimination of PBDEs (Rauert et al. 2018). Persistent and chemically stable, Dechlorane Plus binds to organic carbon, limiting bioavailability and hindering biodegradation. Despite being bioaccumulative, it exhibits adverse effects on mammals and humans, including oxidative damage, neurodevelopmental toxicity, and potential endocrine disruption (POP RC 2021). Concentrations of Dechlorane Plus are notably high in water and sediments near e-waste recycling areas. However, comprehensive studies across various environmental matrices, especially in these areas, remain limited (Dvorska 2023; Li et al. 2018). It was listed in the Annex A to the Stockholm Convention in 2023 (Stockholm Convention 2023).

Per- and Polyfluoroalkyl Substances (PFASs), in 2018 comprised a diverse class of over 4,500 persistent fluorinated chemicals, including PFOS, widely used in packaging, textiles, and plastics (OECD 2018). Concerns about their environmental prevalence led to international calls for limiting production and developing safer alternatives (Blum et al. 2015). More recently NIEHS published that PFASs are a group of nearly 15,000 synthetic chemicals, according to a chemicals database maintained by the U.S. Environmental Protection Agency (NIEHS 2023). In this study, samples were analysed for 31 individual PFAS or their groups (see Table A2). Two major manufacturing methods, electrochemical fluorination (ECF) and telomerisation, produce PFASs. ECF results in complex mixtures, while telomerisation produces purer linear or isopropyl forms (van Hees 2016).

In animal studies, long-chain PFASs exhibit adverse effects such as liver toxicity, disruption of lipid metabolism, immune and endocrine system disruption, neurobehavioral effects, neonatal toxicity, and tumors (Lau et al. 2007; Post et al. 2012). The European Food Safety Authority (EFSA) significantly reduced the permitted intake of PFOS due to health concerns (EFSA CONTAM 2018).

We can encounter PFASs in various consumer items, including single-use paper food packaging, cosmetics, or clothing (Dewapriya et al. 2023; Strakova et al. 2023a; Strakova et al. 2023b; Strakova et al. 2021), and therefore, it is not surprising that the highest concentration was found during sediment research in Belarus in 2012 at the outlet channel of the municipal wastewater treatment plant in Mogilev (Nezhyba et al. 2012). In a study from Malaysia, PFASs concentrations in sediments were generally lower than those measured in water and biota (Mohamad et al. 2022). PFAS remain in the environment for an unknown amount of time (NIEHS 2023), which is why they are also referred to as 'forever chemicals'.

Perfluorooctanesulfonic Acid (PFOS) and its salts, listed in the Stockholm Convention, are extremely persistent and associated with cancer, neonatal mortality, developmental delays, and endocrine

disruption (Du et al. 2013; Jacquet et al. 2012; Luebker et al. 2005; POP RC 2006c; Thomford 2002a; Thomford 2002b). In animal studies, PFOS has been shown to cause cancer, neonatal mortality, delays in physical development, and endocrine disruption PFOS-related substances have been used in the packaging and paper industries in both food packaging and consumer products.

Perfluorooctanic Acid (PFOA): Governments added PFOA to the Stockholm Convention in 2019 for global elimination. PFOA, with diverse uses, is linked to delayed pregnancy, reduced semen quality, and various human health issues (Di Nisio et al. 2018; Fei et al. 2009; Joensen et al. 2009; POP RC 2016).

Perfluorohexane Sulfonate (PFHxS), used in various applications, was the last of the PFASs substances added to the Stockholm Convention (Stockholm Convention 2022). It persists in the environment, with exposure primarily through food, water, and consumer products, causing immune system suppression and various health impacts (Ali et al. 2019; POP RC 2019).

Unintentionally produced POPs represent a large group of POPs which were not produced intentionally and added to any products, but they occurred as unintentional by-products at any phase of the production of chemicals or disposal of waste containing halogenated compounds. These POPs are listed in Annex C to the Stockholm Convention (Stockholm Convention 2010). We have also added polybrominated dioxins (PBDD/Fs), which are not yet listed in Annex C, to our study.

