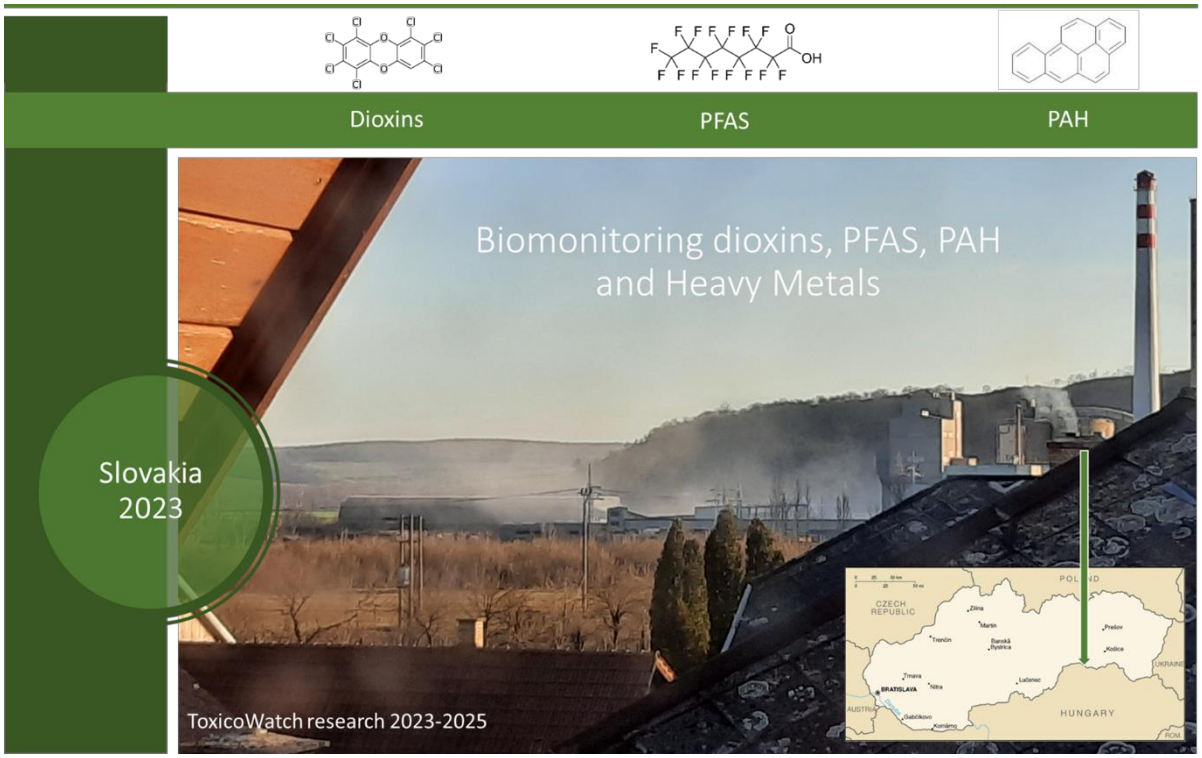
TOXICO WATCH

Biomonitoring research persistent on organic pollutants in the environment surrounding the Cement plant in Turňa nad Bodvou, Slovakia 2023



A.Arkenbout, K.J.A.M. Bouman

March - 2024

ZERO WASTE EUROPE

THE TRUE TOXIC TOLL

Biomonitoring research on persistent organic pollutants in the environment surrounding the cement plant

Turňa nad Bodvou, Slovakia | 2023

Report

ZERO WASTE EUROPE

TOXICOWATCH

Thank you to Zero Waste Europe for enabling this research on persistent organic pollutants (POPs). Special thanks to all the participants in the villages of Dvorníky, Hosťovce, Zádiel, Včeláre and Turňa nad Bodvou for their cooperation and trust in allowing the analysis of their backyard chicken eggs, vegetation, fruit, and roof dust. Your participation has contributed significantly to enhancing our understanding of the environmental health in your communities.

