European Union Water Initiative Plus for the
Eastern Partnership Countries (EUWI+)

Result 2

INVESTIGATIVE MONITORING OF THE DNIEPER RIVER BASIN

POLLUTANTS SCREENING

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Abbreviations

AA-EQS	Annual Average Environmental Quality Standard
BDE	Brominated diphenylethers
DCT	Data Collection Template
DSFP	Digital Sample Freezing Platform
d.w.	dry weight
EMBLAS	EU/UNDP project 'Improving Environmental Monitoring in the Black Sea'
EQSD	Environmental Quality Standards Directive, 2013/39/EU
ESI-QToF-MS	Electrospray Ionization Quadrupole Time of Flight Mass Spectrometry
FoA	Frequency of Appearance
FoE	Frequency of Exceedance
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LC/GC-HRMS	Liquid / Gas Chromatography-High Resolution Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
MAC-EQS	Maximum Allowable Concentration Environmental Quality Standard
NORMAN	NORMAN Association, Network of Reference Laboratories, Research Centers and Related Organisations for Monitoring of Emerging Environmental Substances
NTS	Non-target Screening
PNEC	Predicted No Effect Concentration
QS	Quality Standards for Groundwater Directive (2006/118/EC)
RBSPs	River Basin Specific Pollutants
SDL	Screening Detection Limit
SOP	Standard Operating Procedure
SS	Sampling site
ToR	Terms of reference
TV	Threshold Value
UkrSCES	Ukrainian Scientific Centre of Ecology of the Sea
WFD PS	Water Framework Directive Priority Substances, 2013/39/EU
w.w.	wet weight
WWTP	Wastewater Treatment Plant

1 EXECUTIVE SUMMARY

A first investigative screening of a wide-range chemical pollutants in surface water and biota samples has been conducted within the EUWI+ project in October 2020 at 27 sites in the Dnieper River Basin. Novel methodologies of wide-scope target screening of >2,200 and suspect screening of >65,000 organic pollutants were used for analysis of each sample. The results were complemented with target analyses of metals. Legacy pollutants brominated diphenylethers (BDEs) and dioxins and dioxin-like compounds were analysed in biota samples. The results provided a first overview on the pattern and extent of chemical pollution in the Dnieper River Basin, where several pollution 'hot-spots' were identified. Consequently, a follow-up investigation aiming at pollution cessation was recommended.

Out of 45 Water Framework Directive priority substances atrazine, cadmium and nickel were determined in concentrations above EQS limits according to Directive 2013/39/EU in surface water samples; as well as mercury and BDEs in biota samples. The target and suspect screening revealed 161 and 440 organic pollutants, respectively, to be present in at least one sample. In a simplified prioritization scheme, each detected substance was compared against its toxicity threshold value (Environmental Quality Standard (EQS) or Predicted No Effect Concentration (PNEC)).

A list of 21 candidate Dnieper River Basin Specific Pollutants was proposed for further monitoring and their eventual inclusion into the Dnieper River Basin Management Plan. Results of the screening were provisionally stored in the NORMAN Database System (https://www.norman-network.com/nds/) allowing for their retrospective analysis.

2 INTRODUCTION

The "Investigative monitoring of the Dnieper River Basin" had been organised within the European Union Water Initiative Plus for the Eastern Partnership project (EUWI+ 4 EaP) with the main goal to analyse surface water and biota samples from the Dnieper River Basin for the presence of a wide-range of organic and inorganic pollutants (heavy metals). The sampling was carried out from 7th to 16th of October 2020. During the survey samples of surface water at 27 sites and five samples of biota (fish) at five sites (cf. Table 2) have been collected. The sampling of surface water samples was performed by the team of experts from UKRSCES, Odesa. Biota samples were collected by experts from the Institute of Hydrobiology of the Ukrainian Academy of Sciences. Overall logistics, transport of samples and all analyses were coordinated by the Environmental Institute, Slovakia, which had been assigned for this screening by the EUWI+ project. The analyses were performed by the laboratories listed in Table 1.

Table 1: Overview of laboratories and analytical techniques used for analyses.

Institute/ laboratory	Parameters and matrix	Analytical technique
Environmental Institute (EI) and National Kapodistrian University of Athens (NKUA)	Wide-scope target, suspect and non-target screening in surface water and biota	LC-ESI-QTOF-HRMS
National Kapodistrian University of Athens (NKUA)	Heavy metals in biota and surface water	ICP-MS
Slovak National Dioxins Centre in Bratislava	Dioxins and dioxin-like compounds and brominated diphenyl ethers (BDEs) in biota	HRGC-EI-HRMS

The latest methodologies and infrastructure for data processing developed within the NORMAN network in support of the EU Chemicals Strategy (Dulio et al., 2020) and previously tested in the Joint Danube Survey 4 (Liska et al., 2020) were applied.

The main goals of the chemical screening were as follows:

- Analysis of WFD priority substances (PS) at selected sites in the Dnieper River Basin;
- Identification of potential Dnieper River Basin Specific Pollutants (RBSSs) in water and biota matrices by:
  - (i) wide scope target screening of specific compounds (>2,200 compounds, Annex II); and
  - (ii) suspect screening over 65,000 environmentally relevant compounds;
- Establishment of a chemical pollution baseline for the Dnieper River Basin as an extended starting point for future water quality monitoring compliant with WFD.

High resolution mass spectrometry data were archived in the Digital Sample Freezing Platform (DSFP; https://norman-data.net/Verification/; Alygizakis et al., 2019) developed by the NORMAN Association (https://www.norman-network.net/) and they can be revisited for retrospective analysis of any chemical substance detected within the applicability domain of the used analytical methodology.

The investigative monitoring was inspired by results of the previous screening campaigns in the Dniester River Basin (implemented in the frame of the Environment and Security Initiative (ENVSEC) with guidance from the UN Economic Commission for Europe (UNECE), Organization for Security and Co-operation in Europe (OSCE), UN Environment Programme (UNEP) and UN Development Programme (UNDP)), Siverskiy Donets (OSCE) and Joint Black Sea Surveys performed within the EU/UNDP 'Improvement of the Environmental Monitoring in the Black Sea' (EMBLAS) projects (http://emblasproject.org/). Similar state of the art analytical methodologies applied in all these projects within a span of two years allow for intercomparison of the results and provide an opportunity to establish a holistic view on the chemical pollution of two major Ukrainian river basin and the impacted Black Sea shelf into which they discharge.

3 SAMPLING SITES

All 27 sampling sites were located along the Dnieper River Basin (2,201 km); their GPS coordinates are in Table 2; corresponding spatial distribution is shown in Figure 1. The table provides also information on the sampling locations of the biota samples.

