Persistent Organic Pollutants in Free Range Chicken Eggs from Western Balkan Countries

Bosnia and Herzegovina, Montenegro and Serbia / 2014 – 2015

ARNIKA

CENTRUM PRO PODPORU OBČANŮ

TRANSITION

Persistent Organic Pollutants

in Free Range Chicken Eggs from Western Balkan Countries

Million tons of steels per year is produced by ArcelorMittal in Zenica, Bosnia and Herzegovina. The levels of dust in air are 30 fold higher than in central London.

Photo: Adéla Turková / Arnika

CONTENTS

Persistent Organic Pollutants (POPs) in Free Range Chicken Eggs from Western Balkan Countries
Bosnia and Herzegovina, Montenegro and Serbia 2014–2015

RNDr. Jindřich Petrlík, Arnika – Toxics and Waste Programme, Prague
Peter Behnisch, Bio Detection Systems, Amsterdam
Prague, 2015
ISBN: 978-80-87651-17-9

Arnika – Citizens Support Centre
Chlumova 17, 130 00 Prague 3
The Czech Republic
Phone: +420 222 781 471
e-mail: cepo@arnika.org

Cover photos: Adéla Turková / Arnika (www.adelinagrafika.com)
Graphic design and DTP: Jakub Němeček (www.typonaut.cz)

Read more: http://english.arnika.org

This report was produced with the financial support of the Ministry of Foreign Affairs of the Czech Republic in the framework of Transition Promotion Programme, and Global Greengrants Fund. The content of this publication is a sole responsibility of the authors and in no way can be taken to reflect the views of the donors.

Authors would like to acknowledge NGOs participating in sampling: Green Home (Montenegro), Center for Ecology and Sustainable Development (Serbia), Center for Ecology and Energy Tuzla and Eko Forum Zenica (Bosnia and Hercegovina), and CEE Bankwatch Network.

Giant thermal power plant in Tuzla, Bosnia and Herzegovina, consuming from 3 to 4 million tons of lignite anually, is surprisingly not equipped by desulphurisation filters.

Photo: Jana Sobotková, Arnika

1. INTRODUCTION

Free range chicken eggs were used for monitoring levels of contamination by POPs at certain places in many previous studies (Pless-Mulloli, Schilling et al. 2001, Pirard, Focant et al. 2004, DiGangi and Petrlík 2005, Shelepchikov, Revich et al. 2006, Aslan, Kemal Korucu et al. 2010, Arkenbout 2014). Eggs have been found to be sensitive indicators of POP contamination in soils or dust and are an important exposure pathway from soil pollution to humans, and eggs from contaminated areas can readily lead to exposures which exceed thresholds for the protection of human health (Van Eijkeren, Zeilmaker et al. 2006, Hoogenboom, ten Dam et al. 2014, Piskorska-Pliszczynska, Mikolajczyk et al. 2014). Chickens and eggs might therefore be ideal “active samplers” and indicator species for evaluation of the level of contamination of sampled areas by POPs, particularly by dioxins (PCDD/Fs) and PCBs. Based on this assumption, we have chosen sampling of free range chicken eggs and their analyses for selected POPs as one of the monitoring tools within the projects “Legal Protection of Environmental Pollution Victims and Transfer of Experience from the Czech Republic” and “Arnika Regional & International Support for a Toxic Free Future” in three Balkan states.

The data and analyses of free range chicken eggs discussed in this report were obtained during a two-year joint project of Bosnian and Czech NGOs, and a yearlong joint monitoring project by Bosnian, Montenegrin, Serbian and Czech NGOs. They were obtained during field visits in 2014 and 2015, as in cases of the reports by Dvorská (2015) or Šír (2015). The sampled localities were chosen as those where selected sources of pollution by POPs were expected such as metallurgical plants, coal-fired power plants, and waste disposal sites.

2. SAMPLING AND ANALYTICAL METHODS

Samples of free range chicken eggs were collected at two locations in Bosnia and Herzegovina, two locations in Montenegro – of which one was expected to be clean – and finally one location in Serbia. Pooled samples of more individual egg samples were collected at each of the selected sampling sites in order to get more representative samples. Table 1 summarizes basic data about the size of samples and measured levels of fat content in each of the pool samples. Thirteen pool samples of free range chicken eggs were taken in total. One sample was taken in 2014 and twelve samples in 2015. A sample of cheese was taken in addition to the free range chicken eggs in Pljevlja, Montenegro in 2015.

Free range chicken eggs determined for analysis of PCDD/Fs and dioxin-like PCBs using the DR CALUX® method were sent to a Dutch ISO 17025 certified laboratory (BioDetection Systems B.V., Amsterdam). The procedure for the BDS DR CALUX bioassay has previously been described in detail (Besselink H 2004) but, briefly, H4IIE cells stably transfected with an AhR-controlled luciferase reporter gene construct were cultured in α-MEM culture medium supplemented with 10% (v/v) FCS under standard conditions (37°C, 5% CO2, 100% humidity). Cells were exposed in triplicate on 96-well microtiter plates containing the standard 2,3,7,8-TCDD calibration range, a DMSO blank. Following a 24 hour incubation period, cells were lysed. A solution containing luciferin (Glow Mix) was added and the luminescence was measured using a luminometer (Berthold Centro XS3).

The DR CALUX bioassay method is proven for screening analyses which can give a good picture about the level of pollution[1]; however, for confirmation it is necessary to go for more specific PCDD/Fs and DL PCBs congener analyses, which also allows examination of finger prints of dioxins (PCDD/F congener patterns), specific for different sources of pollution. Most of the samples were analyzed for content of individual PCDD/Fs and an extended list of PCB congeners by HRGC-HRMS at the accredited laboratories Axys Varilab and of the State Veterinary Institute in Prague, Czech Republic.