AUTHORS

A. ARKENBOUT - Head of research at ToxicoWatch Foundation
K. J. A. M. BOUMAN - Research ToxicoWatch Foundation

HARLINGEN, THE NETHERLANDS, TOXICOWATCH FOUNDATION, MARCH 2024
PUBLICATION NUMBER: 2024-SK-01
CLIENT: Zero Waste Europe

DISCLAIMER

The ToxicoWatch Foundation conducted this biomonitoring research on behalf of Zero Waste Europe. ToxicoWatch accepts no liability or responsibility whatsoever to any third party for any loss or damage arising from any interpretation or use of the information contained in this report or reliance on any views expressed herein.

www.toxicowatch.org

Zero Waste Europe gratefully acknowledges financial assistance from the European Union and The Sigrid Rausing Trust. The sole responsibility for the content of this event materials lies with Zero Waste Europe. It does not necessarily reflect the opinion of the funders mentioned above. The funders cannot be held responsible for any use that may be made of the information contained therein.

Introduction

The civil society organisation Zelený živel o.z., representing environmentally conscious residents in Turnianska Kotlina, took the initiative in 2023 to contact Zero Waste Europe and ToxicoWatch (TW) for independent research on the deposition of persistent organic pollutants (POPs) such as dioxins (PCDD/F/dl-PCB), Polycyclic Aromatic Hydrocarbons (PAH) and PFAS, as well as heavy metals in the environment surrounding the cement kiln Cementáreň Turňa nad Bodvou, located in the Košice Region in Slovakia.

According to the Turňa nad Bodvou Cement Plant's website,[1] the plant is equipped with state-of-the-art BAT/BREV equipment. Waste gases with a volume flow rate of 165000 m^3/hour are discharged into the air through a fabric filter and, subsequently, through a chimney with a height of 51.0 meters. The dust separated by the fibre filters is transported as dried clay to the raw material landfill. The conveyor belts used for transporting the clay for crushing within the plant to the sieving station are dust-tight.[2] Cement production ranks among the energy-intensive industries. This plant, which is supported by EU grants, burns waste materials, ranging from plastic agglomerate, worn-out old used car tyres, and PCB oil-containing waste[3] - as a sustainable alternative to fossil fuels. There are plans to increase waste burning from 65,000 to 115,000 tons annually - a nearly 50% increase. Cement kilns are utilised to destroy persistent organic pollutants such as PCBs and PFAS, owing to the higher combustion temperatures they provide.

Emissions of pollutants must adhere to the emission limits set by EU Decree No 410/2003 Coll. (Air Act No. 137/2010 Coll. repeals several regulations) as amended for cement rotary kilns and should refer to Industrial Emissions Directive and BREF 2023.[4] It's noteworthy that emissions of dioxins are measured only a few hours per year. The last publication dates to 2018 with limited information on dioxin emissions and lacking detailed Toxic Equivalent (TEQ) distribution data. No recent data are available on emissions and depositions of other persistent organic pollutants (POPs), like PAH, fluorine compounds (PFAS), and dioxin-like PCBs. This TW research does not (yet) include monitoring of brominated dioxins (PBDD/F) or other halogenated POPs, but it might be necessary to investigate the emission of these abundant flame retardants.