The selected sampling sites can be characterised with different proxy pressures that can be divided into several categories:

- Direct impact by pollution sources;
- Reference site;
- Influence of the Republic of Belarus;
- Wastewater channel from WWTP into the Dnieper River;
- Water used for production of drinking water;
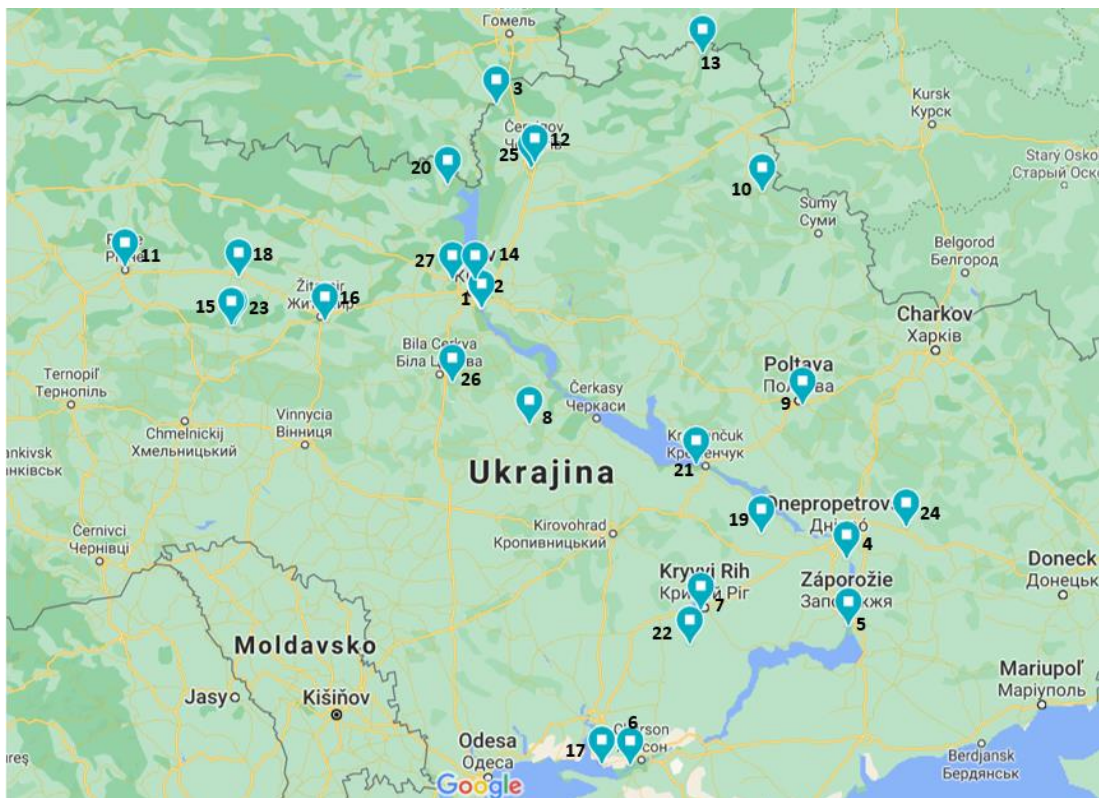- Chernobyl zone.

Figure 1: Map of sampling sites (source: Google maps).

Table 2: Sampling sites of the investigative monitoring of the Dnieper River Basin and their GPS coordinates. Only the five (out of originally 10 nominated) biota samples highlighted in green were collected for the follow up analysis.

№	Sampling site	Water	Biota*	Date of sampling	Weather conditions	GPS coordinates	
						Longitude	Latitude
1	Dnipro river (Kaniv reservoir) below the discharge of Kyivvodokanal (Vyshenka)	+	+	11.10.2020	Sunny (16°C)	30°38'0,09"E	50°19'0,48"N
2	Main canal for sewage - discharge of Kyiv-vodokanal - Bortnytsia aeration station	+		11.10.2020	Sunny (16°C)	30°38'51,46"E	50°19'32,6"N
3	Dnipro river (border with the Republic of Belarus, Chernihiv region, Kamianka)	+		11.10.2020	Cloudy, windless (16°C)	30°49'17,8"E	51°54'41,03"N
4	Dnipro reservoir, below Dnipro city	+	+	9.10.2020	Sunny (16°C)	35°8'38.78"E	48°18'44.52"N
5	Dnipro river, below Zaporizhzhia city	+	+	8.10.2020	Cloudy, windless (17°C)	35°9'57.84"E	47°45'32.53"N
6	Kosheva river, below the waste treatment facilities in Kherson	+		7.10.2020	Cloudy, windless (22°C)	32°28'31,43"E	46°35'32,81"N
7	Inhulets river, Kryvyi Rih (below the mouth of Saksahan river run into), hydrological station	+		8.10.2020	Sunny (22°C)	33°20'31,17"E	47°53'2,95"N
8	Ros river, Korsun-Shevchenkivskyi	+	+	12.10.2020	Sunny (18°C)	31°14'09.6"E	49°24'00.0"N
9	Vorskla river (Nyzhnimlyny reservoir), 144 km, 1,5 km bewlow Poltava city, below mouth of Kolomak river, at Poltava-Kharkiv road bridge (Hydromet)	+		9.10.2020	Sunny (15°C)	34°35'38,4"E	49°33'36"N
10	Seim river, 230 km, Pesky village of Putyvl district, border with the Russian Federation	+		10.10.2020	Cloudy, windless (19°C)	34°5'58.69"E	51°14'2.61"N
11	Ustia river, 24 km, below the wastewater treatment plant (WWTP) of "Rivnevodokanal", Rivne	+	+	13.10.2020	Cloudy, windless (19°C)	26°14'46.05"E	50°39'04.56"N

12	Desna river, below Chernihiv	+	+	11.10.2020	Sunny (12°C)	31°17'58,1"E	51°27'26,5"N
13	Desna river, border of Russian Federation, Muravii	+		10.10.2020	Cloudy, windless (19°C)	33°22'4,63"E	52°17'12,01"N
14	Desna river, 3 km, Desna drinking water intake, Kyiv	+	+	15.10.2020	Sunny (15°C)	30°34'8,4"E	50°33'3,6"N
15	Khomora river, Poninka	+	+	13.10.2020	Cloudy, windless (15°C)	27°33'33,5"E	50°11'19,0"N
16	Teteriv river, below Zhytomyr	+	+	14.10.2020	Cloudy, windless (15°C)	28'42'48,4"E	50°13'28,1"N
17	Dnipro estuary (transitional waters), Stanislav	+		7.10.2020	Cloudy, windless (21°C)	32°07'05,29"E	46°35'54,47"N
18	Slutch river, 203 km, drinking water intake, Novhorod-Volynskyi	+		13.10.2020	Cloudy, windless (17°C)	27'39'2"E	50'34'28,42"N
19	Samotkan river, Vilnohirsk, below mining site	+	+	9.10.2020	Sunny, windless (22°C)	34°5'18,96"E	48°31'14,16"N
20	Prypiat river, border with the Republic of Belarus, Chernobyl zone (Chornobyl)	+		14.10.2020	Cloudy, windless (15°C)	30°13'30,0"E	51'17'29,0"N
21	Dnipro river (Kremenchuk reservoir), 580 km, Kremenchuk, Vlasivskyi water intake SE "Kremenchukvodokanal" of Kremenchuk City Council	+		9.10.2020	Cloudy, windless (18°C)	33°17'9,6"E	49°4'51,6"N
22	Inhulets river, 265 km, Andriivka	+		8.10.2020	Cloudy, windless (22°C)	33°12'43,23"E	47°36'11,71"N
23	Khomora river, 52 km, drink water intake, Polonne	+		13.10.2020	Cloudy, windless (15°C)	27°35'47,24"E	50°11'37.49"N
24	Samara river, 139 km, hydrological point of the Samara river - Pavlohrad, 40 m above the railway bridge Pavlohrad-Lozova	+		9.10.2020	Sunny, windless (19°C)	35°52'14,73"E	48°34'20,99"N
25	Bilous river, Chernihiv	+		11.10.2020	Cloudy, windless (11°C)	31°15'12"E	51°25'6,2"N
26	Ros river, below Bila Tserkva, influence by wastewater "Bilotserkivvoda" LLC	+		12.10.2020	Sunny (18°C)	30°16'40.0"E	49°44'32.3"N
27	Irpin river, 28 km, Hostomel, mouth of Bucha river	+		11.10.2020	Cloudy, windless (12°C)	30°17' 6,42"E	50°33'5,76"N