The egg samples were also analyzed for content of non-dioxin-like PCBs and OCPs in Czech certified laboratories (University of Chemistry and Technology, Department of Food Chemistry and Analysis and Axys Varilab). 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 identification and quantification of the analyte was conducted by gas chromatography coupled with tandem mass spectrometry detection in electron ionization mode.

The mercury content in the samples was analyzed with atomic absorption spectrometry in an Advanced Mercury Analyser (AMA 254, Altec) using standard operating procedure SOP 70.4 (AAS-AMA) at the State Veterinary Institute, Prague.

1 "Bioanalytical methods" means methods based on the use of biological principles like cell-based assays, receptorassays or immunoassays. They do not give results at the congener level but merely an indication of the TEQ level, expressed in Bioanalytical Equivalents (BEQ) to acknowledge the fact that not all compounds present in a sample extract that produce a response in the test may obey all requirements of the TEQ-principle. European Commission (2012). Commission Regulation (EU) No 252/2012 of 21 March 2012 laying down methods of sampling and analysis for the official control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EC) No 1883/2006 Text with EEA relevance European Commission. Official Journal of the European Communities: L 84, 23.83.2012, p. 2011–2022.

In the village of Tetovo, Bosnia and Herzegovina, people keep chicken in their yards distant just few hundred meters from huge steelworks of ArcelorMittal.
Photo: Adéla Turková / Arnika

Table 1: Overview of free range chicken egg samples from selected sites in three Western Balkan states.

No	Sample	Locality	Country	Month of sampling	Number of eggs in pooled samples	Fat content
1	ZEN-1	Podbrežje (Zenica)	Bosnia and Herzegovina	01/2014	10	11.15
2	ZEN-15/1	Gračanica (Zenica)	Bosnia and Herzegovina	04/2015	5	15.7
3	ZEN 15/2 and 15/4	Tetovo (Zenica)	Bosnia and Herzegovina	04/2015	11	14.1
4	ZEN 15/3	Donja Gračanica (Zenica)	Bosnia and Herzegovina	04/2015	6	11.5
5	ZEN 15/5	Donja Vraca (Zenica)	Bosnia and Herzegovina	04/2015	6	15.6
6	BiH-E-01	Divkoviči I (Tuzla)	Bosnia and Herzegovina	04/2015	6	12.3
7	BiH-E-02	Divkoviči II (Tuzla)	Bosnia and Herzegovina	04/2015	5	15.6
8	PLZ-E1+E2+E3	Plužine – Orah	Montenegro	04/2015	3	12.5
9	PLZ-E4+E5+E6	Plužine – Seoce	Montenegro	04/2015	3	10.6
10	PLJ-EGGS-01	Pljevlja	Montenegro	04/2015	2	10.2
11	SRB-EGG-01	Grabovac I (Obrenovac)	Serbia	04/2015	2	13.6
12	SRB-EGG-02 and 03	Grabovac II (Obrenovac)	Serbia	04/2015	4	12.6
13	SRB-EGG-04, 05 and 06	Ušće – Gorjača – Gola bara (Obrenovac)	Serbia	04/2015	6	17.2
14	MN 17 (cheese)	Pljevlja	Montenegro	04/2015	-	32.2

Figure 1: Location of the chosen hot spots on a map of Bosnia and Herzegovina, Montenegro, and Serbia. The hot spots Obrenovac (Serbia), Pljevlja (Montengero), Tuzla, and Zenica (both Bosnia and Herzegovina) are marked by red flags together with the chosen background location Plužine (Montenegro).

3. DESCRIPTION OF HOT SPOTS

The four locations chosen for sampling (Obrenovac, Pljevlja, Tuzla and Zenica) are located in different parts of three Western Balkan states – Bosnia and Herzegovina, Montenegro and Serbia. Three of these locations were chosen as there was larger sampling of soil, sediments, vegetable and fish in relation to coal burning power plants in Obrenovac, Pljevlja and Tuzla. The Stockholm Convention has identified coal burning power plants as a sector *"for comparatively high formation and release"* of persistent organic pollutants such as dioxins, furans, PCBs, hexachlorobenzene, and pentachlorobenzene.[2] More information about these thermal power plants can be found e.g. in Šír (2015). There are more industrial facilities potentially releasing POPs in Tuzla in addition to the power plant, such as for example chlorine chemical industry and others. The fourth location, Zenica, was chosen as there is large steel mill, whose majority owner is the ArcelorMittal corporation. All hot spots were chosen as potential sources of POPs releases.

3.1. Obrenovac

Obrenovac is a town and municipality in northern Serbia. In 2011 the town had a population of 24,568, and the municipality had 71,419 inhabitants. Obrenovac is one of 17 municipalities that make up the greater Belgrade area. The largest Serbian thermal power plant is located on the outskirts of the town. Obrenovac was submerged and completely evacuated during the 2014 Southeast Europe floods (Wikipedia 2015).

2 Stockholm Convention Annex C, Part II

The samples in the Obrenovac area were collected in the surroundings of the Nikola Tesla B power plant and its ash landfill (see map in Figure 2). The Nikola Tesla power plants are located on the right bank of the river Sava, approximately 40 km upstream from Belgrade, near the town of Obrenovac. Nikola Tesla A is by far the largest one in Serbia: it has six blocks with a total installed capacity of 1,650 MW while Nikola Tesla B has two units with a total of 1,240 MW. The ash landfill contains a suspension of ash and water, which sometimes overflows and drains into the river Sava. In addition to the impact on water pollution, landfills represent a surface source of air pollution particles of ash. Due to the unfavourable physical and chemical characteristics of ash and of the way that ash disposal is carried out in open dumps, in dry and windy weather wind erosion of ash occurs. These power plants use lignite mined from the Kolubara mine basin as fuel.