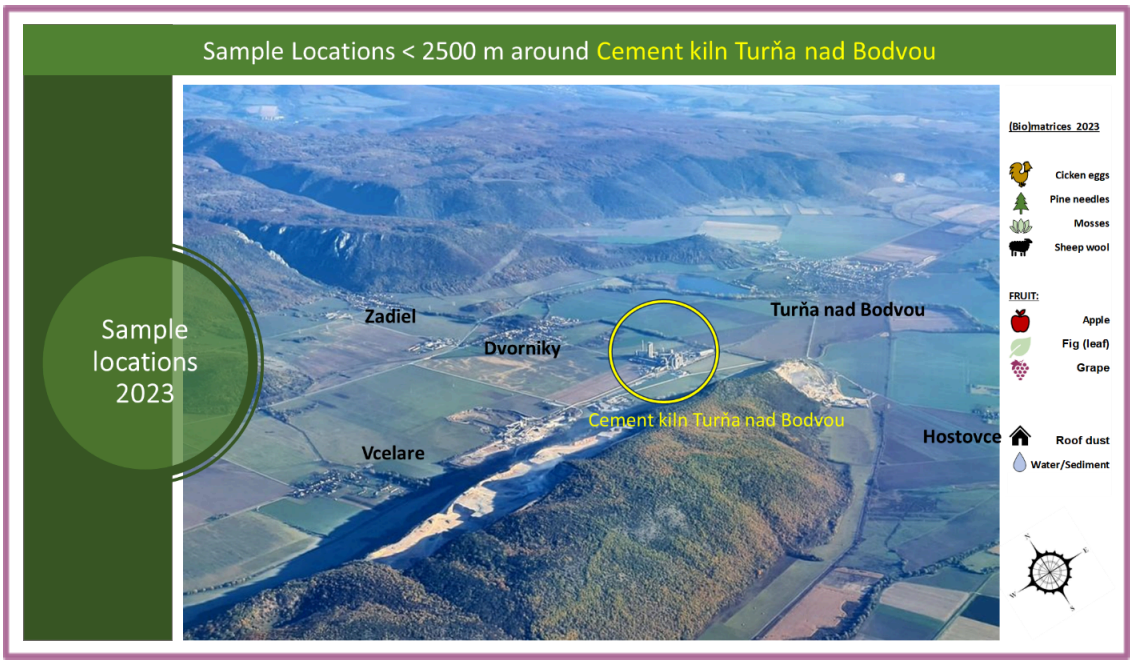
In this report, TW's research focuses on assessing the environmental impact around the cement kiln Turňa nad Bodvou. We employ biomonitoring techniques using eggs from backyard chickens, as well as analysing fruit and vegetation for dioxins, PFAS, PAH and heavy metals. Alongside cement production, the region of Košice faces additional industrial sources of air pollution. Notably, in Včeláre and Hosťovce quarries, limestone, (a basic raw material for cement production) is extracted. There are ecologically significant areas adjacent to the cement kiln, including the Protected Bird Area Slovak Karst (SKCHVÚ 027) and the National Nature Reserve – Zádielska tiesňava (The Zadiel Gorge), which forms part of the Slovak Karst National Park.

---

[1] www.danucem.com/site/2/Turňa -nad-bodvou-cement-plant
[2] Increase in the output of the furnace line VSH, a.s. Turňa nad Bodvou to 3500 tons of clinker per day - OBJECTIVE
[3] Wastes classified under catalogue numbers 191210, 191211, 19121212, 19121212, 191214 and 160119. In addition, wastes are classified under catalogue numbers 191204 (Plastic agglomerate) and 160103 (Worn tyres).
[4] eeb.org/wp-content/uploads/2023/04/Upgrading-Europes-air.pdf

Figure 1 - The cement kiln Turňa nad Bodvou

Figure 2 - Sample locations < 2500m around the cement kiln Turňa nad Bodvou



Sampling

This biomonitoring research focused on analysing various biomarkers: eggs from backyard chickens; eggshells; pine needles (*Picea abies*); mosses (*Bryophyta*); and fruits such as

apples, grapes, and fig leaves. Additionally, matrices such as roof dust, sediment, and water were examined. The area of research encompassed five (5) surrounding villages within a 2500-meter radius of the cement kiln. Samling was conducted at four (4) locations in Dvorníky, three (3) in Včeláre, three (3) in *Hosťovce*, two (2) in Zádiel and one (1) in *Turňa nad Bodvou*.

Eggs
For egg samples, 6-10 fresh eggs were collected at each location. The content (egg yolk and white) was mixed and stored in an HDPE lab container in a freezer until it was analysed. The research team conducted a questionnaire and on-site location inspection to identify any potential confounding factors at each backyard chicken egg location.

Fruit
Fruit samples weighing 200–300 grams were collected from fruit trees and shrubs, placed in special HDPE lab bags, and stored in a cool, dry environment.

Vegetation
Vegetation samples, 200–300-grams of fresh pine needles from Pine trees – *Picea abies* and 200–300-gram mosses (*Bryophyta*), were collected from sheds' roofs at the same locations as the egg sampling. Additionally, moss (*Bryophyta*) samples were collected from a rural open field on a hill near Dvorníky. All vegetation samples were stored in HDPE-lab bags, in a cool, dark, and dry environment.