- Fish samples: bream (*abramis brama)* from SS 1, 5, 8, 14 and roach (*rutilus rutilus)* from SS 4.

4 QUALITY ASSURANCE AND QUALITY CONTROL ASPECTS

All surface water samples for analysis of organic contaminants were sampled into newly purchased 5 l HDPE containers pre-cleaned with HPLC-grade methanol and stored in cooling boxes filled with cooling inserts at 4-8°C during the transport. A special car equipped with cooling facility was used for transport of samples from Ukraine to Slovakia at the constant temperature of 4°C. 500 mL of each surface water sample for determination of heavy metals were sampled into two pre-cleaned 250 ml HDPE containers, filtered on-site via 0.45 µm pore size nylon filter and stabilised with 1 mL of 1 M ultra-pure nitric acid.

Each specimen of biota (fish) was wrapped in pre-cleaned aluminum foil, put in a plastic zip-bag and deep-frozen after sampling at -20°C, until transport to Slovakia.

All samples were stored at 4°C (surface water) and -20°C (biota) until being processed. The samples were analysed within 30 days from the date of sampling.

All analyses were performed in laboratories accredited according to EN ISO/IEC 17025: 2005 and followed internal Standard Operation Procedures. Field blanks were collected and analysed. Procedural blanks were analysed for each batch of samples. If any signal was detected, it was subtracted from the signals of the samples. The potential loss of the substances during the sample preparation was considered and corrected for by the use of standard addition method for quantification. Internal standards were always spiked to all samples as part of quality control. The methodologies applied for Dnieper River Basin surface water and biota samples were identical to those applied in the Joint Black Sea Surveys (Slobodnik et al., 2016) and the Joint Danube Survey 4 (Liska et al. 2020).

5 METALS IN SURFACE WATER AND BIOTA SAMPLES

Introduction

One of the survey tasks was the determination of metals. In order to provide a comparable dataset for metals from the previous surveys (Dniester and Severskiy Donets), eight selected metals: cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), arsenic (As), chromium (Cr), copper (Cu), and zinc (Zn) were analysed in the surface water samples. Additionally, four WFD priority substances (PS) metals: Cd, Pb, Hg and Ni were analysed in the five biota samples.

Methods

Inductively coupled plasma – mass spectrometry (ICP-MS) analysis was conducted in the National Kapodistrian University of Athens (NKUA) on a Thermo Scientific iCAP RQ ICP-MS for the determination of metals and arsenic after acidification (surface water) or microwave digestion and dilution (biota). Kinetic energy discrimination (KED) was performed using helium for the reduction of interferences. Element-specific internal standards were added constantly with a fast on-line autosampler system. The ICP-MS method for both surface water and biota determinations was accredited according to EN ISO/IEC 17025: 2005. Water hardness, which is used in support of assessment of cadmium results, was determined to be in each water sample in the range of 100 -200 mg $CaCO_3$/l. Certified reference materials were used for the analysis of metals in biota.

Results

Surface water samples

Three out of four WFD PS metals (EQSD; EU, 2013) were determined in water samples.

Cadmium exceeded its AA-EQS of 0.15 µg/l **at seven sites**, with the highest concentration of **2.66 µg/l** at the **sampling site 5** (Dnipro river, below Zaporizhzhia city);

Nickel exceeded its AA-EQS of 4.0 µg/l only at the **sampling site 26** of the Ros river, below Bila Tserkva, influence of wastewater "Bilotserkivvoda" LLC (**6.14 µg/L**).

Mercury did not exceed its MAC-EQS of 0.07 µg/l at any of the sampling sites, the only detection was recorded at the **sampling site 16** (Teteriv river, below Zhytomyr; 0.04 µg/L).

Concentration profiles of the remaining non-WFD PS metals (Zn, Cu, Cr) and arsenic are shown in Figure 2. The adverse environmental impact of these substances was evaluated by comparing their concentration values against ecotoxicity limit values (EQS) set in the current legislation in Slovakia (national RBSPs).

Arsenic:

None of the dissolved concentrations determined in water samples was above the Slovak EQS (24 µg/L), the highest concentration was determined at the **sampling site 27** (Irpin river, 28 km, Hostomel, influence of the Bucha river; **10.60 µg/L**).

Zinc:

The dissolved concentrations in **16 water samples** were above the Slovak EQS value (9.6 µg/L); the highest exceedance was determined at the **sampling site 8** (Ros river, Korsun-Shevchenkivskyi; **61.7**

µg/L) and at the **sampling site 7** (Inhulets river, Kryvyi Rih; below the inflow of the Saksahan river; **38.4 µg/L**).

Copper:

The dissolved concentrations in **11 water samples** were above the Slovak EQS value (1.6 µg/L); the highest exceedance at the **sampling site 5** (Dnipro river, below Zaporizhzhia city; **9.39 µg/L**) and at the **sampling site 7** (Inhulets river, Kryvyi Rih, below the inflow of the Saksahan river; **6.06 µg/L**).

Chromium:

None of the dissolved concentration levels was above the Slovak EQS value (9.0 µg/L); the highest concentration was determined at the **sampling site 12** (Desna river, below Chernihiv; **3.89 µg/L**).
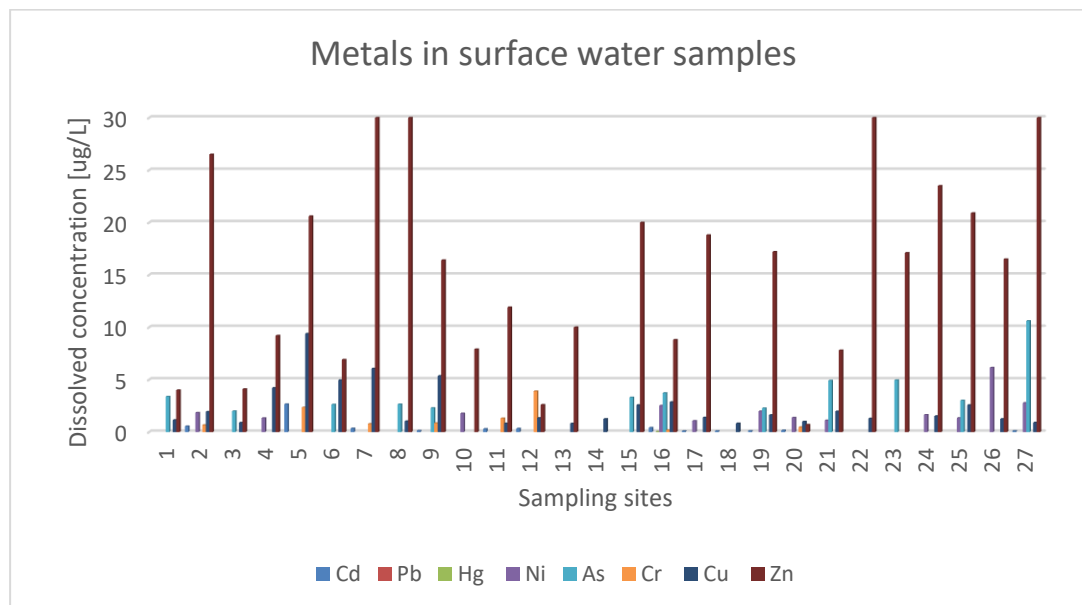
Figure 2: Summary overview of concentrations of metals in the Dnieper river water samples. For details of sampling sites, see Table 2.