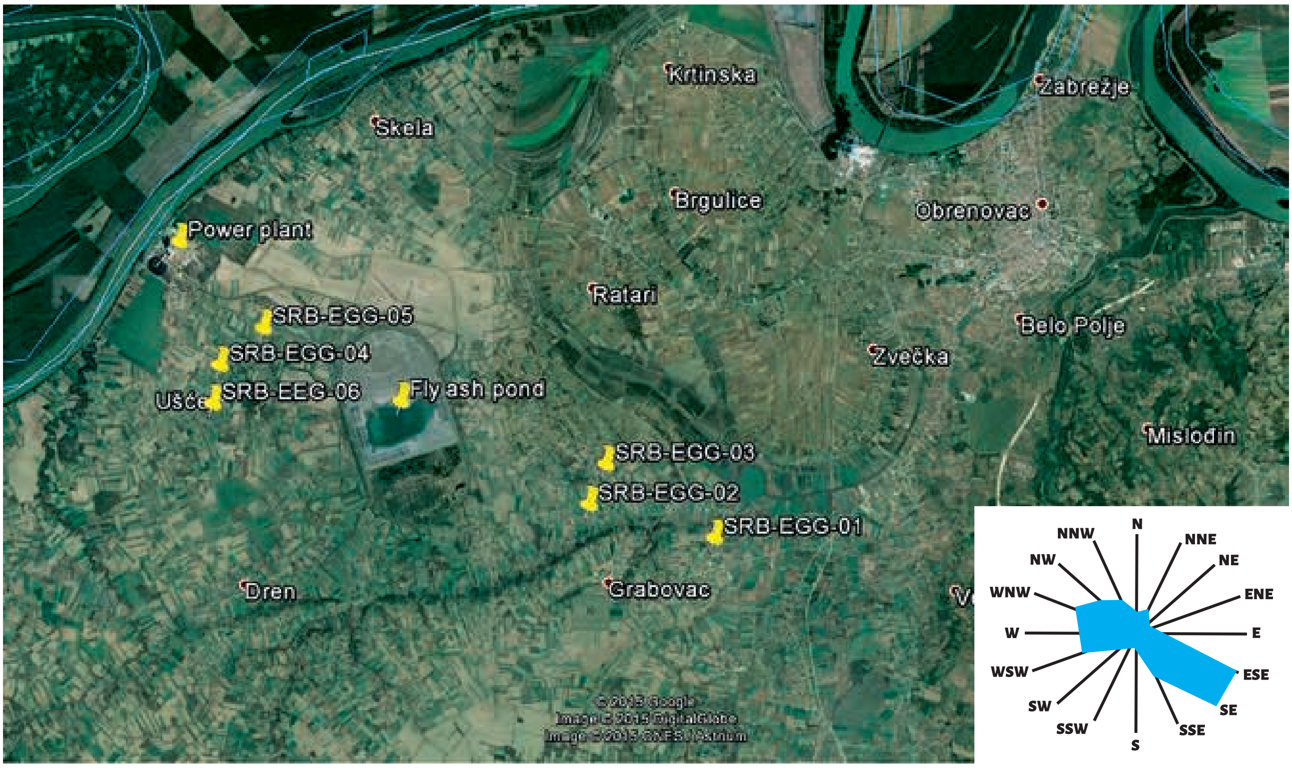


Figure 2: Location of samples taken in the surroundings of Obrenovac, Serbia, on a Google Earth map with a wind rose for this region (on the bottom part of the figure).

In rural areas of Western Balkan, many people consume own chicken eggs daily ; surpluses are often sold at local markets. *Photo: Adéla Turková / Arnika*

3.2. Pljevlja

Pljevlja is a town and the centre of Pljevlja Municipality located in the north of Montenegro. The town lies at an altitude of 770 m. In 2011, the municipality of Pljevlja had a population of 30,786, while the town itself had a population of about 19,489. The municipality borders with the republics of Serbia and Bosnia and Herzegovina. With a total area of 1,346 km^2, it is the third largest municipality in Montenegro. Pljevlja is also one of the main economic centres of Montenegro. The only thermal power plant in Montenegro, which provides 45% of the electric power supply for Montenegro, is situated just outside Pljevlja as well as a coal mine with 100 % of the coal production in Montenegro (Wikipedia 2015). The sample in Pljevlja was taken 100 m from the ash deposit of the thermal power plant, which is 3 km southwest from the town of Pljevlja. After a reconstruction carried out 2009, the new power of the thermal power plant is 218.5 MW. Pljevlja I is fuelled by coal strip mines. The plant annually consumes an average of 1.35 million tonnes of coal, 3,500 tons of fuel oil and 660 tonnes of chemicals (lime, hydrochloric acid, alkali, etc.). Power plant flue gas is separated into the atmosphere through a 252 m high chimney. Its outlet exceeds 1,000 m above sea level. The power plant is supplied from the Coal Mine A.D. Pljevlja.

3.3. Tuzla

Tuzla city, the seat of the Tuzla Canton, is the third largest city in Bosnia and Herzegovina after Sarajevo and Banja Luka. The city is home to more than 80,000 inhabitants and represents the economic and scientific centre of north-eastern Bosnia.

