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Heavy metals and persistent organic pollutants in Moldovan environment

Prague – Chisinau 2021

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TRANSITION

Heavy metals and persistent organic pollutants in Moldovan environment
Prague – Chisinau, 2021

Editors and lead authors: Václav Mach and Jindřich Petrlík
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Part I.

Heavy metals

in selected areas in the Dniester River basin

Editor and lead author: Václav Mach

Contributors: Marek Šír, Jan Matuštík, Ilya Trombitsky, Jitka Straková, Martin Skalský, Jindřich Petrlík

Summary

The study was focused on the monitoring of cadmium, lead, chromium, copper, zinc, nickel, arsenic, and mercury in the drainage basin of the Dniester River in Moldova. The aim of the study was to identify potential heavy metal pollution sources in the Moldovan environment. A set of samples of soil, sediments, and surface water was collected in the surroundings of five potential industrial sources of heavy metals in July 2021. The localities that were sampled included two landfills for municipal waste – the Tintareni Landfill and the Balti Landfill – and three other industrial areas within the towns of Vatra, Rezina, and Rybnitsa. The Tintareni Landfill has apparently been operated in an inappropriate manner for a long time and the Balti Landfill is still very probably, because of its low security and poor operation, a source of pollution for its surroundings. In general, we recommend efficient and sophisticated measures to ensure their safe operation and the introduction of European legislative instruments on land-filling as well as their application in practice. The basic measures that result from this legislation include security against the entry of unauthorised persons, prevention of wild burning of waste, regular compaction of the waste, and the installation of a system for collecting landfill gas and landfill leachate. In particular for the Balti Landfill, where the operating conditions are very poor, immediate measures to prevent it from burning, regular compaction, and overlaying by soil can be recommended. The Vatra Industrial Area is very probably a source of heavy metals – particularly lead, arsenic, and mercury – into the Bic River, a tributary of the Dniester. It is not possible to determine exactly which industrial plant is the source of heavy metal pollution, because the plants are clustered and the impact of each of them cannot be individually separated. The towns of Rybnitsa and Rezina affect the Dniester River by introducing heavy metal pollution into the river basin. This conclusion is driven from a comparison of heavy metal concentrations

in water sediments above and below the towns of Rezina and Rybnitsa showing the lowest measured concentrations of most heavy metals above the towns and concentrations downstream from the towns that are twice as high (lead, chromium, copper, nickel, and mercury). According to our data, the Rybnitsa Industrial Area is a significant heavy metal source for the watershed in comparison to the cement plant in Rezina. The Rybnitsa Industrial Area is most likely to release heavy metals into agricultural land and the Rybnitsa brook, with concentrations of some heavy metals (especially cadmium, lead, and zinc) increasing several times as the brook flows through the town of Rybnitsa. In addition, a small metalworking factory in the town of Rezina is a likely source of heavy metals in the Dniester River. The impossibility of determining the sources of pollution exactly is related to the non-existence of a comprehensive and reliable Pollution Release and Transfer Register. However, the study revealed some of the sources of pollution that have an impact on the environment and should be monitored.

Introduction

The rural population of Moldova is largely dependent on agriculture and forest use. Almost 60% of the population lives in the countryside and agriculture is a vital source of their livelihood. The quality of life of the rural population depends greatly on rivers. A threat to agriculture and human health is posed by pollution of rivers and the environment in general by heavy industries using obsolete technologies, as well as several other anthropogenic sources that create additional burdens which threaten to release toxic substances into the drainage basins of Moldovan rivers. These are mainly poorly operated municipal waste landfills and the discharge of sewage from settlements.

The industrial sector in the Republic of Moldova represents 22.8% of GDP, employing 17.1% of the active population. Traditionally, the country's main industries have been manufacturing, agriculture and food processing, including canning, wine and alcohol production, textiles, tobacco, and apparel and footwear. Transnistria is more industrialised, with steel production in the town of Rybnitsa as the leading industry which accounts for about 60% of the budget revenue of Transnistria. Other industries in Transnistria include cement production, the textile industry, the energy sector, gas transmission, and alcohol production. The existing waste management system in the Republic of Moldova is still in a developing stage and it faces some serious problems such as environmental pollution, illegal dumping, landfill overloading, and insufficient networking of public services for waste collection, waste recycling, or a proper legislative framework.[1] Moldovan rural areas often suffer from a lack of any waste management at all. Some villages currently have no public waste management service, so that village residents rely on transporting their own waste to nearby dumps and there is no possibility of sorting and recycling waste.[2]

This study is devoted to identification of potential sources of heavy metals (i.e., by some municipal waste landfills and industrial areas located in the drainage basin of the Dniester on both banks of the river) in the Moldovan environment. Our investigation is focused on assessment of contamination by heavy metals. Although heavy metals are natural compo-

nents of the earth's crust, certain activities of mankind, such as mining and smelting, have caused increased concentrations of heavy metals in the environmental compartments. [3] In some areas heavy metal concentrations have reached potentially harmful levels. In addition to mining and smelting, sources such as vehicle emissions, industrial waste, and fertilisers also contribute to the accumulation of heavy metals in the soil, sediment, and surface water. [4] The various heavy metals can cause adverse effects to the human body, having toxic and carcinogenic effects and causing the oxidative deterioration of biological macromolecules (see Annex 1 for more information).[5] Exposure to pollutants such as heavy metals is one of the major environmental and public health concerns. In order to determine the possible sources of heavy metals in the environment and watercourses, we conducted a sampling campaign in the vicinity of selected landfills and industrial sites in Moldova.

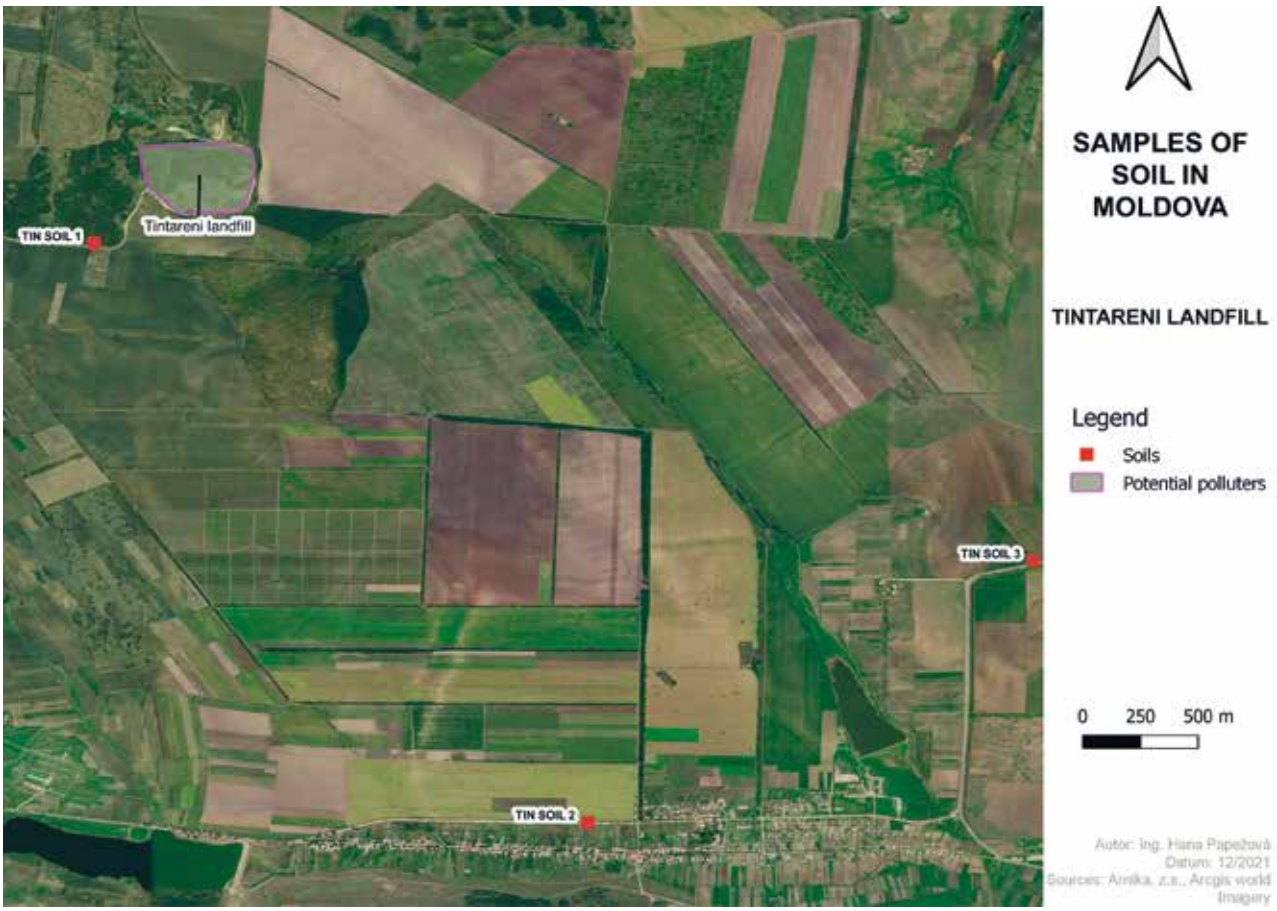
Localities

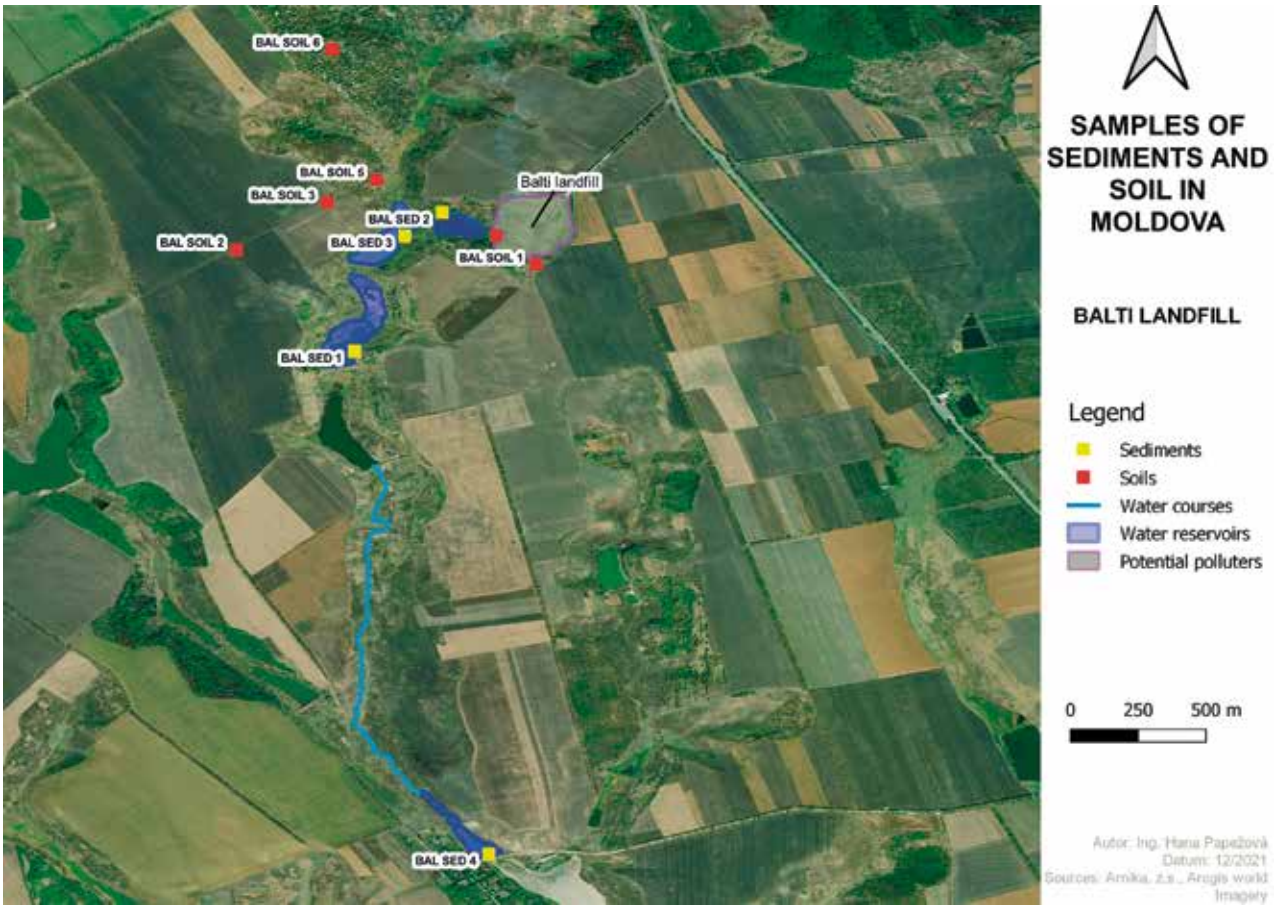
Samples of soil, sediment, and surface water were taken in the surroundings of five potential sources of heavy metals and from the Dniester River. Among the potential sources of heavy metals in the environment there were two landfills for municipal waste – the Tintareni Landfill and the Balti Landfill – and three other industrial areas in the towns of Vatra, Rezina, and Rybnitsa. The section of the Dniester River that was examined is located about 35 km alongside the river downstream from the towns of Rezina and Rybnitsa. A description of the selected potential sources of heavy metals and the section of the river is provided below.

Tintareni Landfill

The landfill near the village of Tintareni serves as a municipal waste landfill for Chisinau. The landfill is situated approximately 40 km south-east of Chisinau in the Anenii Noi district. The body of the landfill is circular, with a diameter of up to half a kilometre. Every day more than 700 metric tonnes of municipal waste came to the landfill. The waste is compressed and periodically covered with soil. According to the project focused on sustainable management of POPs stockpiles funded by Global Environment Facility (GEF) there was more than 2 tonnes of unidentified POPs pesticides transferred from Tintareni to central storage before year 2005[6].

A new landfill leachate treatment facility was placed at the landfill in autumn 2020. Before the new facility was placed there, the landfill leachate had probably not been treated. Locals complain that the water in the wells in Tintareni and other surrounding villages is not suitable for drinking or watering household plots, fruit, and vegetables. The landfill burned for three days at the end of July 2020, and the locals report irregular but frequent fires on the landfill. In December 2020, the European Bank for Reconstruction and Development, the European Investment Bank, and the E5P fund jointly provided loans and grant funds to Chisinau for adjustment of the landfill (e.g., refurbishing of waste transfer station, opening a new waste-sorting plant, installation of a new landfill gas and leachate collection systems).