Biota samples

Four WFD PS metals were analysed: Cd, Pb, Ni, and Hg. Mercury is the only metal legally required to be monitored in biota according to the EQSD and thus having its EQS, whereas the other metals were compared with their PNECs derived for freshwater biota in the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/).

Hg:

Mercury was determined only in one out of five biota samples at concentration of **30.2 µg/kg** in the **biota sample_14** (Desna river, 3 km, Desna drinking water intake, Kyiv) and thus exceeding its EQS value of 20 µg/kg.

Cd:

Cadmium was not determined above its LOD in any biota sample.

Pb:

Lead was not determined above its LOD in any biota sample.

Ni:

Nickel was determined in **biota sample_5** at concentration level of 11.7 µg/kg. In the NORMAN Eco-toxicology Database, the lowest PNECBio_fw was proposed as 23,700 µg/kg and thus there seems to be no need to consider its adverse ecotoxicological impact.

6 DIOXINS AND DIOXIN-LIKE COMPOUNDS

Methods

Fish muscle tissue samples were extracted by accelerated solvent extraction using n-hexane and diethylether solvent (9:1). This was followed by fractionation to PCDD/F, planar PCBs and non-planar PCBs (the same procedure for PBDEs); and analysed by HRGC-HRMS DFS. Quality confirmation and quantification has been performed using Isotope Dilution analysis. GC-EI-HRMS measurements were carried out on the Thermo Scientific DFS high resolution GC-MS system coupled to a Thermo Scientific TRACE GC ULTRA gas chromatograph. GC was operated in pulsed splitless injection mode. The injection volume was 1 μL. A 60 m Agilent J&W DB-5ms column (0.25 mm i.d. x 0.25 μm film thickness) was used with He as carrier gas. The magnetic sector mass spectrometer was automatically calibrated with perfluorotributylamine prior to each injection. In the used method LOQ was set for each sample separately. Values assigned as ,less 'than' (<) in Annex IV correspond to LOQ value of the substance for that particulate sample. All analyses were performed at the Slovak National Dioxins Centre in Bratislava.

Results

The determination of dioxins and dioxin-like compounds was performed in all biota samples. Three classes of compounds were included in this analysis: polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCB-DL). Each category comprises of the following contaminant:

- PCDDs: 2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD.
- PCDFs: 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF and OCDF
- PCB-DL: PCB 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, 189, 28, 52, 101, 138, 153 & 180 (the underlined PCBs – non dioxin-like (NDL) are not included in 2013/39/EU Directive).

According to the EQSD, EQS for dioxins and dioxin-like compounds in biota is a sum of PCDD+PCDF+PCB-DL (**6.5 ng/kg TEQ)**. Dioxins and dioxins-like compounds were determined in all five fish samples in the concentration range from 0.02 to 0.11 ng/kg TEQ. The highest determined concentration was found in **biota sample_1** (0.11 ng/kg TEQ), well below the EQS value. The highest content of sum of (non dioxin-like) NDL-PCBs (**1.66 μg/kg**) was determined in **biota sample_4**, whereas in the rest of the samples NDL-PCBs were in the range from 0.18 to 1.48 μg/kg. For all results, see Annex IV.
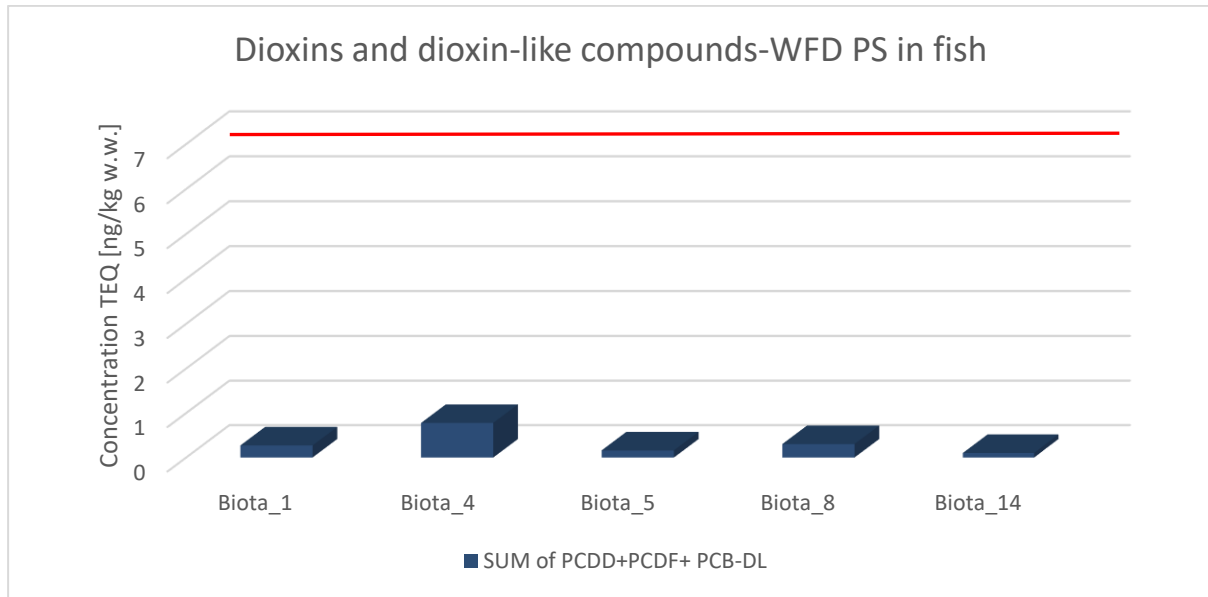
Figure 3: Concentration profile of dioxins and dioxin-like compounds expressed as a sum of PCDD+PCDF+PCB-DL in ng/kg w.w.TEQ in the biota (fish) samples. Red line represents EQS level (6.5 ng/kg w.w.TEQ) for biota. For details of samples, see Table 2.