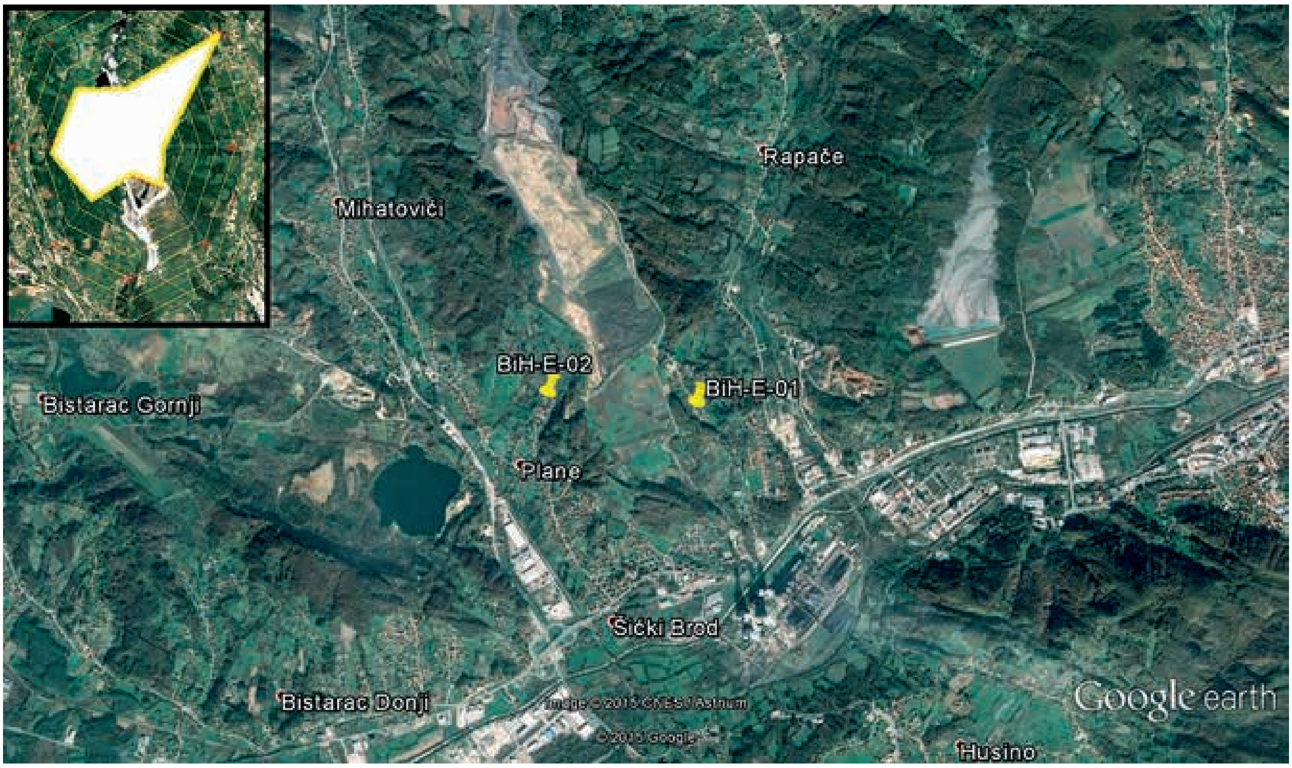


Figure 3: Location of samples taken in the surroundings of Tuzla, Bosnia and Herzegovina on a Google Earth map with a wind rose for this region (on the upper part of the figure).

Samples were taken close to one of the ash ponds on the edge of Tuzla as is visible on the map (see map at Figure 3). The ash pond serves Tuzla Power station which is the largest coal-fired power plants in Bosnia and Herzegovina. The power station has an installed electric capacity of 715 MW (without two 32 MW units that do not operate) and it produces around 3.1 TWh of electricity per year. In addition, it supplies heat for Tuzla and Lukavac. The plant burns 330,000 tonnes of coal annually. Units 1-6 are supplied from the Kreka and Banovići mines.

3.4. Zenica

Zenica is the fourth biggest city in Bosnia and Herzegovina. It lies in Zenica-Doboj Canton, 70 km from Sarajevo on the river Bosna. Zenica is home to around 73,000 inhabitants. The steelworks in Zenica was a state-owned factory built by the Socialist government. The steelworks, which extends over almost 30 km^2, employs around 3,000 people (before the war the production provided 22,000 working places for people from a wider area). The production capacity is 1 million tonnes annually. The direct negative impact of whole the industrial complex in Zenica affects the health and life of more than 130,000 people (Arnika – Citizens Support Centre 2015).

Samples were taken in the surroundings of the steelworks (see maps at Figures 5 and 6, page 15).

4. THE WESTERN BALKAN STATES, EU, AND OTHER LIMITS FOR POPS IN EGGS

Chicken eggs are a quite common part of the diet in many countries including the Western Balkan states. It is also common that people raise their own chicken and partly sell surplus chicken eggs at markets as raw eggs or as food in public restaurants. Limits for POPs in chicken eggs applied in Bosnia and Herzegovina are summarized in Table 2. There is same limit value for PCDD/Fs and PCBs in Bosnia and Herzegovina as in the EU (Bosnia and Herzegovina 2014)(see Table 2). This applies also to limit values for OCPs like DDT or HCHs. For mercury we found for example the limit value used in Kazakhstan. There is no limit set up for mercury content in eggs within the EU or in the three Western Balkan countries in which the egg samples presented in this study were collected.