TIN SOIL 1
Tintareni landfill
TIN SOIL 3
TIN SOIL 2
SAMPLES OF SOIL IN MOLDOVA
TINTARENI LANDFILL
Legend
Soils
Potential polluters
0 250 500 m
Autor: Ing. Hana Papežová
Datum: 12/2021
Sources: Arnika, z.s., Arcgis world Imagery


BAL SOIL 6
BAL SOIL 5
BAL SOIL 4
Balti landfill
BAL SED 2
BAL SOIL 2
BAL SED 3
BAL SOIL 1
BAL SED 1
BAL SED 4
SAMPLES OF SEDIMENTS AND SOIL IN MOLDOVA
BALTI LANDFILL
Legend
Sediments
Soils
Water courses
Water reservoirs
Potential polluters
0 250 500 m
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Datum: 12/2021
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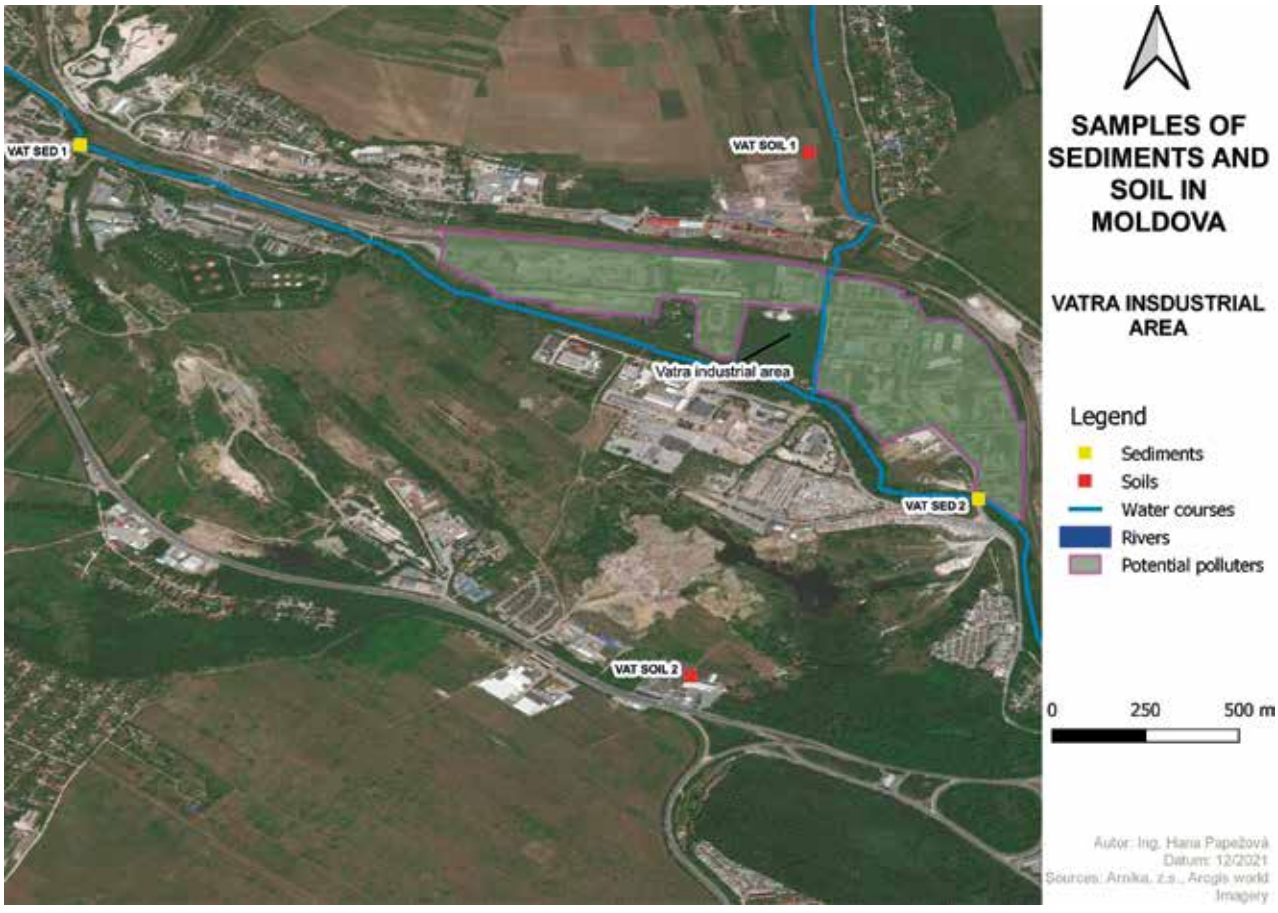
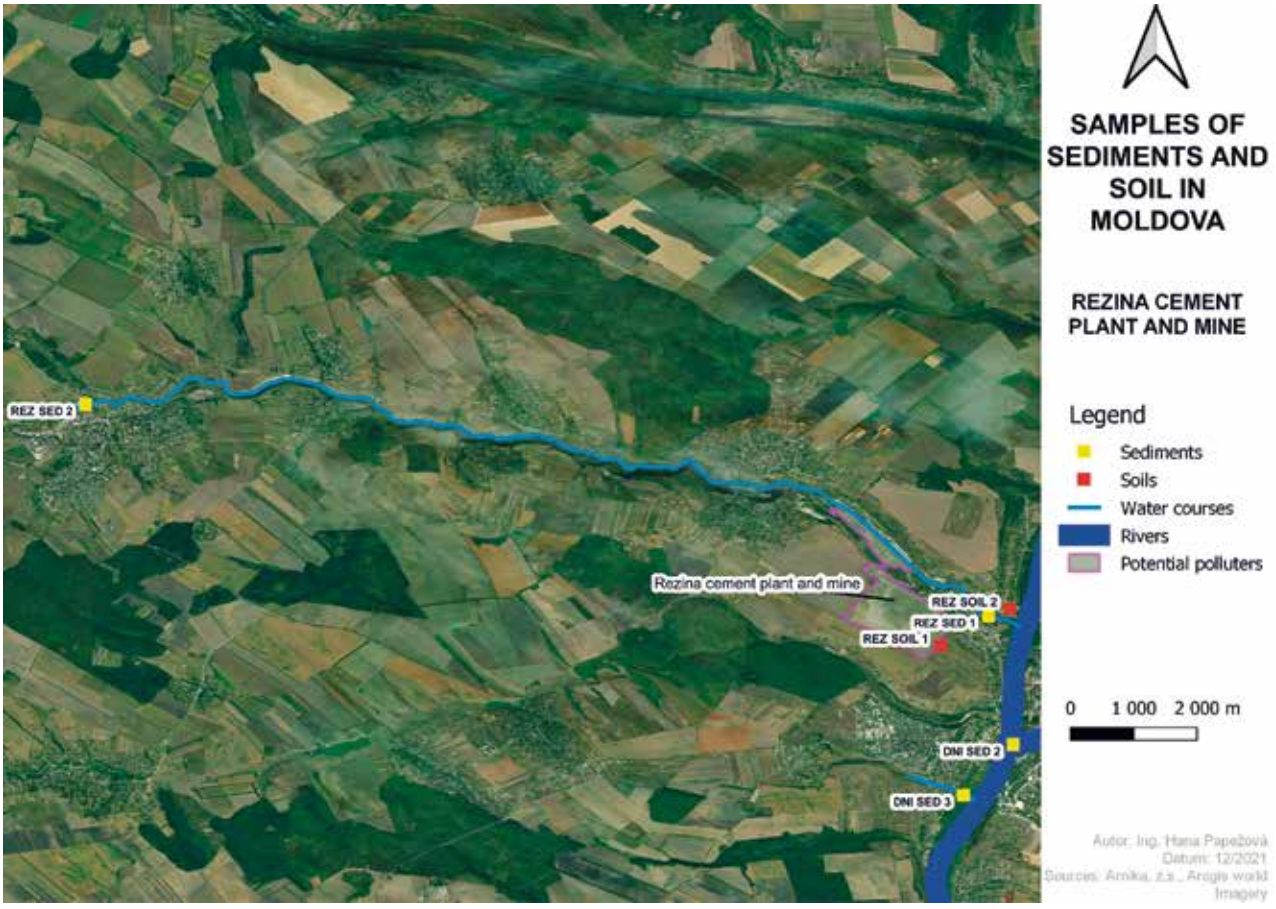
Balti Landfill

The landfill near the town of Balti in the northern part of Moldova serves for the disposal of municipal waste. The landfill is situated approximately 5 km south of Balti. The body of the landfill is elliptical, with a diameter of up to 300 m. The landfill has apparently been vastly mismanaged. The waste has not been compacted on the landfill and the waste remains largely uncovered. No landfill gas collection system has been constructed on the site, and most probably no leachate capture system either. Since the soil is mainly clay, it is probable that the leachate does not infiltrate and the landfill is effectively separated from groundwater. The leachate flows to a series of ponds below the landfill. The water in the first pond is clearly leachate of a dark brown colour. Because the soil around the first pond is mainly clay, it is probable that that pond is also separated from groundwater and the leachate is isolated most of the time and left to evaporate. The first pond periodically overflows during heavy rains. Thus, the landfill leachate could affect the ponds downstream. The second pond is visibly more natural, with thick reed vegetation. The third pond below the landfill is a private fishing ground. At the time of the sampling, the landfill was burning, with a lot of smoke spreading to the vicinity. The smoke was pouring straight on to the agricultural fields (mainly maize) that were all around the landfill, with no barrier. There is a fishing pond located downstream on the cascade of ponds, used as a commercial fishing spot.



Vatra Industrial Area

Vatra is a town located in the district of Chisinau, in the central part of the country, approximately 12 km north-west of Chisinau. There is a large industrial park with various factories in Vatra with various small industrial plants, which are located right next to each other. In total, there may be about two dozen different industrial companies. Among the small industrial plants in the industrial zone, there are mainly tyre pyrolysis, asphalt production, oil and gas transhipment, production of building materials and sheet metal roofs, and packaging repair companies. The exact list of industrial plants was not made available for us. Since the factories are clustered, there is no way to separate the impact of each, and thus we can only evaluate their sum in the results. In addition, there are several former quarries in the vicinity of the industrial area. The Bic River – a tributary of the Dniester River – flows through that industrial area.



Rezina Industrial Area

Rezina is a town located on the right bank of the Dniester River in the north-west of the country. About 5 km north of Rezina a large cement kiln belonging to the company Lafarge Cement is located. In the past the cement kiln probably burned used tyres to heat up a steam boiler as an alternative fuel; however, according to an official statement, the company stopped this practice several years ago. In the immediate vicinity of the cement plant, there is a small brook called the Ciorna, which is a right-bank tributary

of the Dniester River. In addition, there is a limestone quarry between the cement plant and the town of Rezina.

Rybnitsa Industrial Area

Rybnitsa is a town in Transnistria on the same length of the river as the town of Rezina. On the northern outskirts of the town there is a large industrial area, where there are several large industrial plants. The industrial area is dominated by the steelworks and the cement kiln, but there are also several smaller facilities such as a power station or an oil storage site. The steel-producing company in Rybnitsa – the Moldova Steel Works (part of the Russian Metalloinvest holding) – accounts for more than half of Transnistrian industrial output. It was founded in 1985 for the reprocessing of scrap metal. In 2020, the annual production capacity of the company was 464.9 thousand tonnes of crude steel and 451.4 thousand tonnes of rolled products. The cement kiln in Rybnitsa was put into operation in November 1961. The cement production capacity of the plant is 1 million metric tonnes of cement and 955 thousand metric tonnes of clinker per year.

Dniester River

The Dniester runs first through Ukraine and then through Moldova, from which it more or less separates the breakaway territory of Transnistria, finally discharging into the Black Sea on Ukrainian territory again. We have focused on the 35-km-long section of the river downstream from the towns of Rezina and Rybnitsa to Lopatna. This section of the river was selected to capture the impact of the industry in Rezina and Rybnitsa; therefore near the towns we took more samples and further on we took a sample approx each 10 km. The heavy industry in Rybnitsa could affect the river. Furthermore, we saw a small flow with a foul smell on the Rezina side of the river. Apart from that, we did not observe obvious sources of pollution further down the selected section. The river appeared almost pristine, meandering through the landscape. On the banks there were thick reeds, a lot of birds were living there, and large flocks of herons indicate that there are a lot of fish. On the banks and on the bottom of the river there live many mussels and molluscs.

Methodology

Sampling procedures

The sampling campaign was conducted according to a sampling plan covering five localities that were potential sources of heavy metals and the 35-km-long section of the Dniester River below two of the localities. The localities were selected on the basis of reports from local environmental activists about potential sources of contamination. Samples of soil, sediment, and water were taken at selected localities in August 2021. Soil samples were collected in agricultural fields at different distances from the potential sources. Sediment samples were collected from watercourses to compare concentrations of heavy metals upstream and downstream from the potential sources of pollution. Water samples were collected at the outflow from the landfill near the town of Balti and from the Dniester River. During the water sampling, the concentration of total ammonium was measured using an HI-733 Ammonia High Range Handheld Colorimeter (0.0-99.9ppm) Checker®HC. When sampling on the selected section of the Dniester River, we sailed down the river in an inflatable boat from the towns of Rybnitsa and Rezina to the village of Lopatna. In total, 16 soil samples, 20 sediment samples, and 14 water samples were collected at the localities that were investigated. Detailed lists of the samples that were analysed are presented in Tables 1, 2, and 3 in Annex II.

Samples of soils were taken as composite samples formed of five partial subsamples taken from points forming a square shape at each sampling site. The samples were taken with a steel trowel from the surface layer of soil, from which potential vegetal cover was removed. Samples of sediments were usually taken with a core sampler or a steel trowel as composite samples formed of several partial samples taken in various places at the given sampling site. The samples were homogenised in a steel bowl; some of them were quarte-

red after homogenisation and transferred into 250-ml polyethylene containers with screw -on lids. After each sampling, all the sampling equipment was cleaned with tap water or with available river water. Water samples were taken from surface water into 1000-ml PET containers that were rinsed with sampled water. The samples were initially stored in a dark place at a natural temperature and then, after transport to the laboratory, in a refrigerator, where they were kept until the analysis.

Analytical methods

Chemical analyses for determination of the heavy metal (Cd, Pb, Cr, Cu, Zn, Ni, As, and Hg) concentrations were conducted using atomic absorption spectrometry. After transport to the laboratory, the samples of soils and sediments were homogenised and a representative part (50 g) was used for the determination of dry matter by a gravimetric method. Another representative part was taken for analysis of heavy metals by means of a mineralisation procedure. The analytical procedure used for the mineralisation was as follows: 5 g of the sample was placed into a beaker together with 40 ml of distilled water and 10 ml of concentrated acid (hydrochloric acid : nitric acid = 3 : 1). The sample was boiled for a period of two hours. Then it was filtered through a fluted filter paper. Metals were determined in the mineralisation procedure by means of a Microwave Plasma Atomic Emission Spectrometer (Agilent Technologies). Mercury was measured directly in solid samples by means of an Advanced Mercury Analyser (AMA 254, Altec). The analysis was conducted at the University of Chemistry and Technology in Prague.

Results and Discussion

All the results of the analytical measurements for all samples are shown in Tables 4, 5, and 6 in Annex III. In this chapter, the heavy metal concentrations determined in samples from the sampling sites are compared with each other and the sampling sites are discussed with respect to possible contamination from potential sources of contamination. Summary results of the mean values of heavy metals in the soil samples are shown in Figures 1 and 2. The comparison of the mean values of heavy metal concentrations in soils between the five potential sources shows significantly higher values of cadmium, lead, and zinc in Rybnitsa than in the other four locations. Chromium, copper, nickel, arsenic, and mercury occurred at roughly the same levels when locations were compared. Based on the above assessment, we assume that Rybnitsa is the site most affected by cadmium, lead, and zinc of the selected localities.

In this study, we do not compare measured concentrations of pollutants with any legal or health protection limits (not Moldovan or EU or WHO). In none of the samples did the concentration of heavy metals exceed the valid limits. However, exceeding the limits indicates a serious threat to human health, while at the same time, increased levels of pollution near potential sources means that such a serious threat might develop if the pollution is not effectively monitored and regulated. The results of this study are based on a comparison of the concentrations of heavy metals upstream and downstream from the identified potential sources of pollution to assess their possible impact.

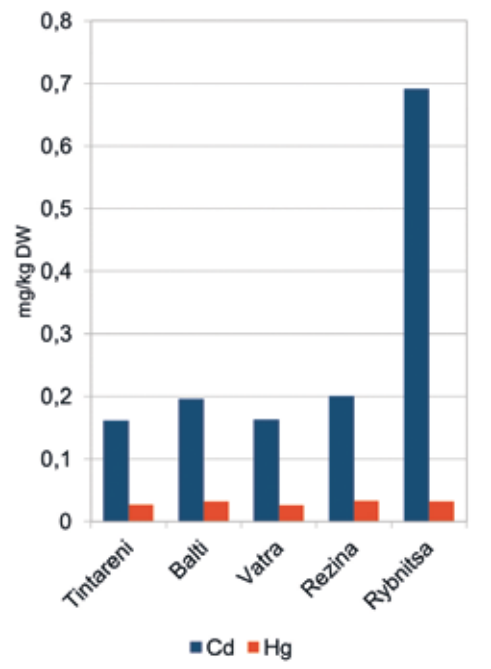


Figure 1:

Mean concentrations of cadmium and mercury in soil samples collected at the localities

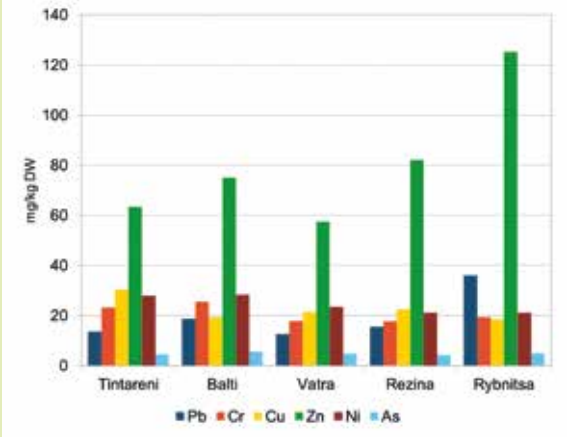


Figure 2:

Mean concentrations of lead, chromium, copper, zinc, nickel, and arsenic in soil samples collected at the localities

Landfills require better operating conditions

Although the Tintareni Landfill has recently undergone modifications to improve its operation, it has apparently been operated in an inappropriate manner for a long time. Three soil samples were t aken at the Tintareni Landfill site. One soil sample (TIN-SOIL-1) was taken directly near the landfill and the other two samples at a distance of several kilometres from the landfill body. The soil sample taken directly near the landfill had higher concentrations of almost all heavy metals (Cd, Pb, Cr, Zn, Ni, As, and Hg) than the other two more distant soil samples. This finding indicates that the Tintareni Landfill is a likely source of heavy metals in the environment. Contrary to this finding, the copper concentration was the lowest in the sample from the vicinity of the landfill. However, copper is also present in pesticides used on agricultural land, and thus the higher concentration of copper in the more distant samples can be explained by agricultural sources.