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), dioxins in short belong to a group of 75 polychlorinated dibenzo-p-dioxin (PCDD) congeners and 135 polychlorinated dibenzofuran (PCDF) congeners, of which 17 are of toxicological concern. Levels of PCDD/Fs and dl-PCBs are expressed in total WHO-TEQ, calculated according to toxic equivalency factors (TEFs) set by a WHO expert panel in 2005 (van den Berg et al. 2006). These WHO TEFs were used to evaluate dioxin-like toxicity in the pooled samples of chicken eggs, soils, sediments, and dust samples in this study.

Chlorinated dioxins (PCDD/Fs) are known to be extremely toxic. Numerous epidemiological studies have revealed a variety of human health effects linked to chlorinated dioxin exposure, including cardiovascular disease, diabetes, cancer, porphyria, endometriosis, early menopause, alteration of testosterone and thyroid hormones, and an altered immune system response, among others (Schecter 2012; White and Birnbaum 2009). Laboratory animals given dioxins suffered a variety of effects, including an increase in birth defects and stillbirths. Fish exposed to these substances died shortly after the exposure ended. Food (particularly from animals) is the major source of exposure for humans (BRS 2017).

Chlorinated dioxins became known to the public in the 1970s as a result of contamination with Agent Orange, a defoliant pesticide mixture sprayed by the U.S. during the Vietnam War.[16] The production of 2,4,5 T pesticide as a basic ingredient for Agent Orange left one of the most seriously contaminated sites in Europe (Kubal et al. 2004; Weber et al. 2008; Zemek and Kocan 1991) and workers sick with many symptoms of exposure to the most toxic of dioxin congeners, 2,3,7,8-TCDD (Bencko and Foong 2013; Pelclová et al. 2006).

[16] According to estimates provided by the Government of Vietnam, 400,000 people were killed or maimed by the pesticide; 500,000 children were born with birth defects ranging from retardation to spina bifida, and an additional two million people have suffered cancers or other illnesses, which also can be related to dioxins as impurities in the Agent Orange mixture. It is estimated that in total, the equivalent of at least 366 kilograms of pure dioxin were dropped. (York and Mick 2018)

Dioxin-like polychlorinated biphenyls (dl PCBs): 12 congeners of PCBs exhibit toxicological properties similar to dioxins and are often referred to as "dioxin-like PCBs" (dl-PCBs). They are suggested to be a part of the total TEQ levels (van den Berg et al. 2006), and this study includes their levels in total PCDD/Fs + dl PCBs TEQ concentrations in all samples except HNK-SOIL-01. The other PCB congeners do not exhibit dioxin-like toxicity but have a different toxicological profile and are referred to as "non-dioxin-like PCBs" (ndl-PCBs) (European Commission 2011).

Pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) are primarily produced unintentionally during combustion, as well as during thermal and industrial processes. They also occur as a by-product during the production of chlorinated hydrocarbons such as perchloroethylene, trichloroethylene, carbon tetrachloride, or pesticides. In the past, they were produced intentionally as pesticides or technical substances. Perchloroethylene is widely used in dry cleaning, and trichloroethylene and carbon tetrachloride have been used extensively as degreasing agents and as solvents for other chlorine-containing compounds. PeCB was used as a component in PCB products, in dyestuff carriers, as a fungicide, as a flame retardant, and as a chemical intermediate in the production of the pesticide quintozene (POP RC 2008).

In high doses, HCB is lethal to some animals and, at lower levels, adversely affects their reproductive success. Researchers also found out that HCB, similarly to other organochlorinated compounds, has a transplacental transfer (Sala et al. 2001). HCB has been found in food of all types (BRS 2017).

Although globally, the consumption of HCB-contaminated food is the primary source of HCB exposure, other potential exposure pathways include the inhalation of HCB-contaminated air, skin contact, in utero exposure, and from breast milk (Reed et al. 2007). The study also found that in addition to cancer, the human health effects associated with HCB exposure encompass systemic impairment (thyroid, liver, bone, skin) and damage to the kidneys and blood cells, as well as the immune and endocrine systems. It also causes a teratogenic effect and impairs nervous systems.