Table 2: Limit concentration values for OCPs, mercury, PCBs and PCDD/Fs TEQs in chicken eggs

	Hen eggs		
	EU ML[2]	EU MRL[3]	KazakhMAC[7]
Unit	pg g^{-1} fat	ng g^{-1} fat	ng g^{-1} *
WHO-PCDD/Fs TEQ	2.5		
WHO-PCDD/Fs-dl-PCB TEQ	5.0		
PCBs[5]	40		
DDT total[6]		50	
γ-HCH (lindane)		10	
α-, β-HCH		20, 10**	
HCB		20	
Mercury			20

2 EU Regulation (EC) N°1259/2011
3 Regulation (EC) N°149/2008. Maximum residue level (MRL) means the upper legal level of a concentration for a pesticide residue in or on food or feed set in accordance with the Regulation, based on good agricultural practice and the lowest consumer exposure necessary to protect vulnerable consumers.
5 sum of PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180
6 sum of p,p´-DDT, o,p´-DDT, p,p´-DDE and p,p´-DDD
7 Kazakhstan SanPin Hygienic safety requirement and nutrition value for food from 11.06.2003 .
* not clear whether calculated for fat content or not
** for each congener is MRL set separately

5. RESULTS

The results of the analyses by using DR CALUX are summarized in Table 3. The results of the analyses for other POPs and congener analyses by using HRGC-HRMS are summarized in Table 4. There are also few results for analyses of mercury content in selected samples of eggs in Table 4. The graph in Figure 7 compares the results of the analyses for 6 PCB indicator congeners. The graph also shows a comparison with the EU limit value for PCB content in chicken eggs. Free range chicken eggs from Belarus, China and Kazakhstan were also analyzed using the same methods (Petrlík, Kalmykov et al. 2015). So we can compare data from the hot spots in three Balkan states with similar locations in other countries as well. The results for DDT on a fresh weight basis are summarized in Table 6 and compared with the respective EU limit value.

5.1. Dioxins (PCDD/Fs) and dioxin-like PCBs measured by DR CALUX

Some samples of chicken eggs collected at hot spots in Western Balkan states during field visits in 2015 were screened for dioxins and dioxin-like PCBs by using the DR CALUX method in the BDS laboratory, Amsterdam. The results are summarized in Table 3.

Table 3: Results of DR CALUX bioassay analyses for both PCDD/Fs and DL PCBs for samples from Bosnia and Herzegovina, Montenegro and Serbia. Data are in pg BEQ g^{-1} fat.

Sample	Locality	Country	PCDD/Fs and DL PCBs (DR CALUX)	PCDD/Fs (DR CALUX)
ZEN-15/1	Gračanica (Zenica)	Bosnia and Herzegovina	12	8.8
BiH-E-01	Divkoviči I (Tuzla)	Bosnia and Herzegovina	7.7	5.6
BiH-E-02	Divkoviči II (Tuzla)	Bosnia and Herzegovina	6.5	4.3
PLZ-E1+E2+E3	Plužine – Orah	Montenegro	0.98	0.34
SRB-EGG-02 and 03	Grabovac II (Obrenovac)	Serbia	7.0	5.2
SRB-EGG-04, 05 and 06	Ušće – Gorjača – Gola Bara (Obrenovac)	Serbia	4.4	2.2

When PCDD/Fs levels determined by the DR CALUX method are discussed, the following has to be considered. This cell based reporter gene assay is a validated method for screening for PCDD/Fs and DL PCB contents in food according to EU Commission Regulation EC/252/2012 (European Commission 2012). Screening methodologies are usually used to exempt those samples that are below the maximum permitted limit (i.e. that are compliant with the limit) and that can, therefore, be released to the market. In addition, one needs to select those samples that require confirmation (i.e. are suspected to be non-compliant) of their PCDD/Fs TEQ level. When bioassays are used as screening tools, the interpretation of the obtained results should consider the higher variability associated with them (van Overmeire, van Loco et al. 2004, Gasparini M 2011).

Six pool egg samples were analyzed using the DR CALUX method for determination of dioxin activity in total. Among those only two samples, one from Plužine and one pooled sample from Ušće – Gorjača – Gola Bara in Obrenovac region were below limits set up by the EU also used for consideration of results obtained by DR CALUX analyses. All other four samples were above 5 pg BEQ g^{-1} fat level for total PCDD/Fs and DL PCBs content. The highest level of 12 was measured in chicken eggs from Gračanica near Zenica, east of the metallurgical plant. The level observed in these eggs is comparable with some samples from Balkhash, Kazakhstan, however in some pooled samples of chicken eggs collected there were also much higher levels of PCDD/Fs and DL PCBs measured by DR CALUX method at some sites in Balkhash (Petrlík, Kalmykov et al. 2015).

5.2. Dioxins (PCDD/Fs), PCBs and other POPs measured by gas chromatography methods

GCMS-HRMS analyses were chosen for bigger number of pooled chicken egg samples. All samples were also analyzed for other POPs, group of OCPs: hexachlorobenzene (HCB), hexychlorocyclohexanes (HCHs) and DDT and its metabolites. HCB is also considered to be unintentionally produced POP (U-POP) in the same processes as dioxins and DL PCBs (Stockholm Convention on POPs 2008), although it is commonly measured together with other OCPs. Nine pooled samples of eggs were analyzed for PCDD/Fs and DL PCBs in total and twelve samples of eggs and one cheese sample for other POPs. Nine samples, including cheese were also measured for mercury content. The results are summarized in Table 4.