On the basis of on-site inspections of the Balti Landfill, it can be stated that because of its low security and its poor operation, the landfill is very likely to be a source of pollution for its surroundings. Soil, sediment, and water samples were taken around the Balti Landfill. The sediment samples from the ponds under the landfill did not show a clear increasing trend in relation to proximity to the landfill. This may be because the subsoil of the ponds consists of low-permeability clay and sediment containing particles from the leachate was not collected during the sampling. The fact that heavy metals are leached from the landfill is revealed by the water samples, because the water sample (BAL-W-2) from the first pond directly below the landfill contained measurable concentrations of chromium and nickel. From the above, we conclude that the landfill can release heavy metals in the drained water. To support this hypothesis, it would be necessary to perform more detailed monitoring in the vicinity of the landfill.

As both landfills can pose an environmental risk by releasing heavy metals, efficient and sophisticated measures can be recommended to ensure their safe operation. In general, the introduction of European legislative instruments on land-filling as well as their application in practice can be recommended. The basic legal instrument in EU is Directive 1999/31/EC on the landfill of waste,[7] which has been amended several times. We recommend EU instruments, because the Association Agreement between the EU and the Republic of Moldova provides for stronger political association and integration between both sides and there should be an approximation to European law and the adoption of EU law by the Republic of Moldova. The main landfill requirements arising from the Directive are listed in Annex IV. In particular for the Balti Landfill, the operating conditions of which are very poor, immediate measures to prevent it from burning, regular compaction, and overlaying by soil can be recommended.

The Vatra Industrial Area is a significant source of heavy metals in the Bic River

According to our sampling in the vicinity of the Vatra Industrial Area, we conclude that the industrial area is a source of heavy metals in the Bic River. Sediments from the Bic River showed a significant increase in all heavy metals below the industrial site compared to sediments collected above the industrial site. In the case of some heavy metals (Pb, As, and Hg), this increase was up to several times. Graphically, the difference between the sediment above the industrial area (VAT-SED-1) and the sediment below (VAT-SED-2) is shown in Figures 3 (Cd and Hg) and 4 (Pb, Cr, Cu, Zn, Ni, and As). On the evidence of the samples taken, it is not possible to determine exactly which industrial plant is the source of heavy metals, because the plants are clustered and the impact of each of them cannot be individually separated. It can only be supposed that the industrial area releases heavy metals into the Bic River. The impact of individual industries in the industrial area should be thoroughly monitored, for example by continuous air and water pollution monitoring stations, and by obliging the industries to report their emissions into Pollutant Release and Transfer Register (PRTR).

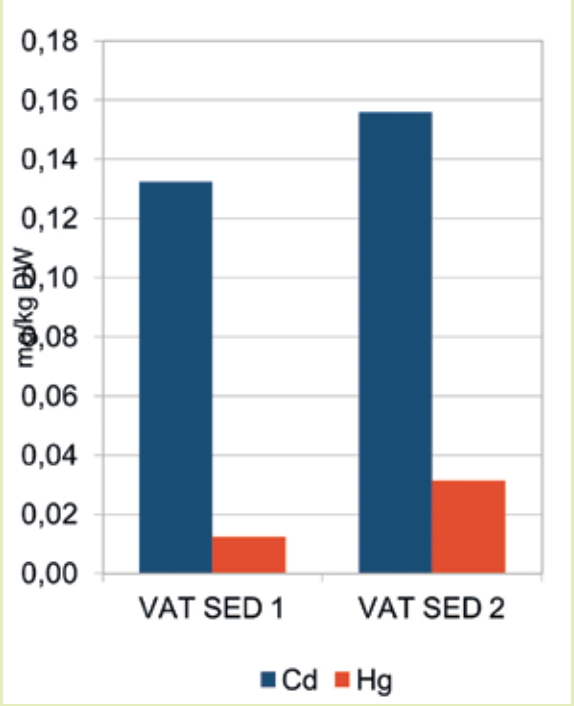


Figure 3:

Concentrations of cadmium and mercury in sediment samples from the Vatra Industrial Area

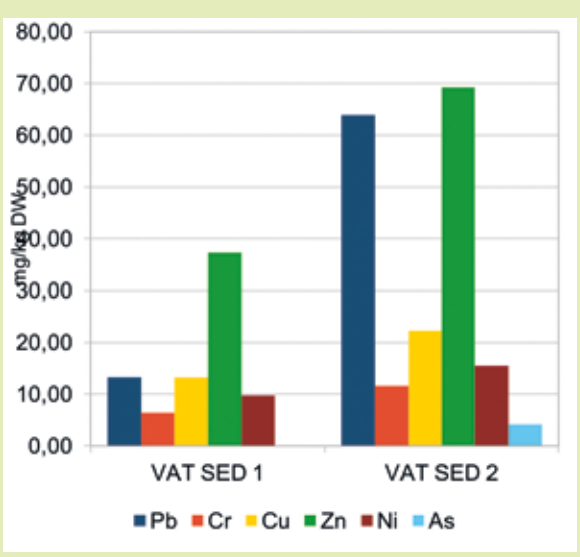


Figure 4:

Concentrations of lead, chromium, copper, zinc, nickel, and arsenic in sediment samples from the Vatra Industrial Area

Other sampling campaigns conducted on the Bic River in 2012 concluded that sediments from Chisinau were moderately polluted concerning heavy metals (Pb, Cd, Cu, Mn, Ni, Cr, and Zn).[8] That research stated that although the entire river is marginally polluted by lead, there is a peak concentration (59 mg/kg DW) of lead in the sediment in Vatra. The authors of the study explain this peak by a point source in Vatra contributing lead to the river.[9] The sediment sample taken by us (VAT-SED-2) below the industrial area contained an even higher concentration (64 mg/kg DW) of lead in the sediment, while the sediment sample above the industrial area contained a concentration of lead that was several times lower. We therefore conclude that the specified point source of lead reported before is located in the industrial area.

The Vatra Industrial Area can thus also be a significant source of heavy metals for the Dniester River, because several other studies that have been carried out showed that the Bic River probably introduces heavy metals to the Dniester River. The first study found significantly higher concentrations of heavy metals (Zn, Cu, Ni, Mo, Mn, Pb, and V) in sediments below the area of the tributary of the Bic River than on other sections of the Dniester River. [10] The second study confirmed increased concentrations of heavy metals (Ni, Pb, Zn, Cd, Cu, Ag, Sn) in sediments in the zone of the confluence of the Dniester and the Bic later. [11] The third study that was concerned about heavy metal concentrations in surface water reached the same conclusion. The surface water sample collected at the mouth of the Bic River discharging into the Dniester River was highly dominated by heavy metals. [12] Moreover, the last-mentioned study assumes that the industry (electronic goods, building materials, machinery, plastics, rubber, textiles) and agricultural activities around the capital, Chisinau, which is located on the banks of the Bic River, can be considered potential sources of anthropogenic inputs of heavy metals into the aquatic environment.

Heavy metals in the Dniester River grow below the towns of Rezina and Rybnitsa

The towns of Rybnitsa and Rezina affect the Dniester River by introducing heavy metals. The comparison of concentrations of heavy metals in sediment samples taken from the Dniester River shows that the sediment sample (DNE-SED-1) taken above the towns of Rezina and Rybnitsa and above the confluences with the brooks flowing around both industrial areas contain the lowest concentrations of most of the heavy metals (Pb, Cr, Cu, Zn, Ni, As, and Hg) in comparison to the sediment samples taken below the towns. The increase in concentrations of heavy metals in the sediment samples taken below the towns is evident and for many heavy metals (i.e., Pb, Cr, Cu, Ni, and Hg) it is up to double in comparison to above the towns. The highest concentrations of all heavy metals except arsenic in the sediments of the Dniester River were found in a sediment sample (DNI-SED-3) from the right bank of the Dniester close to the town of Rezina. In that sediment there was a significantly high concentration of mercury (0.65 mg/kg DW). Near the place where the sediment was collected, which was characterised by an anaerobic odour, there was an outflow of water leading from Rezina. According to map data, it was found that the outflow is the mouth of a small watercourse on which there is a small metalworking factory. That small

factory is the only identified potential source of possible heavy metal pollution that could be responsible for the increased heavy metal concentrations. We recommend that a more detailed investigation of heavy metals in that place be carried out, because according to the map data, there are eight protected sources of seepage water in the vicinity of several hundred metres from the sampling site.

Our results did not confirm the Rezina Industrial Area as a significant source of heavy metals in the Dniester River. Heavy metal concentrations in the sediments collected by the Ciorna brook, which flows through the Rezina Industrial Area, do not show an increase between the samples taken above and below the industrial area. There is a cement plant in the industrial area, which is usually not a source of heavy metals for the environment but can be a source of other potentially harmful contaminants. As industries are located at the outskirts of residential districts of the towns, establishment of continuous air and water quality monitoring – and publishing of its results – is essential to understand the exact burden on the environment and imposing measures to protect public health. The industries should be obliged to report their emissions in the Pollutant Release and Transfer Register (PRTR).

The Rybnitsa Industrial Area is obviously one of major sources of heavy metals into the environment

The Rybnitsa Industrial Area is, according to our measurements of soil and sediment, an important source of some heavy metals. Firstly, this conclusion is supported by the values of heavy metal concentrations in the soil samples. The soil sample (RYB-SOIL-2) which was taken several kilometres from the industrial area south of Rybnitsa contains significantly lower concentrations of all the heavy metals that were monitored than the two soil samples taken in the immediate vicinity of the industrial area. For this reason, we suppose that the industrial area where the large steelworks is located has an impact on the agricultural land in its immediate vicinity. Secondly, the concentrations of heavy metals in the sediments (see concentrations of heavy metals in sediments at individual sampling sites in Rybnitsa in Figures 5 (Cd and Hg) and 6 (Pb, Cr, Cu, Zn, Ni, and As)) suggest that the industrial area is also a source of heavy metals for the Rybnitsa brook, which then flows into the Dniester River. The sediment sample (RYB-SED-3) taken on the Rybnitsa brook above the town of Rybnitsa has significantly lower concentrations of all the heavy metals that were measured than the sediment sample (RYB-SED-2) taken close to where the brook joins the Dniester River. The increment of some heavy metals (especially Cd, Pb, and Zn) in the sediment increases several times as the brook flows through the town of Rybnitsa. High concentrations of heavy metals were also found in the sediment (RYB-SED-1) taken at the mouth of an unnamed watercourse which flows into the Dniester River in the northern part of the town. For this reason, we suppose that the Rybnitsa Industrial Area is a major source of heavy metals into the environment.

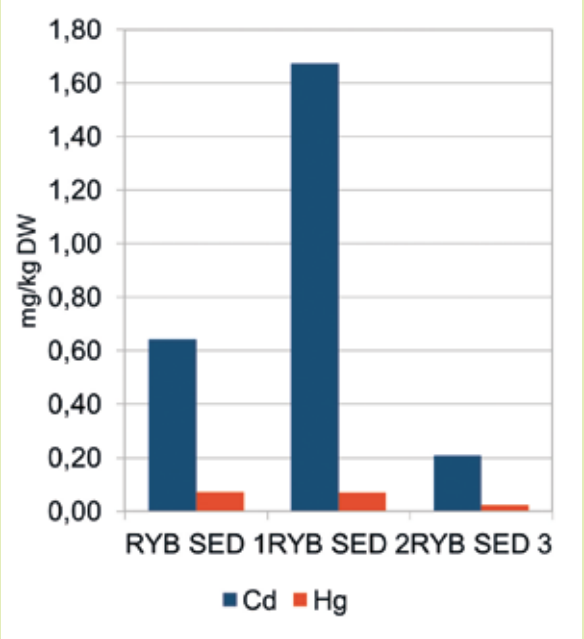


Figure 5:

Concentrations of cadmium and mercury in sediment samples from the Rybnitsa Industrial Area

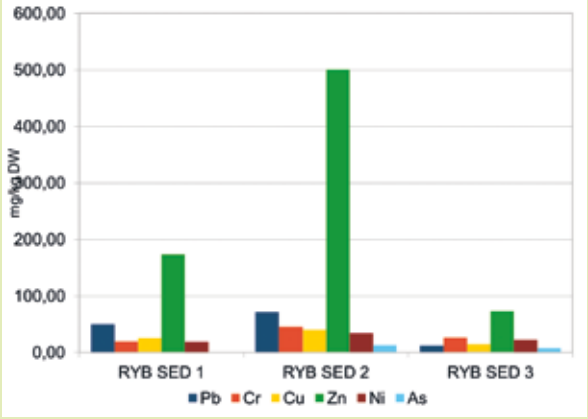


Figure 6:

Concentrations of lead, chromium, copper, zinc, nickel, and arsenic in sediment samples from the Rybnitsa Industrial Area

Some other studies assume that the quality of the Dniester River basin has been seriously impacted by the chemicals released by agriculture, industry, and wastewater discharges. One study examining the presence of heavy metals in fish has even revealed concentrations exceeding the threshold effect concentrations of copper in fish from the Dniester River. However, according to the study, such high copper concentrations are mainly attributed to pollution related to agricultural sources.[13] Other studies focus on the dynamics and sources of individual heavy metals in the Dniester River. Two studies by the same authors conclude that the use of fertilisers and pesticides for agricultural purposes directly affects the dynamics of copper, zinc, and manganese in aquatic systems, and the discharged wastewaters from industry contribute to pollution with nickel, zinc, copper, silver, and cadmium. [14] [15] Our conclusions corroborate the hypothesis that industrial activity contributes to increasing the content of copper, zinc, and nickel in the Dniester River.

Although there are some significant sources of heavy metals on the Dniester River upstream from Moldova in Ukraine, the effect of the industrial areas in Rybnitsa and Rezina is obvious. High concentrations of heavy metals were observed in sediments from the Seret River, a tributary of the Dniester, and upstream from the Zalishchyky reservoir. Both sites are located in the Ternopil Oblast in Ukraine, which is a region with significant industrial

activity.[16] The areas of Rybnitsa and Rezina are also described as sources of heavy metal pollution in other reports. Biomonitoring of mercury pollution of the Dubasari reservoir of the Dniester River has been carried out using macrophytes and lichens. It has been shown that the maximum mercury content in these bio-indicators is found in the area of the Rezina -Rybnitsa industrial complex.[17] In another study examining the content of heavy metals in various abiotic components of the Dubossary Reservoir on the Dniester River, authors stated that the maximal concentrations of heavy metals were in the area comprising the Rezina-Rybnitsa industrial complex. In this area, the contents of the metals under study in the soil exceed the background level by from two up to 11 times.[18]

Besides the above mentioned studies, there is a lack of reliable data on environmental impact of industrial sources of pollution in the area. Pollutant Release and Transfer Register (PRTR) system, that is the most effective standard of collection and publication of information on emissions, was launched recently, however, it does not involve all polluting industries and the latest data published are from 2017. Moldova should improve the system in accordance with the PRTR Protocol to the Aarhus Convention, that would significantly improve monitoring of the sources of pollution.

Conclusions and Recommendations

This study focused on the identification of potential heavy metal contamination sources in the Moldovan environment. According to the data collected in this study, heavy metal pollution sources demanding immediate attention and actions include the following:

1. Although **the Tintareni Landfill** has recently undergone modifications to improve its operation, it has apparently been operated in an inappropriate manner for a long time. Because of its low security and its poor operation, **the Balti Landfill** is very probably a source of pollution for the surroundings. In general, we recommend efficient and sophisticated measures to ensure the safe operation of both landfills and the introduction of European legislative instruments on land-filling as well as their application in practice. The basic legal instrument in the EU is Directive 1999/31/EC on the landfill of waste. The basic measures that result from this legislation include security against the entry of unauthorised persons, prevention of wild burning of waste, regular compaction, and the installation of a system for collecting landfill gas and landfill leachate. In particular for the Balti Landfill, where the operating conditions are very poor, immediate measures to prevent it from burning, regular compaction, and overlaying with soil can be recommended. In addition, we recommend the monitoring of dioxins at both landfills, which may be generated during waste burning, as wildfires have occurred at both landfills.