PeCB is very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment (POP RC 2007b).

Hexachlorobutadiene (HCBD) occurs as a by-product during the production of the same chlorinated hydrocarbons as PeCB and HCB, as a part of the so-called "hexa-residues". It is also formed unintentionally during the incineration processes of such substances as acetylene and chlorine residues. HCBD is very toxic to aquatic organisms and has been shown to cause kidney damage and cancer in animal studies as well as chromosomal aberrations in occupationally exposed humans (Balmer et al. 2019; Pohl et al. 2001; POP RC 2012). Systemic toxicity following exposure via oral, inhalation, and dermal routes may include fatty liver degeneration, epithelial necrotising nephritis, potentially causing chronic inflammation, central nervous system depression, and cyanosis (Balmer et al. 2019; BRS 2017).

5.2 Annex 2: Complete Results of Chemical Analyses of Sediment and Soil Samples from Craters in Zaporizhzhia and Kherson

Table A2: Complete results of chemical analyses

Chemicals	L1	L2	L3	L4	CH	K1	K2	Units
Dry Matter Content	65,3%	62,8%	82,1%	59,4%	97,3%	95,9%	81,2%	%
NEC	16 330	718	272	490	354	NA	NA	mg/kg dm
Hydrocarbons C10-C40	20 705	2 350	<100	<100	<100	NA	NA	mg/kg dm
Cyanides	<0,02	<0,02	<0,02	<0,02	<0,02	NA	NA	mg/kg dm
Acenaphthene	200	0,337	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Acenaphthylene	8,13	0,213	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Anthracene	22,4	0,583	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Benzo(a)anthracene	78,7	0,816	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Benzo(a)pyrene	35,6	0,456	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Benzo(b)fluoranthene	47,3	1,06	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Benzo(k)fluoranthene	36,8	1,33	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Dibenzo(a,h)anthracene	1,73	<0,05	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Fluorene	1,2	0,312	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Fluoranthene	196	2,46	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Chrysene	75,8	1,34	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Indeno(1,2,3cd)pyrene	5,98	0,162	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Naphthalene	5,65	<0,05	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Phenanthrene	45,5	0,746	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Pyrene	130	2,2	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
Benzo(g,h,i)perylen	4,45	0,151	<0,05	<0,05	<0,05	NA	NA	mg/kg dm
16 PAHs	895,24	12,166	0	0	0	NA	NA	mg/kg dm
Antimony	1,44	5,83	<0,611	1,92	3,82	NA	NA	mg/kg dm
Arsenic	7,41	24,5	<0,611	2,83	4,24	NA	NA	mg/kg dm

Boron						NA	NA	
Baryum	101	90,9	17,7	74,5	144	NA	NA	mg/kg dm
Berylium	0,744	<0,804	<0,611	<0,889	<0,515	NA	NA	mg/kg dm
Cadmium	0,299	10,5	0,484	1,31	0,113	NA	NA	mg/kg dm
Cobalt	6,15	6,75	0,793	3,8	3,48	NA	NA	mg/kg dm
Chromium	26,5	256	14,2	40,4	20,9	NA	NA	mg/kg dm
Copper	28,6	55,1	3,56	10	11,1	NA	NA	mg/kg dm
Lead	23	171	8,73	14,4	12,8	NA	NA	mg/kg dm
Manganese	402	1 820	126	805	222	NA	NA	mg/kg dm
Mercury	9,99	0,379	<0,050	0,082	<0,050	NA	NA	mg/kg dm
Nickel	11,5	81,9	4,58	9,08	10,8	NA	NA	mg/kg dm
Selenium	0,521	2,55	<0,611	<0,889	<0,515	NA	NA	mg/kg dm
Silver	<1,33	<1,60	<1,22	<1,77	<1,03	NA	NA	mg/kg dm
Tin	5,4	10,5	2,16	5,64	2,79	NA	NA	mg/kg dm
DDD	2 467,47	6,357	0,18	0,447	1,216	0,159	14,236	ng/g dm
DDE	404,46	7,981	0,240	0,562	2,88	0,058	17,899	ng/g dm
DDT	<0,02	1,418	<0,02	<0,02	0,146	<0,02	32,602	ng/g dm
Sum of DDT	2 872	16	0,42	1	4	0	65	ng/g dm
alfa-HCH	2,30	0,063	0,035	0,067	0,042	0,449	0,402	ng/g dm
beta-HCH	8,24	0,185	0,038	0,088	0,074	<0,02	0,976	ng/g dm
gama-HCH	9,09	0,041	0,031	0,039	<0,02	0,032	0,134	ng/g dm
Sum HCH	19,64	0,29	0,10	0,19	0,12	0,48	1,51	
PCB 28	<0,02	4,35	0,054	0,168	0,183	<0,02	0,036	ng/g dm
PCB 52	5,95	3,48	0,054	1,459	0,230	<0,02	0,092	ng/g dm
PCB 101	15,1	6,83	0,178	2,730	0,619	<0,02	0,213	ng/g dm
PCB 118	17,6	6,99	0,244	3,211	0,821	<0,02	0,269	ng/g dm
PCB 138	10,8	4,93	0,228	1,501	0,685	<0,02	0,339	ng/g dm
PCB 153	6,08	3,68	0,189	0,944	0,486	<0,02	0,217	ng/g dm
PCB 180	1,69	1,12	0,044	0,159	0,113	<0,02	0,122	ng/g dm