Table 4: Summarized results of analyses for POPs and mercury for thirteen pooled free range chicken eggs samples and one cheese sample. There are also EU limit values for comparison. ***(Table continues on page 13.)***

Locality	Podbrežje (Zenica)	Gračanica (Zenica)	Tetovo (Zenica)	Donja Gračanica (Zenica)	Donja Vraca (Zenica)	Divkoviči I (Tuzla)	Divkoviči II (Tuzla)	Plužine – Orah	Plužine – Seoce
Sample	ZEN 1	ZEN 15/1	ZEN 15/2 + ZEN 15/4	ZEN 15/3	ZEN 15/5	BiH-E-01	BiH-E-02	PLZ-E1+E2+E3	PLZ-E4+E5+E
Fat content	11.15	15.7	14.1	11.5	15.6	12.3	15.6	12.5	10.6
PCDD/Fs (pg WHO TEQ g^{-1} fat)	1.93	2.40	5.57	4.73	3.86	2.51	NA	NA	NA
DL PCBs (pg WHO TEQ g^{-1} fat)	5.15	1.55	3.09	3.56	3.75	1.56	NA	NA	NA
Total PCDD/F + DL PCBs (pg WHO TEQ g^{-1} fat)	7.08	3.95	8.66	8.29	7.61	4.07	NA	NA	NA
PCDD/Fs and DL PCB (DR CALUX); (pg BEQ g^{-1} fat)	NA	NA	12	NA	NA	NA	6.5	0.98	NA
PCDD/Fs (DR CALUX); (pg BEQ g^{-1} fat)	NA	NA	8.8	NA	NA	NA	4.3	0.34	NA
HCB (ng g^{-1} fat)	<1.00	1.13	1.18	1.06	2.65	1.55	1.52	2.27	1.36
7 PCB (ng g^{-1} fat)	NA	2.97	12.78	14.69	14.45	NA	16.67	0.73	5.21
6 PCB (ng g^{-1} fat)	NA	2.31	10.03	12.97	12.62	19.38	15.06	0.59	3.01
sum HCH (ng g^{-1} fat)	NA	0.35	2.51	0.27	0.12	0	3.23	0.54	0
sum DDT (ng g^{-1} fat)	NA	3.81	341	144.6	172.73	6.85	933.48	1.83	0
Hg (ng g^{-1})	NA	NA	NA	NA	NA	14	3	1	1

Free range eggs have been found to be sensitive indicators of contamination in soils and are an important exposure pathway from soil pollution to humans.
Photo: Adéla Turková / Arnika

Locality	Pljevlja	Grabovac I (Obrenovac)	Grabovac II (Obrenovac)	Ušće – Gorjača – Gola Bara (Obrenovac)	Pljevlja	EU stand.
Sample	PLJ-EGGS-01	SRB-EGG-01	SRB-EGG-02 + SRB-EGG-03	SRB-EGG-04 + 05 + 06	MN cheese	
Fat content	10.2	13.6	12.6	17.2	32.2	
PCDD/Fs (pg WHO TEQ g-1 fat)	0.20	11.14	3.31	NA	NA	2.50
DL PCBs (pg WHO TEQ g-1 fat)	0.06	2.38	1.58	NA	NA	
Total PCDD/F + DL PCBs (pg WHO TEQ g-1 fat)	0.26	13.51	4.89	NA	NA	5.00
PCDD/Fs and DL PCB (DR CALUX); (pg BEQ g-1 fat)	NA	NA	7.0	4.4	NA	5.00
PCDD/Fs (DR CALUX); (pg BEQ g-1 fat)	NA	NA	5.2	2.2	NA	2.50
HCB (ng g-1 fat)	0.43	5.39	2.12	1.73	4.4	20.00
7 PCB (ng g-1 fat)	0	5.22	1.64	5.45	0	-
6 PCB (ng g-1 fat)	0	2.06	1.13	2.9	0	40.00
sum HCH (ng g-1 fat)	0.24	0.55	0.57	0.68	0.26	-
sum DDT (ng g-1 fat)	5.14	84.2	106.95	119.2	6.91	-
Hg (ng g-1)	2	1	2	3	1	-

5.3. Dioxins (PCDD/Fs) and dioxin-like PCBs (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 which can be divided into two groups according to their toxicological properties: 12 congeners exhibit toxicological properties similar to dioxins and are therefore 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 PCB' (NDL PCBs) (European Commission 2011). Levels of PCDD/Fs and DL PCBs are expressed in total WHO-TEQ calculated according toxic equivalency factors (TEFs) set by WHO experts panel in 2005 (Van den Berg, Birnbaum et al. 2006). These new TEFs were used to evaluate dioxin-like toxicity in nine pooled samples of chicken eggs from three Balkan states.