2. **The Vatra Industrial Area** is very probably a source of heavy metals – particularly lead, arsenic, and mercury – in the Bic River as sediments from the Bic River showed a significant increase in all heavy metals below the industrial site compared to the sediments collected above it. It is not possible to determine exactly which industrial plant is the source of heavy metals, because the plants are clustered and the impact of each of them cannot be separated individually. It can only be assumed that in the industrial area there are sources of heavy metals, which are released into the Bic River. The impact of individual industries in the industrial area should be thoroughly monitored, for example by continuous air and water pollution monitoring stations, and by obliging the industries to report their emissions to the PRTR.
3. **The towns of Rybnitsa and Rezina** affect the Dniester River by introducing heavy metal pollution. We assume that conclusion because the sediment sample taken from the Dniester River above the towns of Rezina and Rybnitsa contains the lowest concentrations of most of the heavy metals. The increase in heavy metal (Pb, Cr, Cu, Ni, and Hg) levels in the sediment below the towns is up to double. The Rybnitsa Industrial Area has a significant influence on the surrounding concentrations of heavy metals. A small metalworking factory in the town of Rezina is probably a noticeable source of heavy metals in the Dniester River, as the highest concentrations of heavy metals in the sediment were found in a sediment sample from the right bank of the Dniester close to the town of Rezina. There is the mouth of a small watercourse, on which there is a small metalworking factory. We recommend a more detailed investigation of heavy metals around the sampling point, as there are eight protected sources of seepage water in the vicinity. The Rybnitsa Industrial Area is most probably an important source of heavy metals for the environment, particularly for agricultural land in its surroundings and for the Dniester River. The sediment sample taken from the Rybnitsa brook above the town of Rybnitsa has significantly lower concentrations of all the heavy metals that were measured than the sediment sample taken close to where the brook joins the Dniester River. The increment of some heavy metals (especially Cd, Pb, and Zn) increases several times as the brook flows through the town of Rybnitsa. As industries are located on the outskirts of residential districts of the towns, the establishment of continuous air and water quality monitoring – and publishing of its results – is essential to understand the exact burden on the environment and imposing measures to protect public health. The industries should be obliged to report their emissions to the PRTR.
4. In general, there is a lack of reliable data on the environmental impact of industrial sources of pollution in Moldova. The PRTR system, which is the most effective standard for the collection and publication of information on emissions, was launched recently; however, it does not involve all polluting industries and the latest data published is from 2017. Moldova should improve the system in accordance with the PRTR Protocol to the Aarhus Convention, which would significantly improve the monitoring of the sources of pollution.

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Annex I: Heavy metals overview and health impact

Arsenic

Arsenic (As) occurs naturally in many forms, either as inorganic compounds (mainly sulphides) or as organic compounds, and accompanies some ore deposits such as gold, silver, lead, copper, nickel, cobalt, antimony, iron, etc (1). A significant anthropogenic source of arsenic is the mining and metallurgical industry (2), as well as the burning of coal (especially lignite) (3).

Acute (short-term) inhalation exposure to arsenic dust or vapours at high levels leads to gastrointestinal effects (nausea, diarrhoea, abdominal pain); disorders of the central and peripheral nervous system can occur in workers acutely exposed to inorganic arsenic (4, 5). Chronic (long-term) inhalation exposure to inorganic arsenic in humans is associated with irritation of the skin and mucous membranes and effects on the brain and nervous system (6-8).

Arsenic itself and arsenic trioxide were allocated by the International Agency for Research on Cancer (IARC) (9) into the group 1 as human carcinogens and their link to the occurrence of lung and bladder cancer is considered sufficient. The IARC considers the evidence of the influence of arsenic on prostate, liver, and kidney cancer only as partially sufficient. Non-carcinogenic health risks of arsenic exposure are connected with the deceleration of foetal development, influencing the neuropsychic development of children, influence on the central and peripheral nervous system, and with heart and vessel diseases (10). The toxicity of arsenic is dependent on its speciation; arsenic (III) compounds are more toxic than AS(V) (11).

Cadmium

Cadmium (Cd) is a heavy metal chemically related to zinc, which is most commonly naturally present with copper, zinc, or lead in ore as sulphides of these metals (12). Cadmium is used as a stabilizer of selected plastics and in metallurgy and other industrial branches. In the past, cadmium was abundantly used in many electric and electronic devices as well; consequently, another significant source of cadmium is the processing of electronic waste (13, 14).

Cadmium has the ability to accumulate within living organisms, including the human body (bioaccumulation). About half of the total amount of cadmium in the body is found in the kidneys, where it binds to metallothionein, a cysteine-rich protein, and itcause damage to these organs (15). In addition, complementary cadmium displaces and replaces calcium absorbed by the intestines. Calcium deficiency in the body is reflected in demineralization, lower bone density, and impaired vitamin D_3 metabolism (16). Cadmium also has a negative effect on the hormonal system, especially sex hormones (17).

According to the IARC, cadmium is considered as a confirmed human carcinogen (group 1) which can disrupt the genetic information in cells (genotoxicity) and cause damage to human foetuses during their prenatal development (teratogenicity). In the case of exposure to cadmium, the IARC confirms the existence of sufficient evidence for the development of lung cancer, and additionally, the influence of cadmium has also been observed in kidney, mammary, and prostate cancer **(18)**.

Lead

Lead (Pb) is present in the soil as a result of human activity or natural processes such as pedogenesis and rock weathering. In soil, lead forms sulphides, sulphates, or carbonates. The presence of lead in the environment is mainly associated with the mining and processing of ores, the disposal of tailings, transport, and the operation of smelting plants, gasworks, and incinerators **(19-21)**. Lead contamination can penetrate the soil to a depth of up to twenty centimetres, thus adversely affecting the quality of biological systems in the long term **(22)**.

Lead has been proved to have a wide spectrum of toxic effects; it is considered one of the persistent HM and is one of the global environmental pollutants. Its presence in the blood is unfavourable in all concentrations as it is a xenobiotic for all life forms. Lead can cause effects on the blood, as well as the nervous, immune, renal, and cardiovascular systems. Exposure to high levels of lead can cause gastrointestinal symptoms and severe damage to the brain and kidneys and may have effects on reproduction **(23)**. Experts consider the so-called developmental neurotoxicity, i.e. damage to brain development in childhood (slow cognitive development, low IQ), to be a possible critically negative effect of lead that can severely affect children **(24)**. Once taken into the body, lead becomes distributed throughout the body in the blood and is accumulated in the bones **(25)**.

The IARC has placed the inorganic compounds of lead into the group of "likely" carcinogens (group 2A), with the explanation that there have been studies conducted on animals, with sufficient but limited results **(26)**.

Chromium

In nature, chromium (Cr) is a component of many minerals. It is used in a wide range of manufacturing, for example in the metallurgical and textile industries and in papermaking, and is also a component of dyes, catalysts, and fertilizers. It enters the environment through release from landfill leaching, contamination during ore extraction, or the combustion of petroleum and coal **(27, 28)**.

Chromium (VI) is known to cause various health effects, such as skin rashes, respiratory problems, a weakened immune system, kidney and liver damage, involve oxidation stress, alterates and damages DNA and proteins **(29, 30)**. The inhalation of chromium (VI) compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms, and oedema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itching. Chromium (VI) is classified by the IARC in group 1.

Significantly, chromium (III) is an essential nutrient for humans, and occurs naturally in many vegetables, fruits, meats, yeasts, and grain (31, 32).

Copper

Copper (Cu) is a metal naturally present mainly in the forms of sulphides, oxides, and carbides and to a lesser extent can also exist in pure metal form. Copper has been used by humans for thousands of years, but the mining and processing of its ores can be a significant source of environmental contamination (33, 34).

On one hand, copper, from a biological point of view, is one of the so-called essential elements; it is involved in the function of many enzymes and in the catalysis of significant enzymatic processes such as cellular respiration or the formation of neurotransmitters (35). On the other hand, higher exposure to copper may pose a health risk. Acute copper toxicity can result in a variety of pathological conditions and, in extreme cases, even death. Chronic toxicity can lead to liver and kidney damage (36) and severe neurological damage (37, 38). It has also been suggested that excess copper could also play a role in Alzheimer's disease (39).

Nickel

Nickel (Ni) is present in the environment especially in the form of sulphides and silicates. The contamination of the environment occurs primarily through ore mining and the metallurgical industry (3).

Prolonged oral exposure to higher doses of nickel causes changes in blood count composition, reduced iodine content in the thyroid gland, and skin irritation, and displaces essential divalent metals such as copper, zinc, calcium, magnesium, or iron from enzymes (40, 41). Some studies on animals have proved a variety of damage done to hereditary information – DNA (9). Moreover, considering its health impacts, nickel also acts as a very strong contact allergen, causing dermatitis (42).

The IARC has classified some compounds of nickel as confirmed human carcinogens (group 1) and nickel itself into group 2B, which is the classification of possible carcinogens.

Mercury

Mercury (Hg) is found naturally in many chemical and physical forms, e.g. in a solid or gaseous state. Each form of mercury has a unique toxicological profile, and differs in the mechanisms of transport and disposition in the body and metabolic fate. Mercury is spread via rock dust particles as a result of the erosion and weathering processes, deposited on the earth's surface, or delivered to water surfaces. The primary route of Hg exposure for humans is the inhalation of mercury vapour. The anthropogenic origin of mercury is associated with combustion processes, the burning of coal or municipal waste, and mining (43).

Elemental Hg is toxic to the central and peripheral nervous system, causing neurological and behavioural disorders. Symptoms include tremors, insomnia, memory loss, neuromus-

cular effects, headaches, and cognitive and motor dysfunction. The inhalation of mercury vapour can have harmful effects on the immune, nervous, and digestive systems, lungs, and kidneys and can be fatal **(44, 45)**.

In aquatic environments inorganic mercury can be converted into an extremely toxic organic form – methylmercury (MeHg). MeHg accumulates in fish and shellfish and has the highest bioavailability compared to the other forms **(46)**. Its ability to penetrate cell membranes causes toxicity of the whole organism, specifically, for example, damage to the nervous system, the development of cardiovascular problems, or problems with the liver and kidneys. The hormonal system is affected even at low concentrations of this metal as a result of the inactivation of receptor sites and suppression of hormone synthesis. Methylmercury is able to cross the placenta and cause brain and nerve disorders in a developing foetus. The presence of mercury in plant tissues inhibits plant growth and affects the intensity of adsorption and accumulation of essential elements **(47)**.

According to the IARC, methylmercury compounds are possibly carcinogenic to humans (Group 2B).

Zinc

Zinc (Zn) is an essential trace element. It is considered to be relatively non-toxic, particularly if taken orally **(48)**. Rather than zinc toxicity, zinc deficiency is observed **(48)**. However, manifestations of toxicity symptoms (nausea, vomiting, epigastric pain, lethargy, and fatigue) will occur with extremely high zinc intakes. Excessive zinc concentrations may lead to the deterioration of copper or iron metabolism **(49)**.

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Annex II: Lists of samples

Table 1: List of soil samples

Locality	Sample ID	Coordinates (N/E)		Date of sampling	Sampling site description	Sampling and sample preparation
Tintareni Landfill	TIN-SOIL-1	46.848305	29.1625498	18.08. 2021	a cornfield by the road leading to the landfill located west of the landfill	surface soil digging
Tintareni Landfill	TIN-SOIL-2	46.8154007	29.1906153	18.09. 2021	a corn field by the small road, north of the village of Ciobaunovca	surface soil digging, composite sample of five subsamples collected in a square 2x2 m
Tintareni Landfill	TIN-SOIL-3	46.8302644	29.2159338	18.08. 2021	a harvested wheat field in the village of Ciobaunovca	surface soil digging, composite sample of five subsamples collected in a square 2x2 m
Balti Landfill	BAL-SOIL-1	47.7112212	279856301	16.08. 2021	spot next to a crop field, between the landfill and the field; the wind usually blows from the NW	surface soil digging, composite sample of five subsamples collected in a square 4x4 m, homogenisation and quotation
Balti Landfill	BAL-SOIL-2	47.7119586	27.9709088	16.08. 2021	a sunflower field a bit further from the landfill	digging surface soil, composite sample of five subsamples collected in a square 2x2 m, homogenisation
Balti Landfill	BAL-SOIL-3	47.7142913	27.9753914	16.08. 2021	a sunflower field and a cornfield	surface soil digging, composite sample of five subsamples collected in a square 2x2 m, homogenisation
Balti Landfill	BAL-SOIL-4	47.7126525	27.983689	16.08. 2021	a patch of grass between the first and second ponds, below the dam	a point sample
Balti Landfill	BAL-SOIL-5	47.7154089	27.9778048	16.08. 2021	a sunflower field just next to the landfill	digging surface soil, composite sample of five subsamples collected in a square 2x2 m
Balti Landfill	BAL-SOIL-6	47.721796	27.9756209	16.08. 2021	a garden in a village	digging surface soil, composite sample of five subsamples collected in a square 2x2 m
Vatra Industrial Area	VAT-SOIL-1	47.0752945	28.7682522	17.08. 2021	a sunflower field quite close to the industry in the village of Ghidighici; the sampling spot is located downwind from the industry in the dominant direction of the wind	digging surface soil, composite sample of five subsamples collected in a square 2x2 m, homogenisation
Vatra Industrial Area	VAT-SOIL-2	47.0568586	28.7640847	17.08. 2021	a cornfield on the edge of the garden village in Dumbrovka	digging surface soil, composite sample of five subsamples collected in a square 2x2 m, homogenisation
Rezina Industrial Area	REZ-SOIL-1	47.7690254	28.9669086	13.08. 2021	a cornfield on a hill, SE of a limestone mine and a field in Rezina-Ciorna, downwind from the plant and the mine	digging surface soil (0-10 cm), composite sample of five subsamples collected in a square 2x2 m

Rezina Industrial Area	REZ-SOIL-2	47.7767585	28.9814251	13.08. 2021	a garden in the village of Rezina-Bosemta; there are some vegetables and flowers	digging surface soil, composite sample of five subsamples collected in a square 2x2 m, homogenisation and quartation
Rybnitsa Industrial Area	RYB-SOIL-1	47.7804975	29.0307887	14.08. 2021	a sunflower field in the town of Rybnitsa	composite soil samples
Rybnitsa Industrial Area	RYB-SOIL-2	47.7528494	25.0380099	14.08. 2021	an agricultural area in the town of Rybnitsa	composite soil sample of five subsamples
Rybnitsa Industrial Area	RYB-SOIL-3	47.7892022	29.019505	14.09. 2021	a harvested wheat field in the town of Rybnitsa	composite soil sample

Table 2: List of sediment samples

Locality	Sample ID	Coordinates (N/E)		Date of sampling	Description of sampling site	Sampling and sample preparation	Corresponding water sample
Balti Landfill	BAL-SED-1	47.7069705	27.9769393	16.8. 2021	the third pond below the landfill; the pond is used for fishing	sampling with sediment core, homogenisation	BAL-W-1
Balti Landfill	BAL-SED-2	47.7138655	27.9809796	16.8. 2021	the first pond below the landfill, probably works as a tailing pond; there is a dam construction	digging from the bank	BAL-W-2
Balti Landfill	BAL-SED-3	47.7126525	27.9793092	16.8. 2021	the second pond below the landfill	sampling with sediment core	BAL-W-3
Balti Landfill	BAL-SED-4	47.6822661	27.9833281	16.8. 2021	the pond with a sort of wetland in the village of Lipovana; fifth pond from the landfill with thick black mud	sampling with sediment core	BAL-W-4
Vatra Industrial Area	VAT-SED-1	47.0740104	28.740925	17.8. 2021	the Bic River in Vatra; the sampling site is in the middle of bush and forest upstream of the industrial area; there was waste dumped on the banks	digging from the bottom	NS
Vatra Industrial Area	VAT-SED-2	47.063097	28.7742245	17.8. 2021	the Bic River in Vatra, under the bridge, downstream from the industrial area	digging from the riverbed, homogenisation	NS
Rezina Industrial Area	REZ-SED-1	47.775238	28.976953	13.8. 2021	the Ciorna brook downstream from the cement kiln		NS