7 BROMINATED DIPHENYLETHERS

The EQS for BDEs in biota (8.5 ng/kg w.w.) refers to the sum of concentrations of congener numbers 28, 47, 99, 100, 153 and 154. BDEs were determined in all five fish samples at concentration levels ranging from 0.97 to 18.56 ng/kg. The highest concentration was determined in biota sample_4 (18.56 ng/kg); exceeding the EQS more than two times. The second highest concentration was found in biota sample_8 (7.77 ng/kg). For all results, see Annex IV.
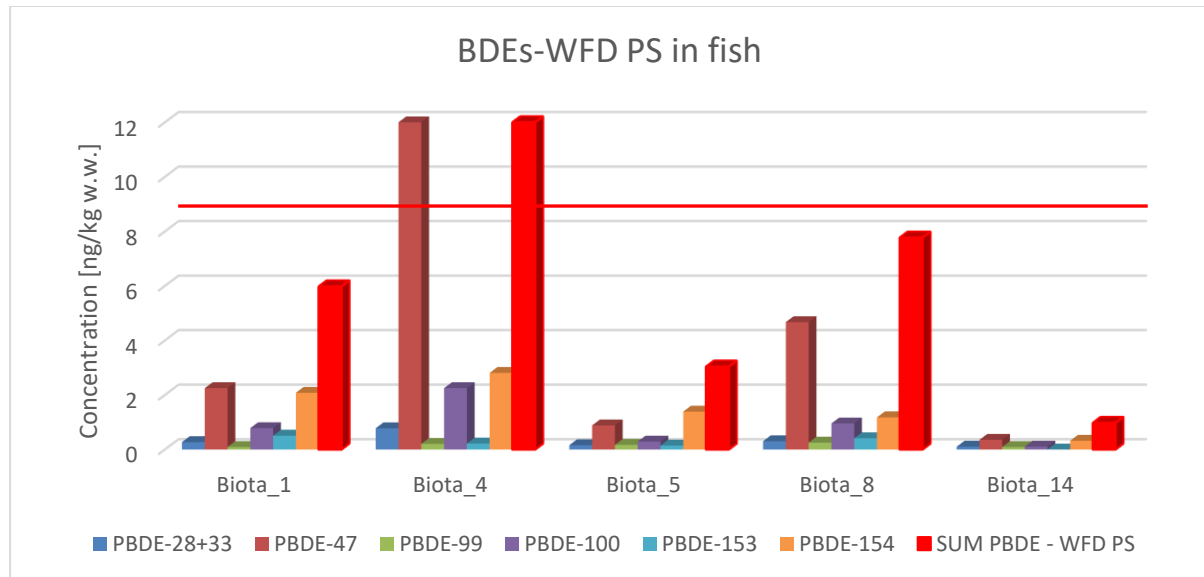

Figure 4: Concentration profile of brominated diphenylethers in biota (fish) samples. EQS for biota is calculated as a sum of all selected congeners (bars in red colour). Red line represents EQS (8.5 ng/kg w.w.) for biota. For details of samples, see Table 2.

8 TARGET, SUSPECT AND NON-TARGET SCREENING OF SURFACE WATER AND BIOTA SAMPLES BY LC-HRMS

Introduction

All collected 27 surface water and five biota samples were subjected to wide-scope target screening (2,232 substances; see Annex II) and suspect screening (>65,000 substances; see NORMAN Substance Database, https://www.norman-network.com/nds/susdat/). The obtained results provided a basis for the development of the list of Dnieper RBSPs.

Methods

Surface water samples were extracted using HORIZON SPE-DEX 4790 device (USA). The samples were concentrated on Atlantic HLB-M Disk with 47 mm disk holder following an automated extraction programme (Alygizakis et al., 2020). The extracts were evaporated using a gentle stream of nitrogen and reconstituted in 50:50 methanol:water (500 µL total volume extract). The extracts were then subjected to analysis by LC-HRMS.

The extraction of biota (fish muscle) was performed using an optimized multiresidue method for fish tissues (Dasenaki and Thomaidis, 2015). Briefly, 0.2 g freeze-dried biota sample was placed into a 15 mL centrifµge tube and extracted with 2 mL of Milli-Q water containing 0.1% formic acid (v/v) and 0.1% EDTA (w/v), 2 mL of methanol, and 2 mL of acetonitrile sequentially, using a vortex mixer (30 sec) and ultrasonic bath at 60°C for 20 min. The samples were centrifµged and the supernatants transferred to new plastic centrifµge tubes to precipitate lipids and remaining proteins at -20°C for 12 h. After an additional defatting step by liquid-liquid extraction with hexane (5 mL), the extract was collected in a glass tube, evaporated to dryness under a gentle steam of nitrogen at 40°C and reconstituted in 0.2 mL methanol/Milli-Q water, 50:50 (v/v). The extract was filtered throµgh a 0.22 µm RC syringe filter of 4 mm diameter (Phenomenex, USA) and transferred into a glass vial for LC-HRMS analysis.

LC-ESI-QTOF-MS analyses were conducted using an ultra high-performance liquid chromatographic (UHPLC) system with an HPG-3400 pump (Dionex Ultimate 3000 RSLC, Thermo Fischer Scientific, Dreieich, Germany) coupled to a QTOF mass spectrometer (Maxis Impact, Bruker Daltonics, Bremen, Germany) in NKUA and evaluated in the Environmental Institute, Slovakia.

Chromatographic separation was performed using an Acclaim RSLC C18 column (2.1 x 100 mm, 2.2 µm) from Thermo Fischer Scientific (Dreieich, Germany) preceded by a guard column of the same packaging material, thermostated at 30°C. For positive ionization mode (PI), the mobile phases were water/methanol 90/10 (solvent A) and methanol (solvent B), both containing 5 mM ammonium formate and 0.01% formic acid. For negative ionization mode (NI), the mobile phases consisted of water/methanol (solvent A) and methanol (solvent B) both acidified with 5 mM ammonium acetate. The adopted gradient elution programme was the same for both ionization modes, starting with 1% B with a flow rate of 0.2 mL min-1 for 1 min and it increased to 39% in 2 min (flow rate 0.2 mL min-1), and then to 99.9 % (flow rate 0.4 mL min^{-1}) in the following 11 min. Then, it was kept constant for 2 min (flow rate 0.48 mL min^{-1}), then the initial conditions were restored within 0.1 min, kept for 3 min and then the flow rate decreased to 0.2 mL min^{-1}. The injection volume was 5 µL.

The QTOF-MS system was equipped with an electrospray ionization interface (ESI), operating in positive and negative mode, with the following operation parameters: capillary voltage 2,500 V (PI) and

3,500 V (NI); end plate offset, 500 V; nebulizer pressure 2 bar; drying gas 8 L min⁻¹ and gas temperature 200°C. The QTOF-MS system was operated in data-independent (broadband collision-induced dissociation (bbCID)) acquisition, as well as in data dependent (Auto MS/MS) acquisition mode and recorded spectra over the range m/z 50−1,200, with a scan rate of 2 Hz. A QTOF-MS external calibration was performed daily with the manufacturer's solution. The instrument provided a typical resolving power (FWHM) between 36,000-40,000 at m/z 226.1593, 430.9137 and 702.8636.