Dust
Roof dust samples weighing 50 grams were collected by direct scraping from a roof at location *Dvorníky*. At the location in *Zádiel*, we sampled roof dust that had naturally deposited in a metal bowl.

Water & Sediment
Water and sediment samples, totalling 200 ml water/sediment were collected directly from the downstream floating into Bodva, near the cement kiln using an HDPE lab container and stored cool and dark environment.

Analysis methods

The collected samples undergo analysis for persistent organic pollutants (POPs) using both bioassays (CALUX) and chemical analyses. The substances of interest are PCDD/F/dl-PCB (dioxins), Per- and poly-fluoroalkyl Substances (PFAS), Polycyclic Aromatic Hydrocarbons (PAH), and analyses of 6-14 heavy metals: Arsenic, Cadmium, Cobalt, Chromium, Lead, Nickel, Aluminium, Barium, Copper, Manganese, Mercury, Silver, Tin, and Zinc.

In this research, bioassay analysis employs DR CALUX® for dioxins/furans (PCDD/F) and dioxin-like PCBs (dL-PCBs), PAH CALUX for PAH substances, and FITC-T4 for the PFAS. Additionally, DR CALUX®, PFAS CALUX®, FITC-T4 and GC-MS are used for dioxins analysis in eggs, when results from DR CALUX exceed the EU Limits for eggs (1.7 pg BEQ/g fat for PCDD/F and 3.3. pg BEQ/g fat for the sum of dioxins (PCDD/F/dl-PCB)). The

analysis is performed by BioDetection Systems in Amsterdam, the Netherlands (NL). BDS is accredited under RvA L401. Chemical analysis for PAH, PFAS and heavy metals re conducted by the accredited laboratory Normec, Groen Agro Control, located in Delft, the Netherlands (NL). PFAS chemical analyses employ LC-MS/MS to detect 24 PFAS, while heavy metals analysis utilises ICP-MS.

Results

Eggs

In October 2023, TW conducted a sampling of eggs from backyard chickens in six (6) private locations across five (5) neighbouring villages near the cement kiln. The values with the DR CALUX range from 1.2 – 9.8 pg BEQ/g fat. **Three (3) locations exceeded the EU limit** of 3.3 pg BEQ/g in backyard chicken eggs (DR CALUX), with **4.70 pg** in *Hosťovce*, **4.80 pg** in *Turňa nad Bodvou* and **9,80 pg BEQ/g fat (MB)**[5] in *Zádiel*. The DR CALUX method assesses the total toxicity of dioxins, including brominated, fluorinated, and other (mixed) halogenated compounds. Chemical analyses, limited to 29 chlorinated dioxins, found in eggs of *Turňa nad Bodvou* **6.6 pg TEQ/g** and in eggs of location *Zádiel* **8.8 pg TEQ/g**. The levels of dl-PCB are from 0.1 – 6.7 pg TEQ/g. The highest-level dl-PCB is found in *Zádiel*. Chemical analysis confirmed this value with 6.6 pg TEQ/g in *Zádiel* and measured 3.9 pg TEQ/g in *Hosťovce*. Both exceed the EU action limit of 1.7 pg TEQ, where action is needed to determine the source. The congener patterns of dl-PCB closely resemble at all these locations.

The chemical analysis (LC-MS/MS) was detected in all eggs PFAS. The **highest value for PFAS** was found at location Zádiel-02, with **4.57 µg ∑ 24 PFAS /kg**. The concentration of PFOS (one of the 4 EU-regulated PFAS compounds and among the 24 analysed PFAS compounds by LC-MS/MS) exceeded the EU limit by 300% with 3.0 µg/kg. Turňa nad Bodvou PFOS level narrowly stayed under the EU limit at 0.75 µg/kg. The findings of 6 different PFAS in the eggs of location *Zádiel* need further investigation to find out the source(s).

Fruit

Dioxins on fruit in *Turňa nad Bodvou* consist of 0.24 pg TEQ/wet weight (MB) for the sum of dioxins (PCDD/F/dl-PCB) and are just below the EU limit of 0.30 pg TEQ.[6] Other locations measured all below the limit of quantification (<LOQ) for dioxins on fruit.