Rezina Industrial Area	REZ-SED-2	47.8198774	28.7866394	13.8. 2021	the Ciorna brook in the town of Soldanesti, upstream from the cement kiln; the sediment is odourless grey clay	sampling with sediment core, composite sample of three subsamples, homogenisation	NS
Rybnitsa Industrial Area	RYB-SED-1	47.7898372	28.9943063	14.8. 2021	a small water stream with private small-scale agriculture and willows in the surroundings; the sediment is black, with the odour of wetlands	composite sample of five subsamples	NS
Rybnitsa Industrial Area	RYB-SED-2	47.754027	28.9962066	14.8. 2021	the Rybnitsa water stream with some vegetation in the surroundings, downstream of the industrial area; the sediment is black	mixture of sediments	NS
Rybnitsa Industrial Area	RYB-SED-3	47.7568587	29.0514722	14.8. 2021	the Rybnitsa water stream with a forest and road in the surroundings upstream from the industrial area; the sediment is black-brown	sampling with sediment core	NS
Dniester River	DNI-SED-1	47.8263915	29.0099375	13.8. 2021	the Dniester River in the village of Solonceni with cattle pastures in its surroundings upstream from Rybnitsa; the sediment is brown-grey and fine-grained	sampling with sediment core, composite sample of three subsamples, homogenisation	NS
Dniester River	DNI-SED-2	47.748706	28.982158	15.8. 2021	the Dniester River in Rybnitsa-Rezina, with a long patch of reeds by the bank	sampling with sediment core, composite sample of three subsamples, homogenisation	DNI-W-1
Dniester River	DNI-SED-3	47.736613	28.971082	15.8. 2021	the right bank of the Dniester River in the Rybnitsa-Rezina area; the sediment is anaerobic black	homogenisation	DNI-W-3
Dniester River	DNI-SED-4	47.706893	28.972801	15.8. 2021	the fishing port on the Dniester River; the sediment is dark grey	sampling with sediment core, homogenisation	DNI-W-5
Dniester River	DNI-SED-5	44.666647	28.99149	15.8. 2021	the right bank of the Dniester River near the village of Vychvatintsi, with a space between reeds where cattle have a drinking spot	sampling with sediment core, composite sample of three subsamples, homogenisation	DNI-W-6

Dniester River	DNI-SED-6	47.619309	28.983869	15.8. 2021	the Dniester River in the village of Zuzalany, with reeds on the bank; many big mussels present in the grey mud at the place	sampling with sediment core	DNI-W-7
Dniester River	DNI-SED-7	47.567938	29.026004	15.8. 2021	the Dniester River in the village of Lalova; the sediment is brown to black	sampling with sediment core, homogenisa-tion	DNI-W-8
Dniester River	DNI-SED-8	47.534994	29.020556	15.8. 2021	the Dniester River in the village of Butucha-ny, with kids swimming at the place; the sedi-ment is black	sampling with sediment core, homogenisa-tion	DNI-W-9
Dniester River	DNI-SED-9	47.507932	29.040099	15.8. 2021	the Dniester River in the village of Lopatna	sampling with sediment core	DNI-W-10

Table 3: List of water samples

Locality	Sample ID	Coordinates (N/E)		Date of sampling	Description of sampling site	Sampling	Ammonium [mg/L]
Balti Landfill	BAL -W-1	47.7069705	27.9769393	16.8. 2021	the third pond below the landfill; the pond is used for fishing; transparent water	bottled sampling	0.09
Balti Landfill	BAL -W-2	47.7138655	27.9809796	16.8. 2021	the first pond below the landfill, probably works as a tailings pond; there is a dam constructed; brown water with black specks	bottled sampling	2.32
Balti Landfill	BAL -W-3	47.7126525	27.9793092	16.8. 2021	the second pond below the landfill; green water	bottled sampling	1.56
Balti Landfill	BAL -W-4	47.6822661	27.9833281	16.8. 2021	the pond with a sort of wetland in the village of Lipovana; fifth pond from the landfill	bottled sampling	0.88
Dniester River	DNI -W-1	47.748706	28.982158	15.8. 2021	the Dniester River in the Rybnitsa-Rezina area; slightly brownish-greenish water	bottled sampling	0.2
Dniester River	DNI -W-2	47.738495	28.9777999	15.8. 2021	the Dniester River in the Rybnitsa-Rezina area; reeds on the banks	bottled sampling from a boat	NA
Dniester River	DNI -W-3	47.736613	28.9747082	15.8. 2021	the Dniester River Reeds in the town of Rezina; some outflow on the bank; slightly brownish water	bottled sampling	2.51
Dniester River	DNI -W-4	47.19431	28.965018	15.8. 2021	the right bank of the Dniester River in Rezina; transparent and slightly brownish water	bottled sampling from a boat	NA

Dniester River	DNI -W-5	47.706893	28.972801	15.8. 2021	the Dniester River in the village of Kipri; fishing port; cattle drinking spot and reeds in the surroundings	bottled sampling from a boat	0.07
Dniester River	DNI -W-6	47.66697	28.99149	15.8. 2021	the Dniester River in the village of Vychvatinti, with reeds in the surroundings		0.07
Dniester River	DNI -W-7	47.619309	28.983969	15.8. 2021	the Dniester River in the village of Zuzulainy, with reeds in the surroundings	bottled sampling from a boat	0.04
Dniester River	DNI -W-8	47.567938	29.026009	15.8. 2021	the Dniester River in the village of Lalova, with bushes in the surroundings; clear water	bottled sampling	0.1
Dniester River	DNI -W-9	47.534994	29.020556	15.8. 2021	the Dniester River in the village of Botachany, with reeds and weeds in the surroundings, with a kids' swimming spot nearby, geese, cattle, and other farm animals; clear and slightly brownish water	bottled sampling from a boat	<LOQ
Dniester River	DNI -W-10	47.507932	29.040099	15.8. 2021	the Dniester River Forest in the village of Lopatna, with pasture in the surroundings	bottled sampling	NA

Annex III: Results

Table 4: Concentrations of heavy metals in soil samples

Locality	Sample ID	Cadmium [mg/kg DW]	Lead [mg/kg DW]	Chromium[1)] [mg/kg DW]	Copper [mg/kg DW]	Zinc [mg/kg DW]	Nickel [mg/kg DW]	Arsenic [mg/kg DW]	Mercury [mg/kg DW]
Tintareni Landfill	TIN-SOIL-1	0.21	16.70	29.45	22.03	78.63	34.54	5.28	0.033
Tintareni Landfill	TIN-SOIL-2	0.14	11.57	18.88	25.29	56.98	25.08	4.55	0.026
Tintareni Landfill	TIN-SOIL-3	0.13	12.20	21.20	43.47	54.60	24.09	3.84	0.023
Balti Landfill	BAL-SOIL-1	0.31	28.47	27.73	30.76	113.56	30.49	6.80	0.026
Balti Landfill	BAL-SOIL-2	0.19	14.39	24.79	17.51	67.97	30.36	5.85	0.030
Balti Landfill	BAL-SOIL-3	0.17	14.37	27.04	18.16	70.36	32.41	7.73	0.031
Balti Landfill	BAL-SOIL-4	0.15	12.91	34.63	13.96	64.21	24.66	4.06	0.024
Balti Landfill	BAL-SOIL-5	0.22	30.92	19.58	22.32	79.81	28.41	4.64	0.052
Balti Landfill	BAL-SOIL-6	0.13	11.41	18.81	13.84	54.14	23.54	4.42	0.031
Vatra Industrial Area	VAT-SOIL-1	0.21	14.59	18.91	31.01	70.42	26.23	5.52	0.026
Vatra Industrial Area	VAT-SOIL-2	0.12	10.71	16.62	12.15	44.48	20.68	3.89	0.027
Rezina Industrial Area	REZ-SOIL-1	0.14	14.32	20.81	13.77	60.24	24.35	4.19	0.028
Rezina Industrial Area	REZ-SOIL-2	0.26	16.64	14.43	31.24	103.94	18.03	≤ 2.0	0.036
Rybnitsa Industrial Area	RYB-SOIL-1	1.16	58.68	25.10	22.67	203.64	22.46	5.73	0.037
Rybnitsa Industrial Area	RYB-SOIL-2	0.23	16.06	15.72	15.39	62.22	20.84	4.04	0.021
Rybnitsa Industrial Area	RYB-SOIL-3	0.68	33.34	17.22	17.60	109.71	19.87	5.30	0.038
Legal standard									
Czech soil pollution indication		20	400	ND	400	150	200	40	20
Regional screening levels – industrial areas (US EPA)		980	800	ND	47,000	350,000	22,000	3	46
Regional screening levels – residential areas (US EPA)		71	400	ND	31,000	23,000	1,500	0.68	11

[1)] Total concentration of chromium

Table 5: Concentrations of heavy metals in sediment samples

Locality	Sample ID	Cadmium [mg/kg DW]	Lead [mg/kg DW]	Chromium[1)] [mg/kg DW]	Copper [mg/kg DW]	Zinc [mg/kg DW]	Nickel [mg/kg DW]	Arsenic [mg/kg DW]	Mercury [mg/kg DW]
Balti Landfill	BAL-SED-1	0.10	5.96	9.63	7.92	26.60	15.19	2.40	0.017
Balti Landfill	BAL-SED-2	0.11	3.40	11.56	4.59	16.94	8.06	2.41	0.014
Balti Landfill	BAL-SED-3	0.16	5.98	19.97	11.38	35.88	25.00	≤ 2.0	0.028
Balti Landfill	BAL-SED-4	0.14	8.73	11.98	12.39	37.98	22.87	5.29	0.022
Vatra Industrial Area	VAT-SED-1	0.13	13.28	6.42	13.32	37.46	9.76	≤ 2.0	0.012
Vatra Industrial Area	VAT-SED-2	0.16	63.99	11.62	22.28	69.34	15.46	4.25	0.031
Rezina Industrial Area	REZ-SED-1	0.09	10.15	18.52	15.76	61.29	19.57	6.96	0.047
Rezina Industrial Area	REZ-SED-2	0.10	9.45	15.21	14.10	52.10	18.67	4.41	0.034
Rybnitsa Industrial Area	RYB-SED-1	0.64	49.96	19.17	25.49	173.87	18.55	≤ 2.0	0.072
Rybnitsa Industrial Area	RYB-SED-2	1.67	71.64	45.39	40.18	501.10	33.81	13.04	0.071
Rybnitsa Industrial Area	RYB-SED-3	0.21	12.55	26.32	14.67	72.93	22.87	7.80	0.024
Dniester River	DNI-SED-1	0.09	3.31	5.31	4.50	17.00	6.38	≤ 2.0	0.019
Dniester River	DNI-SED-2	0.14	7.99	11.77	10.24	37.40	14.53	≤ 2.0	0.040
Dniester River	DNI-SED-3	0.32	27.48	36.98	62.95	253.93	29.83	≤ 2.0	0.648
Dniester River	DNI-SED-4	0.10	7.52	16.90	14.34	44.97	18.10	≤ 2.0	0.052
Dniester River	DNI-SED-5	0.15	6.67	12.06	10.50	34.49	15.88	≤ 2.0	0.038
Dniester River	DNI-SED-6	0.06	6.36	14.38	11.25	35.16	16.99	≤ 2.0	0.033
Dniester River	DNI-SED-7	0.07	5.09	11.29	9.27	31.01	14.35	≤ 2.0	0.051
Dniester River	DNI-SED-8	0.15	6.62	12.51	11.49	36.37	14.99	3.72	0.037
Dniester River	DNI-SED-9	0.09	6.51	13.98	13.10	35.68	17.10	≤ 2.0	0.036

[1)] Total concentration of chromium

Table 6: Concentrations of heavy metals in water samples

Locality	Sample ID	Cadmium [mg/L]	Lead [mg/L]	Chromium[1)] [mg/L]	Copper [mg/L]	Zinc [mg/L]	Nickel [mg/L]	Arsenic [mg/L]	Mercury [mg/L]
Balti Landfill	BAL-W-1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Balti Landfill	BAL-W-2	≤ 0.05	≤ 0.1	0.5	≤ 0.05	≤ 0.1	0.3	≤ 0.4	≤ 0.001
Balti Landfill	BAL-W-3	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Balti Landfill	BAL-W-4	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-2	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-3	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-4	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-5	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-6	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-7	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-8	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-9	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001
Dniester River	DNI-W-10	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.05	≤ 0.1	≤ 0.1	≤ 0.4	≤ 0.001

[1)] Total concentration of chromium

Annex IV: General requirements for landfills in the EU

1. Location

The location of a landfill must take into consideration requirements relating to: the distances from the boundary of the site to residential and recreation areas, waterways, water bodies, and other agricultural or urban sites; the existence of groundwater, coastal water, or nature protection zones in the area; the geological and hydrogeological conditions in the area; the risk of flooding, subsidence, landslides, or avalanches at the site; the protection of the nature or cultural patrimony in the area.

2. Water control and leachate management

Appropriate measures shall be taken, with respect to the characteristics of the landfill and the meteorological conditions, in order to: control water from precipitations entering into the landfill body, prevent surface water and groundwater from entering into the landfilled waste, collect contaminated water and leachate, and treat contaminated water and leachate collected from the landfill to the appropriate standard required for their discharge.

3. Protection of soil and water

A landfill must be situated and designed so as to meet the necessary conditions for preventing pollution of the soil, groundwater, or surface water and ensuring the efficient collection of leachate. Protection of soil, groundwater, and surface water is to be achieved by the combination of a geological barrier and a bottom liner during the operational phase and by the combination of a geological barrier and a top liner during the passive phase. The geological barrier is determined by the geological and hydrogeological conditions below and in the vicinity of a landfill site providing sufficient attenuation capacity to prevent a potential risk to soil and groundwater.

4. Gas control

Appropriate measures shall be taken in order to control the accumulation and migration of landfill gas. Landfill gas shall be collected from all landfills receiving biodegradable waste and the landfill gas must be treated and used. If the gas collected cannot be used to produce energy, it must be flared. The collection, treatment, and use of landfill gas shall be carried on in a manner which minimises damage to or deterioration of the environment and risk to human health.

5. Nuisances and hazards

Measures shall be taken to minimise nuisances and hazards arising from the landfill through: emissions of odours and dust, wind-blown materials, noise and traffic, birds, vermin and insects, formation and aerosols, fires. The landfill shall be equipped so that dirt originating from the site is not dispersed onto public roads and the surrounding land.

6. Stability

The emplacement of waste on the site shall take place in such a way as to ensure the stability of the mass of waste and associated structures, particularly with respect to the avoidance of slippages. Where an artificial barrier is established it must be ascertained that the geological substratum, considering the morphology of the landfill, is sufficiently stable to prevent settlement that may cause damage to the barrier.

7. Barriers

The landfill shall be secured to prevent free access to the site. The gates shall be locked outside operating hours. The system of control and access to each facility should contain a programme of measures to detect and discourage illegal dumping in the facility.


ACCES
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Part II.

Persistent organic pollutants

(POPs) in chicken eggs and soils from three selected localities in Moldova

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Summary

Pooled samples of free-range chicken eggs and composite samples of soils were collected in three villages near the potential sources of persistent organic pollutants (POPs). These samples were analysed for their content of the following POPs: chlorinated dioxins and furans (dioxins; PCDD/Fs), polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs), poly- and perfluoroalkyl substances (PFASs), short-chain chlorinated paraffins (SCCPs), and organochlorine pesticides (OCPs), including DDT and lindane.

The chemical analyses revealed serious contamination of the eggs from Ciobanovca with obsolete POP pesticides (i.e. three HCH isomers and DDT in particular) and PCBs. High levels of dioxins and dioxin-like PCBs, as well as sum of DDT, were measured in the eggs from Dumbrava. The levels of dioxins and dioxin-like PCBs in the eggs from Dumbrava exceeded the EU standard for food by 3.5-fold, showing that tyre pyrolysis or other industrial sources in the nearby Vatra industrial zone can be significant sources of releases of toxic chemicals. Our study shows the importance of filling this gap and also the need for the better evaluati-

on of newly-built potential sources of unintentionally produced POPs (U-POPs), such as, for example, industrial processes including combustion. Tyre pyrolysis in Vatra belongs to this group of sources which are listed as priority sources of U-POPs in Annex C to the Stockholm Convention.

The high level of sum of DDT in one soil sample from Vatra shows in the potentially high residues in the soils from the past use of this pesticide in Moldova. There is also a need to improve the register of stockpiles of obsolete POPs, including buildings left without any remediation after stocks of POPs were removed from them. These contaminated buildings can remain serious contamination hotspots of OCPs, PCBs, and other technical POPs.

Low levels of other POPs such as PBDEs or PFASs in eggs show that waste containing these POPs probably has not reached the landfills in Moldova yet, and/or free-range chicken eggs did not become the final destination of these POPs. There is a lack of data about POPs from which to gain an understanding of sources of POPs in the Moldovan environment.