The wide-scope screening method was fully validated for its linearity, trueness via recoveries, reproducibility and matrix effect by using a set of representative substances. For more details, one may consult reference Gago-Ferrero et al. (2020). Compounds were quantified with standard addition calibration curve (minimum 5-point spike calibration curves) and isotope dilution for specific substances (Flunixin-d3, BPA-d16, Ranitidine-d6, Diuron-d6, SDZ-d4, Fenbendazole d3, Sulfadimethoxine-d4, SDD-d4, Cetirizine-d3, Atrazine-d5, Mefenamic acid-d3, Amisulpride-d5). Quality control checks were carried out throμghout the sequence including the use of internal standards for check of sensitivity and infusion of reference calibrants at the beginning of each chromatographic run. The HRMS equipment was always calibrated before the analysis.

The Screening Detection Limit (SDL) was reported for the contaminants that were determined by the wide-scope LC-QToF-MS screening method. The SDL is established as the lowest concentration level tested for which a compound is detected in all spiked samples, at the expected retention time and with specific mass error of the precursor ion. In the in-house developed method, the SDL was established as the concentration level at which the thresholds of (i) retention time and (ii) mass accuracy of the precursor ion were satisfied. The SDL is not compound-specific, but a generic reporting value derived after method validation. Thus, the SDL for the compounds included in the database of this screening method was 0.63 ng/L in surface water, and 1.25 μg/kg for biota, respectively. For the compounds detected with the screening method, a further thoroμgh compound-specific validation was performed for quantitation purposes. Spiked samples, with the detected compounds and structure-related isotope labeled compounds (IS), were treated with the same method and analyzed. Compound-specific LOD and LOQ values and recoveries were calculated and all detected contaminants were quantitatively determined by the standard addition method with IS.

In order to evaluate the risk of a compound at a polluted site, or to determine its overall priority in the context of other pollutants, quality targets, often referred to as Predicted No Effect Concentration (PNEC), were used. In order to to assess the potential ecotoxicological threat of the detected contaminants their experimental concentration levels were benchmarked against their provisional PNECs, retrieved from the NORMAN Ecotoxicology database (https://www.norman-network.com/nds/ecotox/, last accessed in December 2020) (Dulio at al., 2020). The Ecotoxicology database contains PNECs for the freshwater, sea water, sediments (marine, freshwater) and biota (marine, freshwater). The occurrence of contaminants with concentration levels above PNEC represents potential risk for the ecosystem. In cases when no experimental data on the toxicity of detected substances were available, predicted PNECs (P-PNECs) were derived by Quantitative Structure Toxicity Relationship (QSTR) models (Aalizadeh et al., 2017). For risk assessment purposes, if more PNEC values were available, the lowest PNEC was selected in the order of (a) legacy environmental quality standard (EQS); (b) verified experimental PNEC; (c) *in silico* predicted PNEC.

8.1 WIDE-SCOPE TARGET SCREENING

Surface water samples

Surface water extracts were analysed by the wide-scope target LC-HRMS method, allowing for screening of 2,232 reference compounds from various groups such as pharmaceuticals, pesticides, biocides, personal care products, industrial pollutants, drugs of abuse, flame retardants etc. Compounds detected in at least one sample are listed in Annex III; those exceeding their PNEC or EQS values are highlighted in red. For all results, see *Supplementary Material SM_Wide-scope target screening river water and biota*.

In total **161** compounds were detected in at least one surface water sample. The highest number of detected compounds **(95** and **87)** was observed in samples influenced by wastewater: **sampling site 2** (Main canal for sewage - discharge of Kyivvodokanal - Bortnytsia aeration station) and **sampling site 26** (Ros river, below Bila Tserkva, influence of wastewater "Bilotserkivvoda" LLC), respectively. This was followed by **sampling site 8** (**66 compounds**) and **sampling site 25** (**56 compounds**).

The environmental impact of the detected compounds was evaluated by:

1. Comparing measured concentrations with their toxicity threshold values in freshwater (PNEC_fw).
2. Frequency of appearance (FoA) – % of sites at which the substance was detected.
3. Frequency of exceedance (FoE) of the PNEC value for the particular compound (number of sites with the exceedance in the brackets).

When using a cut-off filter for considering compounds present at minimum 10% (3) of sampling sites and exceeding their toxicity threshold value at minimum one site, a list of **19 candidate RBSPs** was drafted (see Annex V). The list was dominated by pesticides and pharmaceuticals, containing one personal care product (galaxolidone).

High exceedances of PNEC_fw were observed for:

terbuthylazine (herbicide, PNEC 60 ng/L, **40,589** ng/l **- SS 26, FoA 19% (3)**),

nicosulfuron (herbicide, PNEC 9 ng/l , **3,242 ng/l - SS 8, FoA 7%, (2)**),

fipronil (insecticide, PNEC 0.77 ng/l, **190** ng/l **- SS 2, FoA 22% (6)**),

carbendazim (fungicide, PNEC 150 ng/l, **32,793 ng/l - SS 26, FoA 52% (4)**).

Compounds detected with the highest FoA belong to the group of pharmaceuticals: **carbamazepine** (antidepressant; FoA 63%), **lopinavir** (antiretroviral drug; FoA 56%), **fluconazole** (antifungal generic medication; FoA 30%), and **diclofenac** (anti-inflammatory drug; FoA 26%). Here, it might be of interest that lopinavir (and also atazanavir) was proposed as a treatment against COVID-19. Efavirenz is also an antiretroviral medication originally used to treat and prevent HIV/AIDS.

From among WFD PS, only **atrazine** exceeded its EQS at **SS 8 and 26**. EU Surface Water Watch List (2015, 2018) compounds **fluconazole, diclofenac and** neonicotinoid insecticides **imidacloprid** and **thiacloprid** were also determined at concentrations above their PNEC values.

In general, **all substances determined at concentrations exceeding their EQS/PNEC values represent a potential threat for the Dnieper river basin ecosystem** and should be further monitored. Considering the low number of measurements and that the investigative monitoring was performed only once, an arbitrary threshold of FoE 0.1 (exceedance of PNEC at 10% of the sampling sites) could also be proposed to select a more robust list of candidate Dnieper RBSPs.

When comparing results of the wide-scope target screening obtained from the Black Sea samples (EM-BLAS project, Slobodnik et al., 2016, http://emblasproject.org/), 40 out of 161 substances were detected in both the sea water (Joint Black Sea Surveys 2016, 2017, 2019) and Dnieper surface water. This indicates that there is a direct impact of the Dnieper chemical pollution on the ecosystem of the Black Sea.

Fish samples

Five fish extracts were subjected to analysis with the wide-scope target LC-HRMS method. Substances detected in at least one sample are listed in Annex III.

Only **six** out of 2,232 screened for compounds were detected. The highest number of compounds **(3)** was observed in the sample **biota_5** (Dnipro river, below Zaporizhzhia city). **Biota_14** (Desna river, 3 km, at the Desna drinking water intake, Kyiv) has shown the presence of **4-formyl-antipyrine at 59.3 µg.kg w.w.** (**PNEC 42.4 µg/kg w.w**). **4-Formyl-antipyrine,** a metabolite of widely used aminopy-rine with analgesic and anti-inflammatory properties, **was determined in all five fish samples at concentrations above its PNECbio_fw**.