PFAS was detected in grapes in Včeláre, and fig leaves in *Dvorníky,* with 0.14 and 0.22 ng /gram dw (MB) for 6:2 Fluorotelomer sulfonate (6:2FTS), respectively. In the other locations, no PFAS could be found above the limit of quantification (>LOQ). **Although the presence of 6:2 Fluorotelomer sulfonate (6:2FTS) is with great concern, because of the threat of serious health effects, and accumulation potential in people, this PFAS is (still) not included in the EU regulations.**

The PAH levels on apples are between 2.34 – 19.69 ng Benzo(a)Pyrene equivalent per

[5] ½ *LOQ=”medium-bound” (MB)
[6] 2013/711/EU

gram/product with the PAH CALUX. The highest level was found in *Turňa nad Bodvou.* In grapes of *Dvorníky,* and *Včeláre* 19.1 ng and 32.5 ng ∑16 PAH was found with the chemical analysis of GCMS.

Mosses

The values of dioxins measured with DR CALUX in mosses at *Dvorníky* are 3.3 pg TCDD eq./g, in mosses at the top of the hill north, and 23.8 pg TCDD eq./g in mosses on a roof 800 meters distance from the plant. Mosses collected from roofs in *Včeláre* dioxins measured 6.4 pg TCDD eq./g, in *Zádiel* 10.8 pg TCDD eq./g, and *Hosťovce* 19.0 pg TCDD eq./g dw (MB). The dioxin in all the moss samples exceeds the limit (for feed) of 0.83 pg TCDD eq./g 88% dry weight (medium bound, MB). High levels of dioxins were detected in all moss samples collected around the cement kiln. **The levels of dioxins (PCDD/F/dl-PCBs) in mosses of Slovakia are among the highest observed in international biomonitoring research conducted by TW**. Follow-up research in 2024 on moss in this Slovak area will expand to include moss samples from the Slovak Karst National Park region.

In the mosses of *Hosťovce* and *Dvorníky*, values of 4.6 and 5.4 pg TCDD eq./g for dl-PCB are found. This high value could be the result of the incomplete combustion of PCB waste. Semi-continuous measurements of the flue gases are needed to determine the amount and patterns of emissions of dl-PCB. In *Zádiel*, *Dvorníky (Hill North)* and *Včeláre* 0.1, 0.2 and 1.4 pg TCDD eq./g were measured respectively.

Notably, mosses exhibited higher levels of dioxins compared to fruits or pine needles collected from the same locations. This disparity might be attributed to the fact that fruits mature from blossom to ripe fruit within a few months (May-September) whereas mosses grow continuously throughout the year and can live for many years.

PAH in mosses, analyzed with the PAH CALUX varies from 355.4 - 4684.7 ng/g Benzo(a)pyrene equivalent. The chemical analysis tool of the GC-MS on 16 PAH is in the range of 32.5 – 423 ng PAH/g. The lowest level is found at the top of the hill in *Dvorníky* and the highest level in *Hosťovce*. The bioassay PAH CALUX method measures the toxicity of the total PAH instead of 4-16 PAH congeners with chemical analyses (GC-MS).

Pine needles

The levels of dioxins in pine needles measured with the bioassay DR CALUX are 0.77 pg TCDD eq./g in *Dvorníky*, 1.52 pg TCDD eq./g in *Zádiel* and 2.85 pg TCDD eq./g in *Hosťovce* and *Včeláre*. PAH levels at these 4 locations in pine needles are 0.08 – 2.16 ng Benzo(a)Pyrene equivalent/g by PAH CALUX. With the chemical method of PAH analyses, a substantially higher level of 60.1 ng ∑ 16 PAH/g was measured in the pine needles at location *Dvorníky*, which is quite remarkable and needs to be repeated in the next sampling.

Dust

Residents had reported concern about black dust accumulating on their roofs, windows, and windowpanes. **In this research, high levels of PAH were found in roof dust sampled directly from a roof at location *Dvorníky*, and from a metal bowl located on**

the roof with naturally deposited dust in *Zádiel*. Dioxin levels in dust are 5.50 TCDD eq./g in *Dvorníky* and 6.30 pg TCDD eq./g in *Zádiel*. The dl-PCBs are 1.20 and 2.20 TCDD eq./g, respectively.