Introduction

This study is focused on the evaluation of levels of persistent organic pollutants (POPs) measured in three pooled egg samples from sites near potential sources of these chemicals (i.e. by some municipal waste landfills and industrial areas located in the drainage basin of the River Dniester) in the Moldovan environment. Our investigation is focused on the assessment of contamination by chemicals which were either listed in the Annexes to the Stockholm Convention on POPs or fall into the larger group of chemicals with POP characteristics (e.g. brominated flame retardants (BFRs) or per- and polyfluoroalkyl substances (PFASs)). The chemicals that were investigated fall into three groups:

1. some of these chemicals are additives to plastics (BFRs, PFASs, short-chain chlorinated paraffins (SCCPs)) or to paper food packaging or textile consumer products (PFASs) and thus can be found in end-of-life products in waste landfills;
2. the other group of chemicals, such as, for example, dioxins (PCDD/Fs), dioxin-like polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCB), and hexachlorobenzene (HCB), occur as unintentionally created by-products of chemical production, combustion technologies (e.g. pyrolysis), or burning chlorinated wastes (e.g. when a dumpsite burns out or waste is incinerated);
3. we also looked at intentionally used POPs such as the large group of organochlorine pesticides (OCPs) and/or polychlorinated biphenyls (PCBs) used as transformer and condenser oils or additives to paints in the past. There were many obsolete pesticide warehouses in Moldova with OCPs, including DDT, hexachlorocyclohexane (HCH), and others. Tintareni is on the list of such sites, and it is also one of the hotspots within our study.

Our survey builds on the mapping of POPs in the Moldovan environment by the National Implementation Plan (NIP) for the Stockholm Convention [1], and some other studies conducted in Moldova previously [2-6]; however, information is limited as the NIP was not updated to include new POPs added to the Stockholm Convention Annexes after 2004. On

the evidence of the existing information sources, DDT, HCH, and other POP pesticides were widely used in Moldova between 1950 and 1990 [1, 6].

Localities

Samples of free-range chicken eggs were taken in three villages near three localities with potential sources of POPs. These villages were 1) Ciobanovca, located 4.5 km south-east of the Tintareni Landfill, 2) Mebelchik, which is a settlement and a part of Balti, located 0.5 km north-west of the Balti Landfill, and 3) Dumbrava, located approximately 2.5 km north-north-west of the industrial part of Vatra, which includes tyre pyrolysis [7, 8], asphalt production, and other industrial activities. Tyre pyrolysis is clearly visible in Google Earth satellite images (see the map in Figure 1). The Tintareni and Balti landfill sites and Vatra industrial hotspot are described in the first part of this report, which evaluates contamination with heavy metals in the area of the Dniester basin [9].

Figure 1: Tyre pyrolysis in the industrial area in Vatra in a Google Earth satellite image.

With regard to Tintareni, and from the point of view of potential contamination with POPs, it is important to underline that there were more than two tonnes of unidentified POP pesticides transferred from Tintareni to central storage before the year 2005 [5]. There are also

some agricultural structures and buildings that are recognisable in Google Earth satellite images in the village of Ciobanovca.

Over 1000 warehouses for pesticides had been built in Moldova by the early 1990s, according to the National Implementation Plan for the Stockholm Convention [1], so any agricultural structure and/or building can be suspected of formerly being a place where POP pesticides, which were widely used in Moldova, were stored.

The pyrolysis plant for the disposal of used tyres and asphalt production are potential sources of unintentionally produced POPs among the industrial activities taking place in the Vatra industrial area, although we do not have a full list of the industrial plants there (see the first part of this report on heavy metal contamination).

Methodology

Sampling procedures

The sampling of free-range chicken eggs was selected as a sensitive indicator of contamination by POPs in soils/dust and represents an important human exposure pathway [10-12]. As "active samplers" they can be used to reveal contamination by POPs, particularly in areas impacted by dioxins (PCDD/Fs) and PCBs [13-16], DDT, or lindane [17-20], as well as by BFRs [17, 21, 22] or PFASs [23]. We used free-range chicken eggs to study the levels of contamination of certain sites with POPs.

Pooled samples of six individual egg samples were collected at each of the selected sampling sites in the villages of Ciobanovca (near the Tintareni Landfill), Mebelchik (near the Balti Landfill), and Dumbrava (near Vatra) in order to obtain more representative samples. We also used a sample of pooled eggs from a supermarket in Kyiv as a reference sample to exhibit background levels of POPs, as suggested by Dvorská [24]. That pooled sample was obtained in May 2018 as part of another egg study [25]. For some chemicals we also used partly unpublished data from the analysis of a sample of eggs from a supermarket in Prague from 2018 [26, 27].

The soil sampling is specified in the first part of this report, on contamination by heavy metals.

Analytical methods

The egg samples and two soil samples from Vatra were analysed for their content of individual polychlorinated dibenzo-p-dioxins and dibenzofurans (dioxins, PCDD/Fs), and an extended list of PCB congeners by HRGC-HRMS at the accredited laboratory of the State Veterinary Institute in Prague, Czech Republic. Analyses of PBDEs, HBCD, 17 PFASs, including PFOA, PFOS and PFHxS, organochlorine pesticides (DDT and its metabolites, three HCH isomers), pentachlorobenzene (PeCB), hexachlorobenzene (HCB), hexachlorobutadiene (HCBD), and seven indicator PCB congeners were conducted

in a Czech certified laboratory at the Department of Food Chemistry and Analysis of the University of Chemistry and Technology in Prague.

The analytes were extracted by a mixture of organic solvents, hexane: dichloromethane (1:1). The extracts were cleaned by means of gel permeation chromatography (GPC). The analytical procedures for the extraction of PCBs, OCPs, CPs, and BFRs (GC amenable) and PFASs, HBCDs, and TBBPA (LC amenable) from soils are as described elsewhere **[28-30]**.

The identification and quantification of the analyte was conducted by gas chromatography coupled with tandem mass spectrometry detection in electron ionisation mode for OCPs, HCB, PeCB, HCBD, and indicator PCBs.

The extract was transferred into cyclohexane and diluted. The identification and quantification of SCCPs were performed via gas chromatography/time-of-flight high-resolution mass spectrometry (GC/TOF-HRMS) in the mode of negative chemical ionisation (NCI).

The identification and quantification of PBDEs were performed using gas chromatography coupled with mass spectrometry in negative ion chemical ionisation mode (GC-MS-NICI). The identification and quantification of HBCD isomers and selected PFASs were performed by liquid chromatography interfaced with tandem mass spectrometry with electrospray ionisation in negative mode (UHPLC-MS/MS-ESI).

Results and Discussion

All the results of the analytical measurements for the three egg samples, two soil samples, and the reference egg sample from the supermarket in Kyiv are summarised in Table 1 below. A more detailed overview of the results for specific POP chemicals measured in the eggs and soil from the vicinity of the Tintareni Landfill, Balti Landfill, and Vatra industrial area is provided in Table AIII/1 in Annex III.

Table 1: Summary of the results for the individual and grouped POPs measured in three pooled egg samples, two soil samples from Moldova, and the reference egg sample from the supermarket in Kyiv.

Locality	EGGS	Ciobanovca	Mebelchik	Dumbrava	Kyiv	SOIL	Vatra	Vatra
Sample ID	Units	TIN-EGG-1	BAL-E-GG-1	VAT-EGG-1	Kyiv – supermarket	Units	VAT-SOIL-1	VAT-SOIL-2
Fat	%	11.5%	11.6%	11.7%	10.2%			
PeCB	ng/g fat	16.57	0.60	0.42	<0.10	ng/g dw	<0.02	<0.02
HCB	ng/g fat	2.31	1.73	1.59	0.95	ng/g dw	0.04	0.03
HCBD	ng/g fat	<0.10	<0.10	<0.10	<0.10	ng/g dw	<0.02	<0.02
Sum HCH	ng/g fat	3,005	3.84	5.56	1.70	ng/g dw	2.46	0.04
Sum DDT	ng/g fat	554	47	50	0.25	ng/g dw	234	5.63
6 iPCBs*	ng/g fat	144	2.2	209	0.69	ng/g dw	0.40	0.06
7 iPCBs	ng/g fat	222	3.08	229	0.69	ng/g dw	0.56	0.09
SCCP C10-C13	ng/g fat	<50.0	<50.0	<50.0	NA	ng/g dw	NA	NA
Sum PBDEs	ng/g fat	<LOQ	<LOQ	<LOQ	<LOQ	ng/g dw	<LOQ	<LOQ
Sum HBCD	ng/g fat	4.77	<LOQ	14.75	NA	ng/g dw	<LOQ	0.95
6 nBFRs	ng/g fat	<LOQ	0.341	<LOQ	<LOQ	ng/g dw	0.02	0.01
Sum PFASs	ng/g	0.76	0.26	0.38	NA	ng/g dw	NA	NA
PCDD/Fs	pg TEQ/g fat	5.09	1.29	4.81	0.25	pg TEQ/g	0.31	0.29
dl PCBs	pg TEQ/g fat	51.95	3.13	12.7	0.03	pg TEQ/g	0.26	0.13
Total PCDD/F + dl PCBs	pg TEQ/g fat	57.04	4.42	17.51	0.28	pg TEQ/g	0.57	0.42

NA = not analysed; <LOQ = below level of quantification; for PCDD/F and dl PCB congeners half of LOQ was counted in total levels in the case of congeners below LOQs; * sum of PCB28, PCB52, PCB101, PCB138, PCB153, and PCB180.

Organochlorine pesticides (OCPs)

There were high levels of some OCPs measured in the pooled egg sample from Ciobanovca, as is visible in Table 1. The highest level was observed for the sum of three HCH isomers in that sample, among which the alpha and beta isomers had much higher levels than the gamma isomer (lindane). The beta HCH level of 1,536 ng/g fat is comparable to the level of 1,800 ng/g fat measured in free-range chicken eggs from the vicinity of the obsolete plant for the production of lindane in Porto Romano, Albania [31].

The sum of DDT and its metabolites was also very high in this sample, ten times higher than in the eggs from Mebelchik and Dumbrava. The sum of DDT metabolites (554 ng/g fat) was comparable to the levels of 547 and 491 ng/g fat measured in samples of eggs from Kovachevo, Bulgaria in 2005 [32] and Kryvyi Rih, Ukraine in 2018 [25]. The level of the sum of DDT in the eggs from Ciobanovca is lower in comparison to those from some other locations, such as e.g. Peshawar in Pakistan, Helwan in Egypt, or Lysa nad Labem in the Czech Republic, where the levels of the sum of DDT were above 1,500 ng/g fat [18]. The levels of the sum of DDT in the eggs from Mebelchik and Dumbrava are up to 200 times above the reference sample from the supermarket in Kyiv, **indicating that continuing contamination by DDT has remained present in the Moldovan environment since the time when it was applied in the last century in large volumes** [1]. However comparable levels of 26 and 30 ng/g fat to those in the eggs from Mebelchik and Dumbrava were measured in eggs from large farms obtained in Prague [26] and Beijing [33].

We compared the measured levels of OCPs per gram of fresh eggs with the maximum residue levels (MRL) set by the EU. This comparison is summarised in Table 2. **The level of DDT metabolites in the eggs from Ciobanovca (63.6 ng/g fresh weight) exceeded the EU maximum residue level set for eggs, 50 ng/g fresh weight. It also exceeded the EU MRL for lindane and, by several times, the levels for alpha and beta HCH isomers (see Table 2).**

Table 2: Summarised levels of OCPs in eggs from three villages in Moldova compared with the EU MRL.

Locality	Units	Ciobanovca	Mebelchik	Dumbrava	EU MRL
Sample ID		TIN-EGG-1	BAL-EGG-1	VAT-EGG-1	
Fat	%	11.5%	11.6%	11.7%	
HCB	ng/g	0.27	0.20	0.19	20
α-HCH	ng/g	155.90	0.12	0.16	20
β-HCH	ng/g	176.60	0.28	0.41	10
γ-HCH	ng/g	13.03	0.04	0.08	10
Sum HCH	ng/g	345.53	0.45	0.65	–
o,p'-DDE	ng/g	0.02	0.01	0.01	–
p,p'-DDE	ng/g	47.27	4.64	5.01	–
o,p'-DDD	ng/g	0.10	0.01	0.02	–
p,p'-DDD	ng/g	3.78	0.43	0.51	–
o,p'-DDT	ng/g	2.45	0.31	0.25	–
p,p'-DDT	ng/g	10.11	0.08	0.03	–
sum 4 DDT	ng/g	63.62	5.47	5.80	50

A significant level of the sum of DDT was also measured in a composite sample of soil (VAT-SOIL-1) from a sunflower field near the industrial area. This level is much higher than the levels observed in arable land soils from the Czech Republic [34], for example.

It is obvious from the analytical results that the levels of OCPs in the eggs from Ciobanovca were caused by some local pollution hotspot, while the levels of OCPs in the other two samples from Moldova may result from the remaining overall contamination of the Moldovan environment. Some agricultural structures and buildings are recognisable in Google Earth satellite images in the village of Ciobanovca. Over 1000 warehouses for pesticides had been built in Moldova by the early 1990s, according to the National Implementation Plan for the Stockholm Convention [1], so any agricultural structure and/or building can be suspected of being a former warehouse for the POP pesticides that were widely used in Moldova. Another source of contamination might be that the Tintareni Landfill became the destination for obsolete POP pesticides. According to the project focused on sustainable management of POP stockpiles funded by the Global Environment Facility (GEF), more than two tonnes of unidentified POP pesticides were transferred from Tintareni to central storage before the year 2005 [5]. The above-mentioned potential sources of pollution in Ciobanovca need to be investigated.

Polychlorinated biphenyls (PCBs)

This chapter focuses on PCBs, which were used, for example, in transformer oils in the past. The results for dioxin-like PCBs will be discussed further in the section that focuses on U-POPs. The level of six indicator PCB congeners[1] (iPCBs) in the free-range chicken eggs from Ciobanovca and Dumbrava exceeded the EU maximum limit of 40 ng/g fat [35] by almost four- and more than fivefold, respectively. In the eggs from Dumbrava it is well below that limit and it is slightly above the level in the reference egg sample from Kyiv; however, it is lower in comparison to the level of 13 ng/g fat in eggs from a large farm obtained in a supermarket in Prague [27]. The levels of PCBs in the eggs from Ciobanovca and Dumbrava indicate the influence of some potential PCB sources near the sampling sites. These can be either obsolete transformers and/or capacitors with PCBs or obsolete stockpiles of PCBs in the near vicinity. PCBs are more volatile in comparison to, for example, dioxins, so the influence of a source in the industrial area in Vatra should be considered.

The levels of iPCBs in the eggs from Ciobanovca and Dumbrava are comparable to those observed in eggs from some locations in central Kazakhstan, e.g. Rostovka or Shabanbai Bi [36, 37], but are much higher than the levels found in eggs from certain localities in Ukraine, Armenia, and Balkan countries [38] or south-western Kazakhstan [39].

PCBs were not found in the transformers in Moldova that were checked; however, they can rather be found in old capacitors, according to the Moldovan NIP from 2004 [1]. The NIP also stated that: "The sectors/industries where a certain amount of PCBs could be presently used in Moldova are as follows: hydraulic fluids; lubricating oils; adhesives; paints; surface treatment for textiles; plasticizers; sealants; fluorescent lamp ballasts and other

1 Sum of PCB28, PCB52, PCB101, PCB138, PCB153, and PCB180.

consumer goods" [1]. The NIP also mentioned many gaps regarding the monitoring, management, and data collection for PCBs in Moldova prior to 2004. Moldova has not provided an updated NIP to the Stockholm Convention Secretariat, so no update on the matter of PCBs is available.

Dioxins (PCDD/Fs) and other unintentionally produced POPs (U-POPs)

Polychlorinated dibenzo-p-dioxins and dibenzofurans (dioxins, PCDD/Fs) were measured together with twelve dioxin-like PCB congeners (dl PCBs) and expressed in toxic equivalence levels (TEQ) in all the egg and soil samples in this study. Their levels in the free-range chicken eggs from Ciobanovca, Mebelchik, and Dumbrava are compared with the EU standards for food in Table 3.

Table 3: Comparison of levels of PCDD/Fs and dl PCBs in free-range chicken egg samples from Moldova and reference samples of eggs from supermarkets in Kyiv and Prague with the EU standards for food.