7 PCB cong.	57,209	31,384	0,992	10,171	3,137	0,000	1,288	ng/g dm
Hexachlorobenzene (HCB)	2,29	10,8	0,172	0,188	0,059	<0,02	0,075	ng/g dm
Pentachlorobenzene (PeCB)	1,03	3,31	0,047	0,066	<0,02	<0,02	0,061	ng/g dm
Hexachlorobutadiene (HCBD)	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
Sum of OCPs	2894,883	30,196	0,742	1,458	4,417	0,698	66,384	ng/g dm
Sum of PBDEs	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ng/g dm
Sum of HBCD	<0.05	2,718179	0,093678	<0.05	4,339474	<0.05	51,97838	ng/g dm
PCDD/Fs – DR CALUX	6	10	3,6	1,4	1,1	<0,2	2,8	pg TEQ/g dm
dl PCBs – DR CALUX	29	3,7	3	0,43	0,59	0,24	0,71	pg TEQ/g dm
PCDD/Fs + dl PCBs – DR CALUX	35	13,7	6,6	1,83	1,69	0,24	3,51	pg TEQ/g dm
SCCP C_{10}-C_{13}	<5	<5	<5	<5	<5	57,0	12,2	ng/g dm
MCCP C_{14}-C_{17}	<10	191	<10	<10	<10	<10	290	ng/g dm
PFBA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFPeA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFHxA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFHpA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFOA	<0,02	<0,02	0,100	<0,02	<0,02	<0,02	0,054	ng/g dm
PFNA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFDA	<0,02	<0,02	<0,02	0,024	<0,02	<0,02	<0,02	ng/g dm
PFUnDA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFDoDA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFTrDA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFTeDA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFHxDA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFODA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFPrS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFBS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFPeS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFHxS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm

PFHpS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFOS	<0,02	0,025	<0,02	<0,02	0,028	<0,02	0,043	ng/g dm
PFNS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFDS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PFUnDS	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	ng/g dm
PFDoDS	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	ng/g dm
PFTrDS	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	<0,04	ng/g dm
PFOSA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
N-MeFOSA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
N-EtFOSA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
HFPO-DA	<0,04	<0,04	<0,04	0,144	<0,04	0,104	<0,04	ng/g dm
ADONA	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
9Cl-PF3ONS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
11Cl-PF3OudS	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
Sum of PFASs	0,000	0,025	0,100	0,168	0,028	0,104	0,098	ng/g dm
PCN 4	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 9	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 18	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 20	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 41	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 42	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 52	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 56	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 66	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 70	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 73	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 74	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PCN 75	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	ng/g dm
PBDE 28	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm

PBDE 47	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 49	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 66	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 85	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 99	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 100	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 153	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 154	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 183	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBDE 196	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	ng/g dm
PBDE 197	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	ng/g dm
PBDE 203	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	ng/g dm
PBDE 206	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	ng/g dm
PBDE 207	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	ng/g dm
PBDE 209	<5	<5	<5	<5	<5	<5	<5	ng/g dm
BTBPE	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
DBDPE	<10	<10	<10	<10	<10	<10	<10	ng/g dm
anti-DP	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
syn-DP	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
HBBz	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	0,662	ng/g dm
α-HBCD	<0.05	0,647	<0.05	<0.05	0,569	<0.05	8,35	ng/g dm
β-HBCD	<0.05	0,100	<0.05	<0.05	0,134	<0.05	1,73	ng/g dm
γ-HBCD	<0.05	1,97	0,094	<0.05	3,64	<0.05	41,9	ng/g dm
Sum of HBCD	<0.05	2,718	0,094	0,000	4,339	0,000	51,978	ng/g dm
OBIND	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	ng/g dm
PBEB	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm
PBT	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	ng/g dm

NA – not analysed

5.3 Annex 3: Comparative Analysis of Sediment Contamination in Various River Systems

1. Huveaune River, France (Kanzari et al., 2014): The study of Huveaune River sediments revealed varying concentrations of contaminants. PAH levels ranged from 572 to 4235 μg·kg−1 dw, with a mean of 1966 ± 1104 μg·kg−1 dw. PCB concentrations ranged from 2.8 to 435 μg·kg−1 dw, with a mean of 148 ± 164 μg·kg−1 dw. Organochlorine pesticides ranged from 0.07 to 1.25 μg·kg−1 dw, with a mean of 1.23 ± 1.29 μg·kg−1 dw. While most levels complied with guidelines, specific stations exhibited PCB concentrations exceeding safe limits, suggesting potential toxicity, especially at the river's mouth. Molecular indices indicated pyrolytic and biogenic sources of hydrocarbons (Kanzari et al. 2014).
2. Ammer River, Germany, and Liangtan River, China (Liu et al., 2013): A comparative study between the Ammer River and Liangtan River indicated variations in PAH concentrations. The Ammer River showed higher levels, ranging from 184 to 26,780 μg·kg−1 dw, with a mean of 6126 ± 8006 μg·kg−1 dw, primarily from diffuse sources or legacy pollution. The Liangtan River exhibited ongoing point source emissions, with PAH concentrations ranging from 1399 to 11,202 μg·kg−1 dw (Liu et al. 2013).
3. Durance River and Berre Lagoon, France (Kanzari et al., 2015): The investigation revealed elevated levels of aliphatic hydrocarbons, PAHs, PCBs, and pesticides. Aliphatic hydrocarbons showed high levels, ranging from 1399 to 11,202 μg·kg−1 dw. PAH concentrations in Durance River ranged from 57 to 1528 μg·kg−1 dw, and in Berre Lagoon from 512 to 863 μg·kg−1 dw. PCB concentrations ranged from 0.03 to 13.13 μg·kg−1 dw, with higher levels in northern Berre Lagoon (stations B1 and B3) (Kanzari et al. 2015).
4. Portuguese Coastal and River Areas (Ribeiro et al., 2016): The comprehensive review highlighted the occurrence of POPs in Portuguese aquatic environments. PAHs were found in Sado estuary sediments, reaching concentrations up to 7,350 ng g(-1). PCBs were detected in Ria de Aveiro sediments, with levels up to 62.2 ng g(-1). POPs, including PCBs, were found in biota, such as sentinel fish from the Douro River estuary exhibiting PCB concentrations up to 810.9 ng g(-1), and pesticides in bivalves from the Sado River estuary (Ribeiro et al. 2016).
5. Toce River, Northern Italy (Marziali et al., 2017): Despite low concentrations, legacy contaminants impacted benthic invertebrates in Toce River sediments. Traditional metrics showed no significant differences upstream/downstream, emphasizing the need for specialized tools in risk assessment (Marziali et al. 2017).
6. Somesu Mic River, Romania (Barhoumi et al., 2019): The study provided baseline information on organic and inorganic contaminations. Trace metals (Cd, Cr, Cu, Pb, Ni, Zn) ranged from 0.04 to 236.8 mg kg(-1) dw. Total PAHs, PCBs, and OCPs ranged from 24.8 to 575.6, 2.7 to 252.7, and 2.1 to 44.3 ng g(-1) dw, respectively (Barhoumi et al. 2019).
7. Port of Prahovo, Danube, Serbia (Radomirović et al., 2023): The investigation assessed concentrations, sources, and ecological risks of heavy metal(loid)s and PAHs. The most abundant heavy metal was Cu (38.3 mg/kg), and Σ16PAHs concentrations ranged from 25 to 112.5 μg/kg. The mean and maximum values of HMs and PAHs obtained in this study were below the national regulatory limits and within environmental criteria (Radomirović et al. 2023).
8. Nura River, Kazakhstan (Petrlik et al. 2015): The study investigated contamination of the river Nura and its surroundings by mercury, methylmercury, polychlorinated biphenyls (PCBs), and organochlorinated pesticides (OCPs). Samples of sediments, soils, fish, and eggs were collected during field visits conducted in 2013 and 2014. The research aimed to determine mercury concentrations along the river profile and