Similar to surface water, all compounds determined at concentration levels above or close to their PNECs indicate a high level of pollution and should be considered for further monitoring and inclusion into the list of Dnieper RBSPs.

Surface water used for production of drinking water

Four sampling sites (14, 18, 21, 23) were located in reservoirs used for the production of drinking water. The EU Groundwater Directive, and also the Drinking Water Directive, contain an arbitrary value of 100 ng/L for pesticides and their transformation products not to be exceeded as a safety threshold, above which adverse effects on human health may be expected. This applies even in cases when the human health toxic effects are not known. This threshold is frequently used by groundwater experts for assessment of any substance of anthropogenic origin. From the substances detected by wide-scope target screening only fungicide **carbendazim (SS 23),** mosquito repellent **DEET (SS 18),** a degradation product of the herbicide propazine: **2-hydroxy propazine (SS 18 and 23)** and the plasticizer **bisphenol S (SS 23)** exceeded this threshold value. For all results, see Annex VI.

In general, a presence of any chemical substance in the water resources used for the production of drinking water is of serious concern and their presence should be closely monitored.

8.2 SUSPECT AND NON-TARGET SCREENING

Methods

The averaged peaks of the calibrant substance were used to recalibrate the whole chromatogram using HPC fitting algorithm, which is embedded in DataAnalysis 4.3. (Bruker Daltonics, Bremen, Germany). This calibration method ensures mass accuracy below 2 mDa during whole chromatographic run for m/z from 50-1,200. For exporting files in mzML format, CompassXport 3.0.9.2. (Bruker Daltonics, Bremen, Germany) was used. Chromatograms acquired under data-independent acquisition (termed as 'bbCID' in Bruker instrument) were separated in low and high collision energy layer chromatograms. All mzML files and their meta-data (instrumental, sample meta-data, matrix-specific meta-data and retention time of RTI calibrant substances) were uploaded to Digital Sample Freezing Platform (DSFP; http://www.norman-data.eu/). DSFP has integrated standard operating procedure (SOP) to process the mzML files and all meta-data for the generation of Data Collection Templates (DCTs). This data reduction technique resulted in an automatic generation of DCTs, which includes condensed information from LC-HRMS files.

The two collision channels (4 and 25 eV) in data-independent acquired files were separated using the "Contribution module" of DSFP. Data files together with meta-data (contributor details, instrumental information, sample and sample-preparation information) were uploaded to DSFP. This allowed the application of a workflow which enabled generation of the DCTs. DCTs have been established for all types of environmental samples within the NORMAN network and support the inclusion of non-target (NTS) data.

Peak picking using centwave algorithm (MassSpecWavelet package) with optimized parameters was applied in the files. For each sample, peaks produced from one compound (isotopes and adducts) were grouped to form components. $[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$, selected for positive ESI, whereas $[M-H]^-$, $[M+Na-2H]^-$, $[M+K-2H]^-$, $[M+Cl]^-$, $[M+Br]^-$ were selected for negative ESI. Component's molecular ions and one-peak components were matched against the NORMAN SusDat (https://www.norman-network.com/nds/susdat/susdatSearchShow.php, 65,691 substances as of 21st January 2021).

A fully automated identification screening scheme was applied. SusDat was mapped against the component lists of the samples using the following settings: mass accuracy below 3 mDa, match of retention time index (RTI) and predicted RTI (derived from quantitative structure retention relationships (QSRR) prediction models and a set of calibrant substances) less than 30% for compounds within the applicability domain of the model and match of at least 3 experimental or 6 in-silico fragments either in the higher collision energy layer or in the low collision energy layer (in-source fragments). The criterion of 3 experimental or 6 in-silico fragments was relaxed for substances with poor fragmentation. A match that fulfilled these three criteria was termed as "possible annotation". The "possible annotations" were further investigated based on the isotopic pattern and the HRMS/MS spectral match. To express the confidence in the findings, the detected substances were allocated in identification levels, where level 1 corresponds to confirmed structures (reference standard is available), level 2 to probable structures, level 3 for tentative candidate(s), level 4 to unequivocal molecular formulas, and level 5 to exact mass(es) of interest (Schymanski et al., 2014). During the manual investigation of the "possible annotations", naturally occurring compounds such as aminoacids, nucleosides, vitamins and others which were detected in the samples were discarded, since their presence does not induce risk to the ecosystem. The tentatively identified compounds were semi-quantified based on the standard addition calibration curve of the most similar spiked reference compound. To find the most similar spiked reference compound, 2D-linear fragment descriptors of atom pairs and atom sequences were calculated and compared using Tanimoto

coefficient as the similarity distance function. The semi-quantified concentration levels were compared with PNEC values extracted from the NORMAN Ecotoxicity database (https://www.norman-net-work.com/nds/ecotox/).

Results

The river water and biota samples obtained within the Dnieper monitoring campaign were screened for 65,691 organic substances from the NORMAN SusDat database. The suspect screening revealed the presence of **440 compounds** in at least one sample after the removal of wide-scope target screening substances (see *Supplementary Material SM_Suspect screening*). The biota proved to contain several naturally occurring substances, which were not removed at this stage, in order not to overlook any important compound. The detected suspects were accompanied with their semi-quantitative concentration estimates calculated based on chemical similarity standard addition calibration curves. All raw mass chromatograms allowing to reproduce these results, or even to look for specific compounds of interest retrospectively, were stored in the NORMAN Digital Sample Freezing Platform (DSFP; Alygizakis et al., 2019).

Prioritisation of the suspect screening data was performed to narrow down the detected compounds to a few specific substances that can potentially affect the ecosystem. More specifically, the detected compounds were ranked based on the risk score, which is the linear combination of three indicators: (i) Frequency of Appearance (FoA), expressing at how many sites the compound was detected above the limit of detection (LOD), (ii) Frequency of PNEC exceedance (FoE), considering the frequency of monitoring sites with observations of a compound above a certain effect threshold (lowest PNEC), and (iii) Extent of PNEC exceedance (EoE), ranking compounds with regard to the extent of the effects expected (exceedance of PNEC normalized to the exceedance for all detected compounds). The resulting risk score was then scaled from 0 to 1 (Dulio et al., 2013). Compounds with risk score of more than 0.5 are listed in Table 3.

Finally, the ranking of substances was aided also by the Exposure Index developed by KEMI, Sweden, which is based on normalised values (between 0-1) reflecting (i) the degree of uncontrolled release during use, (ii) annual tonnage and (iii) range of use on the market. The underlying data are confidential (the industries argue that making them public would undermine their competitiveness on the market), but the index allows the use of this information for prioritisation purposes and is available in the NORMAN Database System (https://www.norman-network.com/nds/susdat/).

The top-prioritized substances were dominated by industrial chemicals registered also in the European Chemicals Agency (ECHA) database. The KEMI Exposure Index (>0.5) indicates that isodecyl diphenyl phosphate and bis(2-propylheptyl) phthalate are produced in high annual tonnage and have a widespread use. The sources of the remaining **three substances** causing their widespread presence in the Dnieper river basin **should be further investigated**.