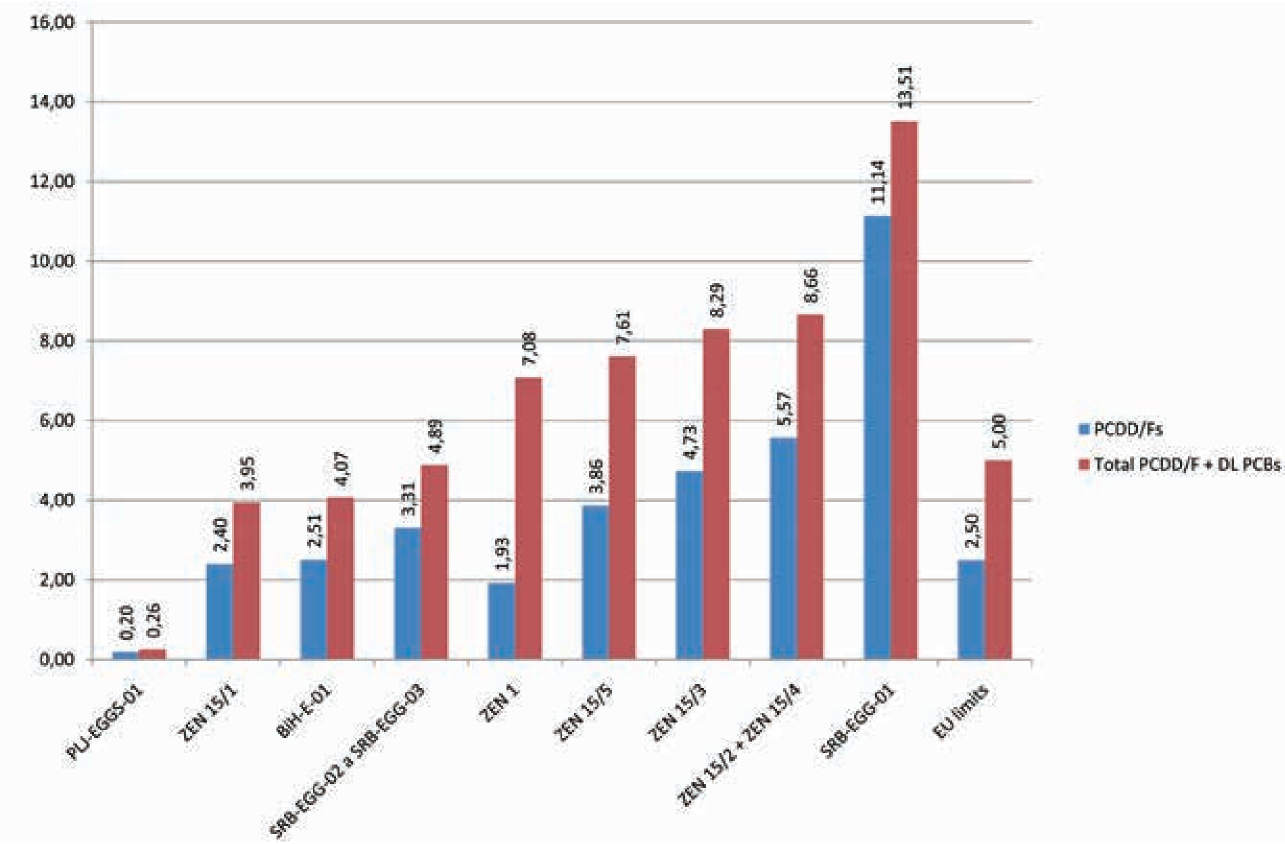


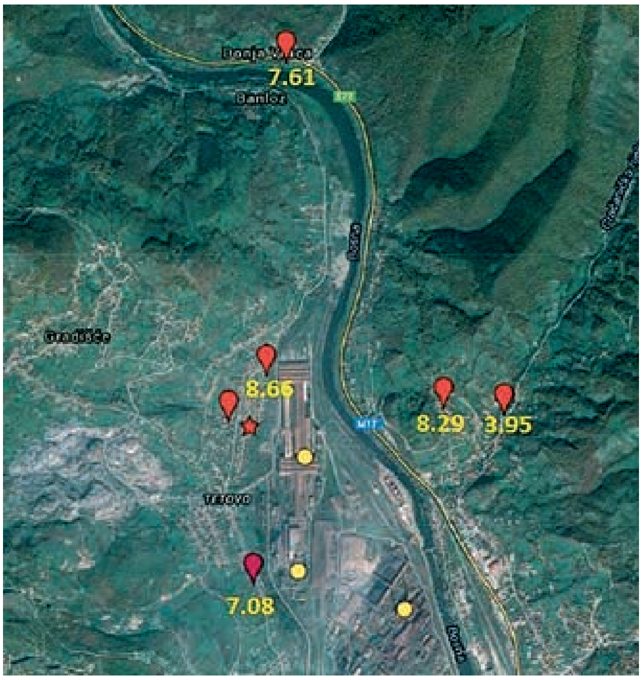
Figure 4: Graph showing comparison of total PCDD/Fs + DL PCBs, and PCDD/Fs only in pg WHO-TEQ g⁻¹ of fat for different pooled chicken eggs samples from Zenica (Bosnia and Herzegovina), Tuzla (Bosnia and Herzegovina), Pluzine (Montenegro, background location) and Obrenovac (Serbia), measured by GCMS – HRMS.