identified localized contamination hotspots, particularly with elevated PCB levels. Additionally, methylmercury in fish exceeded reference doses. Overall, the study revealed significant pollution concerns in the river Nura region during the period under investigation (Petrlik et al. 2015).

9. Rivers in three Western Balkan countries (**Šír** et al. 2015): In 2015 - 2016, a study investigated heavy metal contamination in the Balkans, focusing on sites in Montenegro, Bosnia and Herzegovina, and Serbia. Samples of soils, sediments, water, and biological sources near industrial areas revealed elevated levels of nickel, chromium, arsenic, and cadmium, surpassing local limits. Sediments were specifically analysed for heavy metals. Areas near ash landfills showed higher concentrations of heavy metals. Tuzla's river water exhibited pollution, impacting aquatic life. Fish from the Sava and Cehotina Rivers exceeded mercury advisories, and onions near Tuzla's ash landfills had elevated cadmium (Šír et al. 2015).
10. Labe, VItava, Odra Rivers in the Czech Republic (Mach 2015; Mach and Petrl**í**k 2016): The study conducted a thorough analysis of river sediment and fish samples across various locations in the Czech Republic, focusing on POPs such as PCBs, PCDD/Fs, PAHs, PFASs, and BFRs. With a primary aim to contribute to the historical monitoring of POPs contamination in Czech water ecosystems and investigate heightened PCB concentrations in the Labe (Elbe) River, the research analysed 15 sediment samples from diverse sites. The findings revealed elevated concentrations of indicator-PCBs, surpassing legislative criteria at specific locations. Additionally, certain sites exhibited increased levels of PCDD/Fs, affecting both sediments and fish. Sediment PAH concentrations exceeded legal criteria at specific locations, while PFASs levels were relatively low. The study also identified the presence of BFRs in sediments, exceeding normal values for PBDEs.
11. Loei, Map Ta Phut and Tha Tum hot spots in Thailand (Bystriansky et al. 2018): In the 2018 study focusing on ten hotspot areas in Thailand, including industries like metallurgy, gold mining, pulp and paper, petrochemicals, power generation, cement kilns, waste incineration, and a potentially contaminated landfill fire, elevated concentrations of various pollutants were identified. Specifically, in locations such as Loei, Map Ta Phut, and Tha Tum, increased concentrations of heavy metals in sediments were observed, surpassing pollution criteria and background levels (Bystriansky et al. 2018). Figures included arsenic concentrations reaching 162.17 mg/kg and cadmium reaching 39.25 mg/kg in Loei sediments, while Map Ta Phut showed increased levels of arsenic (highest at 1.48 mg/kg), mercury (highest at 1062.24 mg/kg for zinc), cadmium (highest at 2.95 mg/kg), and copper (highest at 23.56 mg/kg). Similarly, Tha Tum demonstrated elevated concentrations of arsenic (highest at 47.77 mg/kg), cadmium (highest at 12.17 mg/kg), and chromium (highest at 402.55 mg/kg) in sediments. The study underscored the significant toxic pollution near industrial sites in Thailand and the need for effective remediation measures (Mach et al. 2018).