Locality (sample ID)	Units	Ciobanovca (TIN-EGG-1)	Mebelchik (BAL-EGG-1)	Dumbrava (VAT-EGG-1)	Kyiv – supermarket	Prague – supermarket	EU standards
PCDD/Fs	pg TEQ/g fat	5.09	1.29	4.81	0.25	0.03	2.5
dl PCBs	pg TEQ/g fat	51.95	3.13	12.7	0.03	0.34	–
Total PCDD/Fs + dl PCBs	pg TEQ/g fat	57.04	4.42	17.51	0.28	0.37	5.0

Dioxins exceeded the EU standard set at the level of 2.5 pg TEQ/g fat [35] twofold in the samples from Ciobanovca and Dumbrava, while in the sample from Mebelchik they reached half of it. **There were very high levels of dl PCBs, with almost 52 pg TEQ/g fat measured in the sample from Ciobanovca, and the total TEQ level exceeded the EU standard of 5 pg TEQ/g fat [35] by more than ten times in this sample.** The sample from Dumbrava also had a relatively high content of dl PCBs and contributed significantly to a 3.5-fold exceeding of the EU standard. The sample from Mebelchik did not exceed the EU standard for PCDD/Fs + dl PCBs. **All the samples had levels that were many times higher in comparison with the reference samples from supermarkets in Kyiv and Prague.**

The situation in Ciobanovca seems to be somewhat similar to the Shabanbai Bi location in Kazakhstan, where we also found high levels of both indicator and dioxin-like PCB congeners in free-range chicken eggs. This is probably caused by some hidden sources of PCBs in Shabanbai Bi, as well as in and/or near Ciobanovca. See also the discussion in the chapter above focused on PCBs. The congener profile for PCBs is shown in Figure 2. There is no significant difference between the samples themselves, which is typical for most of

the countries where Arnika sampled eggs. The PCDD/F profile can vary greatly, as is also shown for the samples from Moldova in Figure 3.

The dioxin congener profiles for the eggs from Ciobanovca, Mebelchik, and Dumbrava vary greatly between the samples, showing that the potential sources of pollution with these chemicals are most probably also different at all three sites. The sample of eggs from Mebelchik, with a dominant OCDD congener, is very similar to the profile observed in eggs from Bangun, Indonesia [40], where plastic waste is often burned. The profile of PCDD/F congeners in the eggs from Dumbrava is closer to the waste incineration one demonstrated in a study from China [41]. **We consider tyre pyrolysis to be a potential source of the contamination of the eggs from Dumbrava.** However, we were not able to compare these profiles with any local data from Moldova as the measurements of PCDD/Fs are not available from Moldovan sources.

An increased level of PeCB (16.57 ng/g fat) was measured in the eggs from Ciobanovca, much higher in comparison with the eggs from Mebelchik and Dumbrava. This level is close to the 22 ng/g fat of PeCB measured in eggs from the Agbogloshie scrapyard in Ghana in 2018 [42]. This relatively high level can also be the result of a potential hidden hotspot of obsolete pesticides, as PeCB was used for pesticide production in the past as well. PeCB is also present at low levels as an impurity in several herbicides, pesticides, and fungicides [43]. The levels in the eggs from Mebelchik and Dumbrava exceeded LOQ by six and four times respectively, which is not much. This is, for example, lower than the level of PeCB measured in eggs from a supermarket in Karaganda [37].

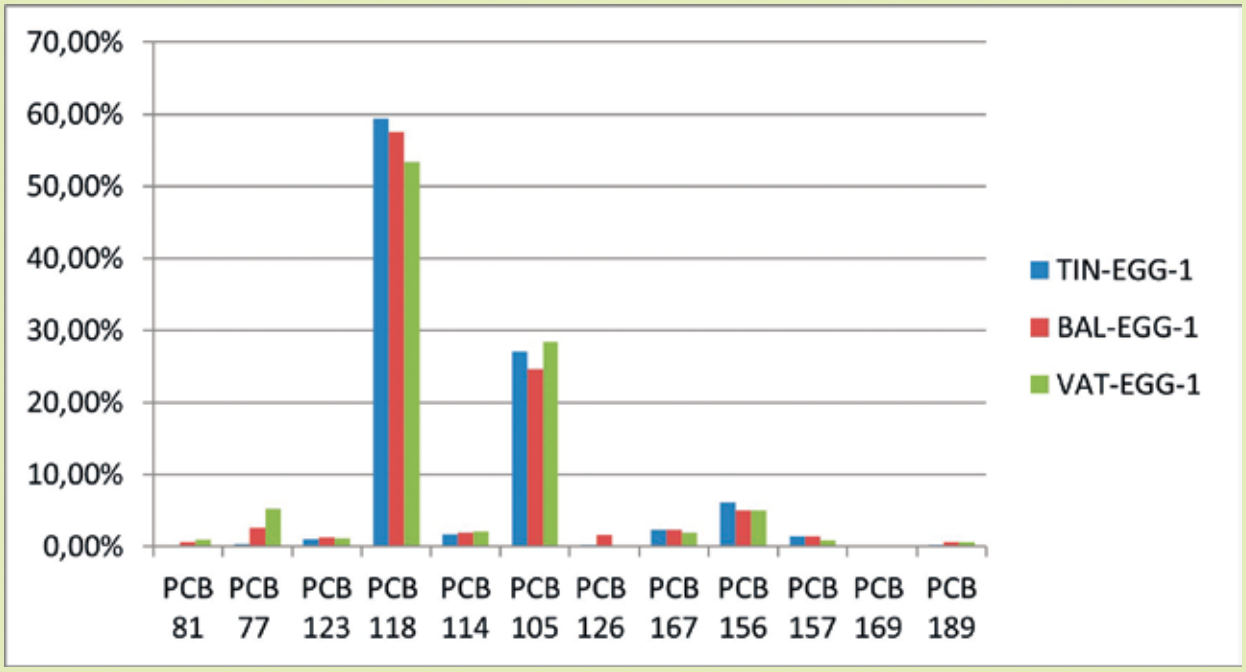

Figure 2:

Graph showing the percentage contribution of dl PCB congeners to the total level, expressed in pg/g fat.

Other POPs measured in eggs from Moldova

Other groups of POPs in the eggs from three Moldovan localities and two composite soil samples from Vatra were also measured. The analytical results summarised in Table 1 show levels below LOQ for PBDEs, SCCPs, and HCBD. The levels of HBCD, six novel BFRs, or PFASs were also below LOQ or low in comparison with studies from other countries [22]. The level of the sum of HBCD isomers of 14.75 ng/g fat in the egg sample from Dumbrava is higher in comparison to the levels in the samples from Ciobanovca or Mebelchik; however, it is still a very low level when compared to samples from Kazakhstan or Thailand [22]. The sum of HBCD isomers was also below LOQ in the reference sample from Prague [26]. The levels of PFASs in all three pooled egg samples were lower than, for example, in eggs from the vicinity of plastic waste yards in Java, Indonesia [40] and comparable to the levels observed at some other locations in Java [40] or to the levels observed in reference egg samples from other countries [44].

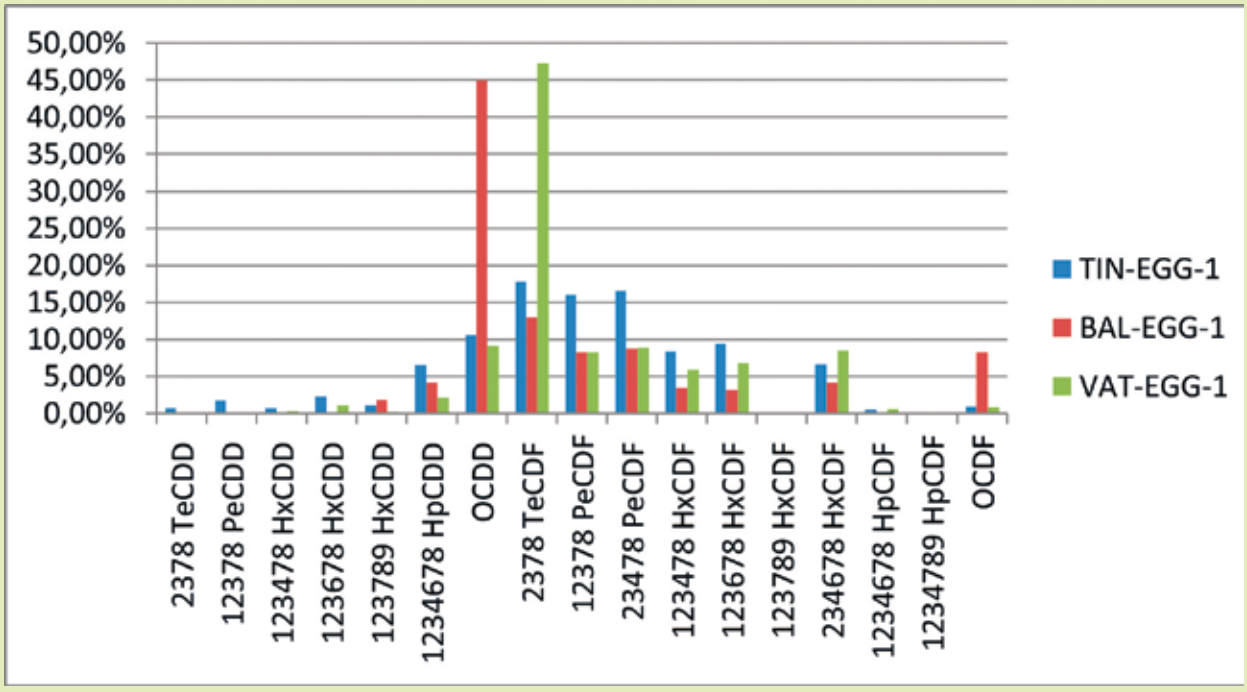

Figure 3:

Graph showing the percentage contribution of PCDD/F congeners to their total level, expressed in pg/g fat.

Conclusions and Recommendations

This study focused on the contamination of free-range chicken eggs from three Moldovan villages, Ciobanovca, Mebelchik, and Dumbrava, with various persistent organic pollutants (POPs). All three villages are located near potential POP sources, two of them, Ciobanovca and Mebelchik, near large landfills, and one near the industrial zone in Vatra, where tyre pyrolysis and asphalt production are also located.

Chemical analyses revealed serious contamination of the eggs from Ciobanovca with obsolete POP pesticides, i.e. three HCH isomers and DDT and PCBs. High levels of dioxins and dioxin-like PCBs, as well as of sum of DDT, were measured in the eggs from Dumbrava. A high level of sum of DDT was measured in a soil sample from Vatra, showing potentially high residues in the soil from past use of this pesticide in Moldova.

Ciobanovca/Tintareni Landfill: The contamination with HCH and PeCB in the eggs from Ciobanovca is most probably related to a hidden stockpile of obsolete OCPs or a building remaining contaminated after it was used as a warehouse for OCPs in the past. The very high levels of PCBs in the pooled egg sample from this village also show a potential source

of contamination with technical PCBs. The situation is somewhat similar to what was revealed in Shabanbai Bi in Central Kazakhstan.

Dumbrava/Vatra industrial zone: The levels of U-POPs in the eggs from Dumbrava also show that tyre pyrolysis or another industrial source in Vatra can be a significant source of the release of dioxins and dioxin-like PCBs.

Mebelchik/Balti Landfill: The POP levels in the eggs from Mebelchik collected in the very near vicinity of the Balti Landfill were not so high in comparison with those in the eggs from Ciobanovca or Dumbrava and the dioxin profile shows the open burning of mainly plastic waste at the landfill as a potential source of contamination, although the level of PCDD/Fs in the eggs was below the EU standard for eggs as food.

There is a lack of data about POPs in the Moldovan environment. Our study shows the importance of filling this gap and the need also to better evaluate new potential sources of U-POPs, including combustion processes. Tyre pyrolysis in Vatra belongs to this group of sources. Tyre pyrolysis is a known priority source of U-POPs identified in Annex C to the Stockholm Convention.

There is also a need to improve the register of obsolete POP stockpiles, including buildings left without any remediation after POP stocks were removed from them. These contaminated buildings can remain serious hotspots for contamination by OCPs, PCBs, and other technical POPs.

The low levels of other POPs such as PBDEs or PFASs in the eggs show that waste containing these POPs has probably not reached the landfills in Moldova yet, and/or that free-range chicken eggs did not become the final destination of these POPs.

Moldova also needs to update its NIP for the Stockholm Convention. Moldova should improve the system in accordance with the PRTR Protocol to the Aarhus Convention, which would significantly improve the monitoring of the sources of pollution, and POPs should be included in the list of such a national PRTR system. The use of a PRTR is also suggested in Article 10 of the Stockholm Convention[2] as an appropriate system for the collection of data on POPs.

2 "Each Party shall give sympathetic consideration to developing mechanisms, such as pollutant release and transfer registers, for the collection and dissemination of information on estimates of the annual quantities of the chemicals listed in Annex A, B or C that are released or disposed of" 45. Stockholm Convention, Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009. Text and Annexes. 2010: Geneva. p. 64.

Annex I: Persistent organic pollutants: overview and health impact

1.1 Organochlorine pesticides (OCPs)

The group of organochlorine pesticides can contain a very wide range of chemicals used as pesticides. While some of them are already listed as POPs under the Stockholm Convention, many are not and they do not even necessary meet all the criteria for POPs. We focused on some examples of this wide group of chemicals in this study: DDT and its metabolites, three isomers of hexachlorocyclohexane (and including gamma isomer lindane), hexachlorobenzene (HCB), pentachlorobenzene (PeCB), and hexachlorobutadiene (HCBD). The last three are also among the group of unintentionally produced POPs (UPOPs) as they might occur during various chemical and combustion processes, so more information about these chemicals is included in the subchapter focused on UPOPs.

The Moldovan NIP stated that: "In the 1950-1990s an estimated total amount of 560,000 tons of pesticides were used in Moldova, including 22,000 tons of persistent organochlorinated compounds (OCPs). Pesticide use registered a peak in 1975-1985" [1].

1.1.1. Dichlorodiphenyltrichloroethane (DDT)

DDT was widely used during World War II to protect soldiers and civilians from malaria, typhus, and other diseases spread by insects. After the war, DDT continued to be used to control disease, and it was sprayed on a variety of agricultural crops, especially cotton. DDT continues to be applied against mosquitoes in several countries to control malaria. Its stability, its persistence (as much as 50% can remain in the soil 10-15 years after application), and its widespread use have meant that DDT residues can be found everywhere; residual DDT has even been detected in the Arctic.

Perhaps the best-known toxic effect of DDT is eggshell thinning among birds, especially birds of prey. Its impact on bird populations led to bans in many countries during the 1970s. Although its use has been banned in many countries, it has been detected in food from all over the world. Although residues in domestic animals have declined steadily over the last two decades, food-borne DDT remains the greatest source of exposure for the general population. The short-term acute effects of DDT on humans are limited, but long-term exposure has been associated with chronic health effects. DDT has been detected in breast milk, raising serious concerns about infant health [46].

1.1.2. Hexachlorocyclohexane (HCH), including its isomer lindane

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 [47].

Lindane is persistent, bioaccumulates easily 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.

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, are classified as potentially carcinogenic to humans [48], and have an adverse effect on wildlife and human health in contaminated regions **[49]**.

Lindane is highly toxic to wildlife, including fish, bees, birds, and mammals **[50]**. 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. It is, therefore, more reliable to measure the latter.

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 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) **[49]**.

1.2 Polychlorinated biphenyls (PCBs)

These compounds are used in industry as heat exchange fluids, in electric transformers and capacitors, and as additives in paint, carbonless copy paper, and plastics. Of the 209 different types of PCBs, 13 exhibit a dioxin-like toxicity. Their persistence in the environment corresponds to the degree of chlorination, and half-lives can vary from ten days to one-and-a-half years **[46]**.

PCBs are toxic to fish, killing them at higher doses and causing spawning failures at lower doses. Research also links PCBs to reproductive failure and suppression of the immune system in various wild animals **[46]**.

Large numbers of people have been exposed to PCBs through food contamination. Consumption of PCB-contaminated rice oil in Japan in 1968 and in Taiwan in 1979 caused pigmentation of nails and mucous membranes and swelling of the eyelids, along with fatigue, nausea, and vomiting. As a result of the persistence of PCBs in their mothers' bodies, children born up to seven years after the Taiwan incident showed developmental delays and behavioural problems. Similarly, children of mothers who ate large amounts of contaminated fish from Lake Michigan showed poorer short-term memory function. PCBs also suppress the human immune system **[46]** and are listed as human carcinogens **[48]**.

1.3 Brominated flame retardants (BFRs)

Brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) are known as endocrine-disrupting chemicals (EDCs) and have an adverse impact on the development of the nervous system and of children's intelligence [51-53].