Table 3. Compounds with Risk score > 0.5. Risk score considers the Frequency of Appearance (FoA), Frequency of PNEC exceedance (FoE) and Extent of PNEC exceedance (EoE) in river water and biota; Exposure Index (EI KEMI) indicates the produced amounts and widespread use of chemicals. All values are normalized to a range between 0 and 1.

Compound	River water				Biota				EI KEMI
	Risk score	FoA	FoE	EoE	Risk score	FoA	FoE	EoE	
Isodecyl diphenyl phosphate	**0.80**	0.70	0.70	1.00	0	0	0	0	0.62
Pentylphenyl octyloxybenzoate	**0.72**	0.93	0.93	0.30	0.27	0.80	0	0	0.13
6-Heptadecyl-1,3,5-triazine-2,4-diamine	**0.54**	0.41	0.41	0.82	0	0	0	0	0.13
Bis(2-propylheptyl) phthalate	**0.50**	0.70	0.70	0.10	0.13	0.40	0	0	0.79
Peroxide, 1-methyl-1-[4-methyl-2(or 3)-(1-methylethyl)phenyl]ethyl 1-methyl-1-phenylethyl	**0.50**	0.40	0.40	0.70	1.00	1.00	1.00	1.00	0.17

9 CONCLUSIONS

Investigative screening of 27 surface water and five biota samples provided a first overview on the pattern and extent of chemical pollution in the Dnieper River Basin. State of the art analytical methodologies were applied for target screening of >2,200 substances and suspect (presence/absence) screening of >65,000 substances in each sample. Substances detected by suspect screening could then be semi-quantified. Additionally, a classic target analysis of metals, BDEs, dioxins and dioxin-like compounds was carried out.

Out of 45 legacy WFD PS only herbicide **atrazine**, whose production and application has already been banned in the EU since 2004 and metals **cadmium and nickel** exceeded their EQS values in surface water samples. Rather surprisingly, WFD PS **mercury** exceeded its EQS value only in one biota sample, whereas, as expected, flame retardants **BDEs** were present in all biota samples at high concentrations. Analysis of 'expensive' dioxins and dioxin-like compounds in biota has shown their presence well below EQS value and thus the absence of their regular monitoring does not seem to be of an immediate high environmental concern.

Analyses of additional metals indicated that **copper and zinc** are ubiquitous in the basin and present at environmentally relevant concentration levels of pollution. This is making them candidates for the Dnieper RBSPs. Wide-scope target screening revealed the presence of **161 compounds** detected in at least one surface water sample, out of which **19** were found at more than 10% of sampling sites with minimum one measurement exceeding the ecotoxicity threshold value. Thus, they are suggested to enter the list of Dnieper RBSPs. The substances were mostly from the group of pesticides and pharmaceuticals. Here, it might be of interest that the antiretroviral drugs **lopinavir** widely present in samples was proposed as a treatment against COVID-19. High concentrations of several pesticides at sampling sites 26, 8 and 2 are of serious environmental concern.

The highest number of detected compounds **(95** and **87)** was observed in samples influenced by wastewater: **sampling site 2** (Main canal for sewage - discharge of Kyivvodokanal - Bortnytsia aeration station) and **sampling site 26** (Ros river, below Bila Tserkva, influence of wastewater "Bilotserkivvoda" LLC), respectively.

Four sampling sites (14, 18, 21, 23) were located in reservoirs used for the production of drinking water. The fungicide **carbendazim (SS 23),** the mosquito repellent **DEET (SS 18),** a degradation product of the herbicide propazine: **2-hydroxy propazine (SS 18 and 23)** and the plasticizer **bisphenol S (SS 23)** exceeded the arbitrary threshold value of 100 ng/L.

In biota samples only **six** out of 2,232 screened for compounds were determined. **4-Formyl-antipyrine,** a metabolite of widely used aminopyrine with analgesic and anti-inflammatory properties, **was determined in all five fish samples at concentrations above its toxicity threshold value** and its presence should be further monitored.

The suspect screening revealed the presence of **440 compounds** in at least one sample; additional to those detected by the wide-scope target screening. Concentrations of **five industrial chemicals** were estimated to be above their PNEC values at more than 50% of the sites and their presence in the basin should be monitored. The high-resolution mass chromatograms with 'fingerprints' (mass spectra) of thousands of substances detected in each sample were stored in the NORMAN Digital Sample Freezing Platform and allow for retrospective analysis of any substance, even those not on the suspect list and unknown today, detected during this investigative screening.

The list of candidate RBSPs is proposed to be a part of the Dnieper RBMP, which is currently under preparation. This would oblige environmental authorities to agree on the environmental quality standards of each substance finally selected as the RBSP, include them into the official monitoring programme and reporting schemes and propose via the Programme of Measures for their cessation in the environment within a committed time-scale.

There is an obvious link between the chemical pollution of the Dnieper river and the impacted Black Sea coastal zone areas (water bodies); 40 out of 161 substances were determined in both sea water and river water. Dnieper as a potential major pollution source of the Black Sea should be further investigated, and the related Programmes of Measures developed for the Dnieper River Basin and for the Ukrainian part of the Black Sea become harmonized.

10   OUTLOOK AND RECOMMENDATIONS

In order to obtain a more detailed picture of the pattern and extent of the chemical pollution in the Dnieper River Basin with the aim to reduce levels of contamination and for decision-making, **follow-up actions** are clearly recommended, such as:

- **Further chemical and biological surveys, in particular at the most polluted sites at different times of the year**. Particular attention should be given to parameters, which have been found during this pollutant screening:
    - Monitoring of heavy metals, especially cadmium, nickel, copper and zinc in surface water;
    - Monitoring of BDEs and formyl-antipyrine in biota;
    - Monitoring of the detected contaminants carbendazim (SS 23), DEET (SS 18), 2-hydroxy propazine (SS 18 and 23) and bisphenol S (SS 23) in reservoirs used for production of drinking water;
    - Monitoring of atrazine and additional 19 substances (pesticides and pharmaceuticals) found in the wide-scope target screening in surface water;
    - Monitoring of five additional industrial chemicals revealed by the suspect screening in surface water.
- Analysis of other environmental matrices, such as sediments (which have not been analysed within this pollutant screening).
- A **targeted investigation about the sources of pollution and the possible wider impact of the detected pollutants on the ecosystem and human health**; this would for instance include the analysis of influent and effluent water samples of WWTPs as well as sewage sludge and compost samples applied on agricultural fields.
- Concrete plans on how to **reduce and terminate the pollution** at an ambitious timeframe, closely involving the responsible governmental institutions, identified polluters, water users and other stakeholders with a vested interest. These pollution cessation plans should become part of the Dnieper RBMP.
- **Immediate action** is recommended at sampling sites 18 and 23 located in Dnieper reservoirs used for the production of drinking water in order to assess the scale, origin and impact of the excessive pollution by pesticides and their transformation products. This information will enable health authorities to decide on any possibly needed precautionary measures.

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12 ANNEXES

Action funded by the
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