In conclusion, these studies underscore the importance of region-specific assessments and ongoing monitoring to understand and manage the environmental challenges posed by sediment contamination in various river systems.

Table A3: Comparison of concentrations of selected chemical substances detected in sediments within the above specified studies.

Chemical	This study (Zaporizhzhia, Dnipro River)	Study 1 (Huveaune River)	Study 3 (Durance River and Berre Lagoon)	Study 6 (Somesu Mic River, Romania)	Study 7 (Port of Prahovo, Serbia)	Study 8 (Nura River, Kazakhstan)	Study 9 (1) Pljevlja - Montenegro; 2) Tuzla – BiH; 3) Obrenovac -Serbia; Balkan st.)	Study 10 (1) Labe, Vltava, Bílina, Klíšský Creek; 2) Odra, Černý Creek)	Study 11 (1) Loei, 2) Map Ta Phut, and 3) Tha Tum, Thailand)
PAHs mg/kg dm	<0.05 - 895	0.572 – 4.235	0.057-1.528; 0.512-0.863	0.0248 – 0.5756	0.025 – 0.1125	NA	1) NA 2) NA 3) NA	1) 0.384 – 6.49 2) 43.3 – 90.2	1) NA 2) NA 3) 85 - 631
Sum of OCPs ng/g dm	0.742-2893	1.23 ± 1.29	0.02-7.15	2.1 – 44.3	NA	<LOD – 78.7	1) NA 2) NA 3) NA	NA	1) <LOD 2) <LOD – 1.294 3) <LOD
PCBs ng/g dm	<0.02 - 57	2.8 - 435	0.03 to 13.13	2.7 – 253	NA	0.81 – 34,920	1) NA 2) NA 3) NA	1) 1.26 – 361 2) 9.05 – 61.5	1) <LOD 2) <LOD – 0.258 3) <LOD – 2.2
Mercury mg/kg dm	<0.050 – 10	NA		NA	0.01 – 0.41	<LOD – 178	1) 0.38-0.50; 2) 0.37 – 0.50; 3) 0.35 – 0.90	NA	1) <LOD – 0.046; 2) 0.004 – 1.479; 3) 0.004 – 0.151
Arsenic mg/kg dm	<0.611 - 24.5	NA		NA	0.45 – 5.0	<LOD [17]	1) 27.1 – 41.3; 2) 32.4 – 42.3; 3) 28.8 – 49.9	NA	1) 0.188 – 162.17; 2) 0.213 – 27.719; 3) 0.137 – 47.772
Lead mg/kg dm	8.73 - 171	NA		12.3 – 131.4	1.7 – 19.0	<LOD - 232	1) 1.2 – 29.7; 2) <0.1 – 34.7; 3) 17.4 – 22.3	NA	1) NA 2) NA 3) 1.78 – 5.73

[17] Arsenic was not analysed in all samples in a study from Kazakhstan.

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Arnika is uniting people seeking a better environment. We believe that natural wealth is not only a gift, but also an obligation to save it for the future. Since its foundation, Arnika has become one of the most important environmental organisations in the Czech Republic. We base our activities on three pillars: engaging the public, professional arguments, and communication. Since the beginning, we have led public campaigns both in the Czech Republic and internationally. The organisation focuses on nature conservation, toxics and waste, access to information, and public participation in decision-making.

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Clean Air for Ukraine is a joint project of Arnika and an informal network of local non-governmental organizations from the industrial regions of Ukraine. Our objective is to improve access to information and strengthen public participation in decision-making. A public monitoring network of air pollution, analysis of soil, river sediments, and foodstuffs in five regions, and capacity building programmes for civil society are some of our main achievements. We bring the experience of transformation of the Czech Republic, involve scientists and experts in public campaigns, publish analyses, and suggest solutions.

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