The indisputable toxicity and persistency of the main types of brominated flame retardants, i.e. PBDEs and HBCD, resulted in governments listing them in the Stockholm Convention for global elimination. Scientists have raised serious concerns over substitutes for flame retardant chemicals, but they continue to be used without precautions or restrictions [54].

PBDEs are of primary interest for this study as these hazardous chemicals were and still are used in many plastic products, including recycled plastics. PBDEs were allowed to be recycled from waste materials into new products despite their well-known adverse environmental and human health effects. HBCD and a few substitutes for PBDEs, described as new brominated flame retardants (nBFRs), are also investigated in this study. The new flame retardants are being introduced to the market much faster than they are being evaluated, so there is an accumulating worldwide inventory of potentially problematic chemicals.

Only limited information is available on the current global market volume, but approximately 390,000 tons of brominated flame retardants were sold in 2011. This represents 19.7% of the flame retardant market [55].

1.3.1 Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are a group of brominated flame retardants 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 breast milk in Indonesia in research from more than a decade ago, and *"the levels were in the same order as those in Japan and some European countries, but were one or two orders lower than North America"* [56].

PBDEs have adverse effects on reproductive health as well as developmental and neurotoxic effects [51-53]. DecaBDE and/or its degradation products may also act as endocrine disruptors [53].

PentaBDE has been used in polyurethane foam for car and furniture upholstery, and Octa- and DecaBDE have been used mainly in plastic casings for electronics. OctaBDE formed 10%-18% of the weight [57] of CRT television and computer casings and other office electronics made of acrylonitrile butadiene styrene (ABS) plastic. DecaBDE forms 7%-20% of the weight [53] of many different plastic materials, including high-impact polystyrene (HIPS), polyvinylchloride (PVC), and polypropylene (PP) used in electronic appliances. As this study examines eggs from sites affected by the presence of plastic waste, all of the above-mentioned PBDEs were part of the main focus of our investigation.

1.3.2 Hexabromocyclododecane (HBCD)

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 [58]. 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 **[59]**. This chemical also belongs among the SVHC substances under the REACH legislation.

1.3.3 Novel BFRs (nBFRs)

Novel BFRs (nBFRs) are a group of chemicals that in many cases replaced already restricted BFRs. 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 **[60]**. 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"* **[61]**.

The scientific panel of the EFSA evaluated 17 "emerging"[3] and ten "novel"[4] 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"* **[62]**. 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 to make it possible to draw meaningful conclusions.

3 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.

4 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.

Decabromodiphenyl ethane (DBDPE) was introduced in the early 1990s as an alternative to DecaBDE in plastic and textile applications [63]. BTBPE was first produced in the 1970s and is used as a replacement for OctaBDEs [64]. HBB has commonly been used for the manufacture of paper, woods, textiles, plastics, and electronic goods [65, 66] and it is *"likely widely distributed, as verified both by chemical analysis and estimated properties"* [67]. Thermal degradation of the DecaBDE technical mixture and polymeric PBDE pyrolysis could also be sources of the HBB found in the environment [68, 69].

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).

1.4 Short-chain chlorinated paraffins (SCCPs)

Short-chain chlorinated paraffins (SCCPs) are a group of POPs added by governments to the Stockholm Convention for global elimination in 2017. SCCPs are toxic to aquatic organisms at low levels, disrupt endocrine function, and are suspected of causing cancer in humans [70]. SCCPs are other additives in plastics that might also be expected in landfill waste. A 2017 study of 60 plastic products for children from ten countries found SCCPs in 45% of them [71, 72].

1.5 Per- and polyfluoroalkyl substances (PFASs)

Per- and polyfluoroalkyl substances (PFASs) are a large class [73] of more than 4,500 very persistent fluorinated chemicals (including PFOS) that have been widely used in packaging, textiles, and plastics. Scientists are concerned with their widespread presence in the environment, and in the Madrid Statement said that they: *"call on the international community to cooperate in limiting the production and use of PFASs and in developing safer nonfluorinated alternatives"* [74]. Later, in the Zurich Statement, they called upon regulators to address PFASs in chemically-related groups rather than as individual substances [75].

In animal studies, some long-chain PFASs have been found to cause liver toxicity, disruption of lipid metabolism and of the immune and endocrine systems, adverse neurobehavioural effects, neonatal toxicity and death, and tumours in multiple organ systems [76, 77]. More health effects are summarised in the Madrid and Zurich statements, as well as in the toxicological profiles of PFASs [74, 75, 78, 79].

The EFSA has sharply lowered the permitted intake of PFOS from 150 ng/kg body weight/day to 13 ng/kg body weight/week [80]. An investigation of PFAS substances in Indonesia found that they are unregulated and contaminate both coastal sediments and breast milk [81].

Electrochemical fluorination (ECF) and telomerisation are the two major methods employed to produce PFASs. The manufacturing process of PFASs can help us understand the differences in the presence of their isomers in the environment, and their links to potential sources of contamination. *"The branched isomers of PFASs are mainly manufactured in the ECF method, which has historically been used to produce the major part of the two dominant PFASs, PFOS and PFOA. ECF gives rise to complex mixtures of linear and branched compounds. PFOA produced by this method has typically had an isomer composition of 78% linear (n-PFOA) and 22% branched isomers (br-PFOA). ECF-PFOS shows a distribution of around 70% linear (n-PFOS) and 30% branched (br-PFOS). ... the telomerisation process keeps the structure of the starting telogen and a pure linear or isopropyl form is produced* **[82, 83]***"* **[84]**.

1.6 Dioxins (PCDD/Fs) and other unintentionally produced POPs

Annex C of the Stockholm Convention lists seven unintentionally produced POPs: HCB, hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB), PCBs, polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and polychlorinated naphthalenes. The analyses of eggs in this study covered HCB, HCBD, PeCB, PCBs, and PCDD/Fs. Polychlorinated naphthalenes were not analysed.

1.6.1 PCDD/Fs and dl-PCBs

Dioxins 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. Polychlorinated biphenyls (PCBs) are a group of 209 different congeners that can be divided into two groups according to their toxicological properties: 12 congeners exhibit toxicological properties similar to dioxins and often referred to as "dioxin-like PCBs" (dl-PCBs). The other PCBs do not exhibit dioxin-like toxicity but have a different toxicological profile and are referred to as "non dioxin-like PCBs" (ndl-PCBs) **[85]**. Technical mixtures of PCBs are characterised by six, sometimes seven indicator PCB congeners (i-PCBs). 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 **[86]**. These WHO TEFs were used to evaluate dioxin-like toxicity in the pooled samples of chicken eggs, soils, ash, and other 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 altered immune system response, among others **[87, 88]**. 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 **[89]**.

Chlorinated dioxins became known to the public in the 1970s as a result of their contamination of Agent Orange, a defoliant pesticide mixture sprayed by the U.S. during the

Vietnam War.[5] 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 [91-93] and sick workers with many symptoms of exposure to the most toxic of dioxin congeners, 2,3,7,8-TCDD [94, 95].

1.6.2 PeCB and HCB

Pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) are primarily produced unintentionally during combustion, as well as during thermal and industrial processes. They also occur as a byproduct 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 for the production of the pesticide quintozene [96].

In high doses, HCB is lethal to some animals and, at lower levels, has an adverse effect on their reproductive success. Researchers also found out that HCB, similarly to other organochlorinated compounds, has a transplacental transfer [97]. HCB has been found in food of all types [89].

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 [98]. 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 [43].

1.6.3 HCBD

HCBD occurs as a byproduct during the production of the same chlorinated hydrocarbons as PeCB and HCB, as a part of 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 [99-101].

5 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 can also 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 was dropped. York, G. and H. Mick. Last ghost' of the Vietnam War. 2008 April 27, 2018 [cited 2018 19-11-2018]; Available from: https://www.theglobeandmail.com/incoming/last-ghost-of-the-vietnam-war/article1057457/?page=all.

Annex II: Lists of samples

Table II/1: List of soil samples

Locality	Sample ID	Coordinates (N/E)		Date of sampling	Sampling site description	Sampling and sample preparation
Vatra Industrial Area	VAT-SOIL-1	47.0752945	28.7682522	17.08. 2021	a sunflower field quite close to the industry in the village of Ghidighici; the sampling spot is located downwind from the industry in the dominant direction of the wind	digging surface soil, composite sample of five subsamples collected in a square 2x2 m, homogenisation
Vatra Industrial Area	VAT-SOIL-2	47.0568586	28.7640847	17.08. 2021	a cornfield on the edge of the garden village in Dumbrovka	digging surface soil, composite sample of five subsamples collected in a square 2x2 m, homogenisation

Table II/2: List of egg samples

Locality	Sample ID	Coordinates (N/E)		Date of sampling	Description of sampling site	Sampling and sample preparation
Tintareni Landfill/ Ciobanovca	TIN-EGG-1	46.813826	29.2081190	16.8. 2021	a garden in the village of Ciobanovca	six eggs collected from fancier/ boiled
Balti Landfill/ Mebelchik	BAL-EGG-1	47.720624	27.975267	16.8. 2021	a garden with fruit trees, chickens can access the whole garden area; in a garden colony with “dachas”	six eggs collected from fancier/ boiled
Vatra Industrial Area/Dumbrava	VAT-EGG-1	47.054162	28.730733	17.8. 2021	a house with a garden in the centre of the village	six eggs collected from fancier/ boiled

Annex III: Results

Table AIII/1: Concentrations of persistent organic pollutants in egg and soil samples

Locality	EGGS	Ciobanovca	Mebelchik	Dumbrava	SOIL	Vatra	Vatra
Sample ID	Units	TIN-EGG-1	BAL-EGG-1	VAT-EGG-1	Units	VAT-SOIL-1	VAT-SOIL-2
Fat	%	11.5%	11.6%	11.7%			
PeCB	ng/g fat	16.6	0.602	0.418	ng/g dw	<0.02	<0.02
HCB	ng/g fat	2.31	1.73	1.59	ng/g dw	0.035	0.029
HCBD	ng/g fat	<0.10	<0.10	<0.10	ng/g dw	<0.02	<0.02
α-HCH	ng/g fat	1 356	1.06	1.40	ng/g dw	0.130	<0.02
β-HCH	ng/g fat	1 536	2.40	3.48	ng/g dw	2.21	0.036
γ-HCH	ng/g fat	113	0.379	0.680	ng/g dw	0.122	<0.02
Sum HCH	ng/g fat	3005	3.84	5.56	ng/g dw	2.46	0.04
o.p'-DDE	ng/g fat	0.164	<0.10	<0.10	ng/g dw	2.70	0.026
p.p'-DDE	ng/g fat	411	40.0	42.9	ng/g dw	153	1.96
o.p'-DDD	ng/g fat	0.839	<0.10	0.204	ng/g dw	3.69	0.066
p.p'-DDD	ng/g fat	32.9	3.68	4.37	ng/g dw	24.3	0.506
o.p'-DDT	ng/g fat	21.3	2.69	2.10	ng/g dw	9.77	0.328
p.p'-DDT	ng/g fat	87.9	0.720	<0.50	ng/g dw	40.9	2.75
Sum DDT	ng/g fat	554.2	47.1	49.5	ng/g dw	234.1	5.6
PCB 28	ng/g fat	4.48	1.07	151	ng/g dw	0.024	<0.02
PCB 52	ng/g fat	0.889	0.108	1.33	ng/g dw	0.041	<0.02
PCB 101	ng/g fat	2.91	<0.10	0.730	ng/g dw	0.081	<0.02
PCB 118	ng/g fat	78.7	0.917	19.8	ng/g dw	0.161	0.029
PCB 138	ng/g fat	69.1	0.604	19.4	ng/g dw	0.134	0.037
PCB 153	ng/g fat	51.5	0.381	21.0	ng/g dw	0.091	0.025
PCB 180	ng/g fat	14.6	<0.50	15.9	ng/g dw	0.029	<0.02
7 iPCB	ng/g fat	222.2	3.1	229.1	ng/g dw	0.56	0.09
SCCP C10-C13	ng/g fat	<50.0	<50.0	<50.0	ng/g dw	/	/
PBDE 28	ng/g fat	<0.10	<0.10	<0.10	ng/g dw	<0.01	<0.01
PBDE 47	ng/g fat	<0.10	<0.10	<0.10	ng/g dw	<0.01	<0.01
PBDE 49	ng/g fat	<0.20	<0.20	<0.20	ng/g dw	<0.01	<0.01
PBDE 66	ng/g fat	<0.20	<0.20	<0.20	ng/g dw	<0.01	<0.01
PBDE 85	ng/g fat	<0.20	<0.20	<0.20	ng/g dw	<0.01	<0.01
PBDE 99	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.01	<0.01
PBDE 100	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.01	<0.01
PBDE 153	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.01	<0.01
PBDE 154	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.01	<0.01
PBDE 183	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.01	<0.01

PBDE 196	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.10	<0.10
PBDE 197	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.10	<0.10
PBDE 203	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.10	<0.10
PBDE 206	ng/g fat	<1.5	<1.5	<1.5	ng/g dw	<0.50	<0.50
PBDE 207	ng/g fat	<1.5	<1.5	<1.5	ng/g dw	<0.50	<0.50
PBDE 209	ng/g fat	<1.5	<1.5	<1.5	ng/g dw	<5.0	<5.0
Sum PBDEs	ng/g fat	<LOQ	<LOQ	<LOQ	ng/g dw	<LOQ	<LOQ
α-HBCD	ng/g fat	4.77	<4.2	14.8	ng/g dw	<0.75	<0.75
β-HBCD	ng/g fat	<4.2	<4.2	<4.2	ng/g dw	<0.75	<0.75
γ-HBCD	ng/g fat	<4.2	<4.2	<4.2	ng/g dw	<0.75	0.947
Sum HBCD	ng/g fat	4.773	<LOQ	14.752	ng/g dw	<LOQ	0.947
BTBPE	ng/g fat	<0.30	<0.30	<0.30	ng/g dw	<0.01	<0.01
DBDPE	ng/g fat	<3.3	<3.3	<3.3	ng/g dw	<10.0	<10.0
HBBz	ng/g fat	<0.20	0.341	<0.20	ng/g dw	<0.01	<0.01
OBIND	ng/g fat	<1.5	<1.5	<1.5	ng/g dw	<0.10	<0.10
PBEB	ng/g fat	<0.20	<0.20	<0.20	ng/g dw	<0.01	<0.01
PBT	ng/g fat	<0.20	<0.20	<0.20	ng/g dw	0.018	0.010
nBFRs	ng/g fat	<LOQ	0.341	<LOQ	ng/g dw	0.018	0.010
PFBA	ng/g	0.055	0.079	0.151	ng/g dw	NA	NA
PFPeA	ng/g	<0.013	<0.013	<0.013	ng/g dw	NA	NA
PFHxA	ng/g	0.017	<0.006	0.022	ng/g dw	NA	NA
PFHpA	ng/g	0.020	0.034	0.092	ng/g dw	NA	NA
PFOA	ng/g	0.030	0.032	0.030	ng/g dw	NA	NA
PFNA	ng/g	0.122	0.029	0.017	ng/g dw	NA	NA
PFDA	ng/g	0.113	0.025	0.021	ng/g dw	NA	NA
PFUnDA	ng/g	0.074	0.013	0.007	ng/g dw	NA	NA
PFDoDA	ng/g	0.038	0.010	<0.006	ng/g dw	NA	NA
PFTrDA	ng/g	0.017	<0.006	<0.006	ng/g dw	NA	NA
PFTeDA	ng/g	0.018	0.006	<0.006	ng/g dw	NA	NA
PFBS	ng/g	<0.006	<0.006	<0.006	ng/g dw	NA	NA
PFHxS	ng/g	0.008	<0.006	<0.006	ng/g dw	NA	NA
br-PFOS	ng/g	0.060	0.009	0.013	ng/g dw	NA	NA
L-PFOS	ng/g	0.189	0.024	0.025	ng/g dw	NA	NA
PFDS	ng/g	<0.006	<0.006	<0.006	ng/g dw	NA	NA
PFOSA	ng/g	<0.006	<0.006	<0.006	ng/g dw	NA	NA
Sum PFASs	ng/g	0.762	0.263	0.378	ng/g dw	NA	NA
PCDD/Fs	pg TEQ/g fat	5.09	1.29	4.81	pg TEQ/g	0.31	0.29
dl PCBs	pg TEQ/g fat	51.95	3.13	12.7	pg TEQ/g	0.26	0.13
Total PCDD/F + dl PCBs	pg TEQ/g fat	57.04	4.42	17.51	pg TEQ/g	0.57	0.42

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