The levels of PAH in *Zádiel* were 34,000 ng and in *Dvorníky* 45,000 ng Benzo(a)Pyrene equivalent per gram. However, on apples and grapes, much lower levels in the range of 0.32 – 2.50 ng Benzo(a)Pyrene equivalent per gram is found in uncleaned fruit samples.

Water & Sediment

A screening test with the FITC-T4[7] was conducted on water and sediment near the cement kiln. The level of PFAS in water was found to be **21,000 ng PFOA.eq. /l**. (These significantly exceed the limit set by the Dutch regulation[8]- **0.3 nanograms per litre for PFOA**[9] - by **more than a factor of 70,000)**. Sediment sampling downstream showed PFAS levels of **1,300 ng PFOA eq./g (dry weight)** with the method of FITC-T4. (This greatly surpasses the limit set by the Dutch regulation)[10] Further research is necessary on water and sediment samples, as well as upstream samples in the Slovak Karst National Park. Extended analyses will employ chemical analysis LC-MS/MS and the bioassay ERA-CALUX.

Heavy metals

The results of analyses of heavy metals on mosses (*Bryophyta*) in *Zádiel are* 6293 mg/kg Zinc, 76 mg/kg Lead, 71 mg/kg Nickel, 918 mg/kg Manganese and 2.2 mg/kg Cadmium in *Zádiel*. More research at reference locations is needed to interpret the results in the context of this region.

The heavy metals levels in the mosses are among the highest recorded in biomonitoring research conducted by TW in Europe (2019-2023). Subsequent samples will be collected in the nearby Slovak Karst National Park and AGGTELEK National Park, located very close to the cement kiln in Hungary.

Heavy metal analysis in pine needles - *Picea abies* in *Zádiel* of 592 mg/kg of Manganese is found to be high, compared to other TW-biomonitoring results in pine needles. Heavy metal analysis of eggshells of backyard chickens found 0.024 mg/kg Lead (Pb), 0.056 mg Nickel (Ni) and no Mercury (Hg) was detected above the limit of detection (< LOD). Only the relatively high content of Aluminium (Al) of 8.3 mg/kg in eggshells of *Dvorníky* needs to have more attention.

---

[7] The FITC-T4 is a method that measures the total toxic effect of a mixture of PFAS congeners and is currently used by the Dutch government to screen for PFAS in surface water and inform policy measures for source reduction.

[8] The reference to Dutch regulation is due to the proactive stance of the Netherlands government in establishing limits for Persistent Organic Pollutants (POPs) emissions ahead of broader European Union regulations. This includes limits for substances such as PFAS, Dioxins (set at 0.01 ng TEQ/Nm3), and heavy metals (enforced from January 1, 2023). It is important to note that while Dutch regulations are cited here, there is a lack of readily available information regarding equivalent limits in Slovakia, where further investigation is warranted.

[9] *Smit C.E., Verbruggen E.M.J. (2022). Risicogrenzen voor PFAS in oppervlaktewaterRIVM-briefrapport 2022-0074 C.E. Smit | E.M.J. Verbruggen*

[10] The Dutch regulation for soil is set at 4.8 ng PFOA eq./kg (to compare equally this means: 0.048 ng PFOA eq./g).

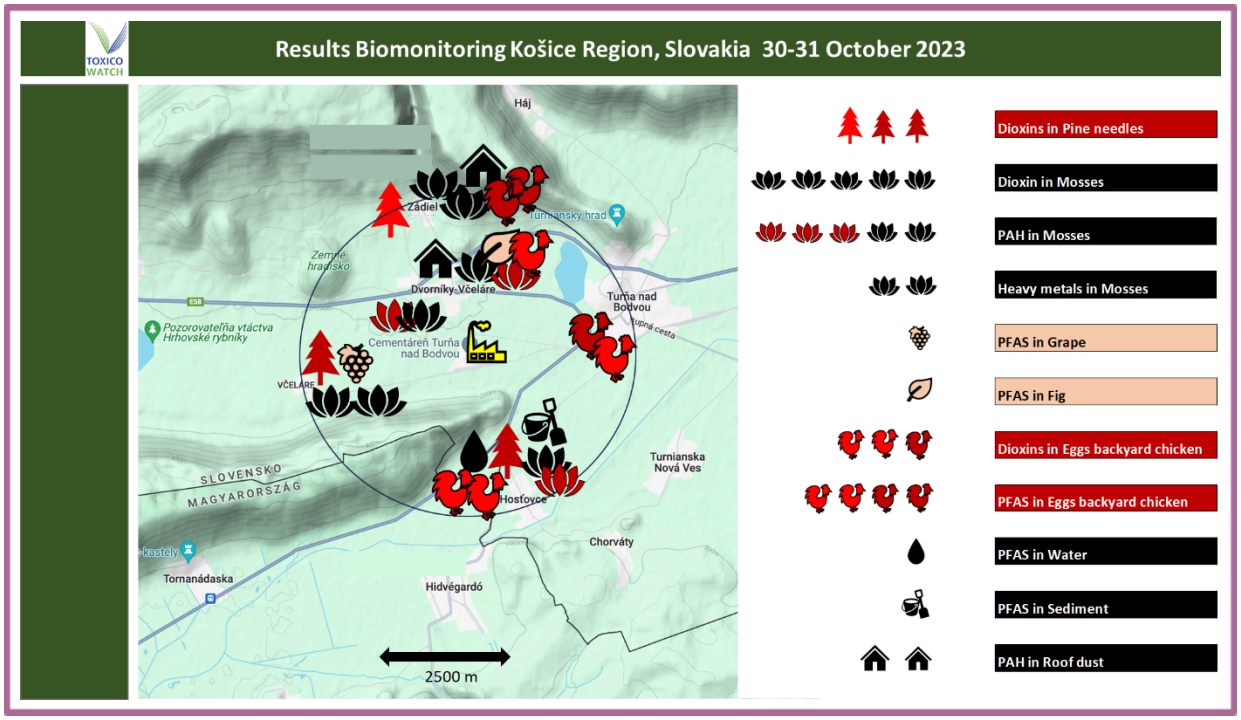
Results

The infographic below presents the initial findings from the TW biomonitoring research conducted around the cement kiln Cementáreň Turňa nad Bodvou, situated in the Košice Region in Slovakia in 2023. Samples were taken within a radius of 2500 meters around the kiln, in the surrounding five (5) villages and analysed for persistent organic pollutants (POPs) - such as dioxins, PFAS, PAH and heavy metals. **Eggs, pine needles, and mosses exhibited high concentrations of dioxins (PCCD/F/dl-PCB), polycyclic aromatic hydrocarbons (PAHs), and per- and poly-fluoroalkyl substances (PFAS)**. In *Turňa nad Bodvou* six (6) PFAS compounds could be determined in eggs. **PFOS level in eggs of location Zádiel- exceeding the EU limit for PFOS by 300%.**

Of particular concern are the screening test results in the surface water stream near the cement kiln and sediment for the alarmingly high levels of PFAS. The heavy metal levels in mosses are among the highest recorded in TW-biomonitoring research conducted in Europe (2019-2023). Additionally, elevated levels of PAH were found in dust depositions on the roofs of houses in the villages of *Dvorníky* and *Zádiel*.

Overall, the findings from this initial biomonitoring project raise worrying concerns regarding the presence of dioxins (PCDD/F/dl-PCB), PAH, PFAS and heavy metals in the environment of this region of the Košice. Further research is imperative to comprehend these contaminants' source(s) and deposition patterns.

Figure 3 - Biomonitoring research results, Košice region, Slovakia, 30-31 October 2023



THE TRUE TOXIC TOLL

To find out more, please visit

www.zerowasteeurope.eu

Zero Waste Europe gratefully acknowledges financial assistance from the European Union. The sole responsibility for the content of this event materials lies with Zero Waste Europe. It does not necessarily reflect the opinion of the funder mentioned above. The funder cannot be held responsible for any use that may be made of the information contained therein.

ZERO WASTE EUROPE

TOXICOWATCH