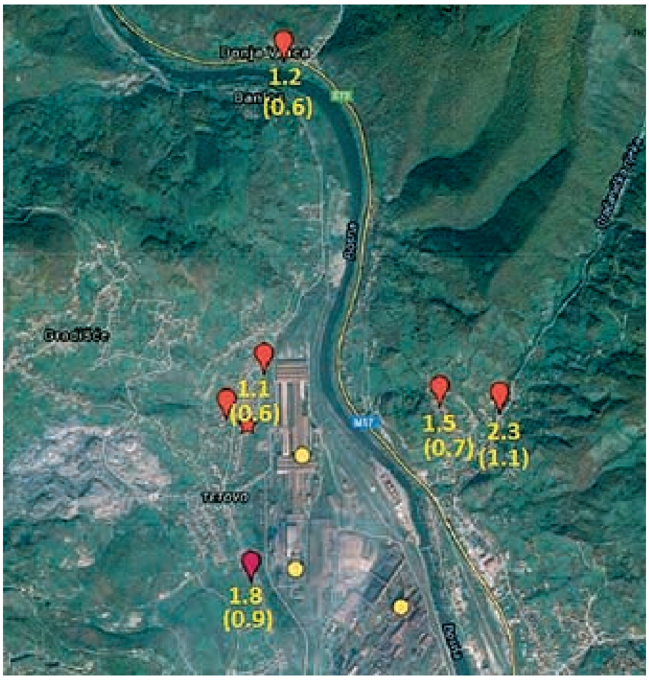
Six out of nine samples from Western Balkan states exceeded the EU ML of PCDD/Fs congeners in chicken eggs, (compare Tables 4 and 2 and see graph at Figure 4) and five samples exceeded the EU limit value for both PCDD/Fs and DL PCBs in chicken eggs (European Commission 2011). The background levels for PCDD/Fs and DL PCBs measured in chicken eggs from Pljevlja were 0.20 and 0.06 pg WHO-TEQ g^{-1} fat, respectively (see also the discussion about background levels further in chapter 4.1). The highest level of dioxins (11.14 pg WHO-TEQ g^{-1} fat) was measured in the sample from the Grabovac I site, near Obrenovac, and the second highest level (5.57 pg WHO-TEQ g^{-1} fat) was measured in the sample from Tetovo (ZEN 15/2 + ZEN 15/4), near the steelworks of ArcelorMittal in Zenica. In both samples the toxicity of PCDD/Fs exceeded the total WHO-TEQ value for PCB congeners. Most of the egg samples showing high levels of total WHO-TEQ had a prevalence of PCDD/Fs share over DL PCBs on total WHO-TEQ, as shown by the graph in Figure 3. This doesn't apply to two samples from Zenica (ZEN 1 and ZEN 15/5).

We tried also to answer the question: How many free range chicken eggs can be eaten by an adult man or woman with an approximate body weight of 70 kg and how many of them can be eaten by a 10-year-old child with an approximate body weight of 35 kg? We stick to the lower bound of TDI of 1 pg WHO-TEQ/kg of body weight per day (van Leeuwen, Feeley et al. 2000) in our calculation, bearing in mind that dioxin and DL PCBs occur not only in eggs but also in other food according to data available for the region (Petrović, Jovanović et al. 2008, Aslan, Kemal Korucu et al. 2010). The calculation was made by using the following formula: N adult = 70 g WHO-TEQ / (pg WHO-TEQ g^{-1} fresh weight×50 g); N 10years = 35 g WHO-TEQ / (pg WHO-TEQ g^{-1} fresh weight×50 g). The results are summarized in Table 5. The calculations are based on the precondition that one chicken egg weight is on average 50 g and the TDI for PCDD/Fs and DL PCBs is within the range of 1 – 4 pg WHO-TEQ/kg of body weight per day (van Leeuwen, Feeley et al. 2000).

Table 5: Calculation of suggested maximum consumption of free range chicken eggs from pool samples by adults and/or 10-year-old children per day in order to meet the TDI lower bound level for PCDD/Fs and DL PCBs, which is 1 pg WHO-TEQ/kg body weight/day.

Sample	ZEN 1	ZEN 15/1	ZEN 15/2 + ZEN 15/4	ZEN 15/3	ZEN 15/5	BiH-E-01	PLJ-EGGS-01	SRB-EGG-01	SRB-EGG-02 + SRB-EGG-03
Fat content	11.2	15.7	14.1	11.5	15.6	12.3	10.2	13.6	12.6
pg TEQg^{-1} of fat	7.08	3.95	8.66	8.29	7.61	4.07	0.26	13.51	4.89
pg TEQg^{-1} fresh weight	0.79	0.62	1.22	0.95	1.19	0.50	0.03	1.84	0.62
pg TEQ in 1 egg	39.45	30.99	61.07	47.68	59.38	25.03	1.32	91.89	30.80
Number of eggs per adult / day	1.8	2.3	1.2	1.5	1.2	2.8	53	0.76	2.3
Number of eggs per 10 year old child / day	0.89	1.1	0.57	0.73	0.59	1.4	27	0.38	1.1





Figures 5 and 6: Locations of samples taken in the surroundings of Zenica on Google Earth map with marked levels of PCDD/Fs and DL PCBs measured in pooled chicken egg samples (on the left Figure 5) and maximum amount of eggs consumed per day in order to meet the WHO's TDI for adults and for 10-year- old children in brackets (on the right, Figure 6). For the explanation of the calculation see the text and Table 5.

Appart the eggs collected in Pljevlja, where the PCDD/Fs and DL PCBs were at a level considered as a background level in general (DiGangi and Petrlik 2005, Petrlík, Kalmykov et al. 2015), all other locatios showed considerably high levels of dioxins and dioxin-like PCBs and their consumption should be minimized. The most critical situation is in Grabovac I, where the calculation suggested that three quarters of an egg can be consumed per day by adults. The contamination of eggs from Zenica is also quite serious. Evaluation of levels of dioxin-like compounds in eggs from that area is shown on maps at Figures 5 and 6. It is clear that contamination of eggs is higher in the valley where the steelworks are located while the side of the valley has a slightly lower level of dioxin like compounds in free range chicken eggs.

The total WHO-TEQ levels of PCDD/Fs and DL PCBs in samples from selected hot spots in three Western Balkan states varies. The total WHO-TEQ level in the pooled egg sample from Pljevlja is comparable to those generally considered as background levels, as mentioned already above. The levels of PCDD/Fs and DL PCBs in one sample from Zenica (ZEN 15/1), one sample from Grabovac II in the Obrenovac area (SRB-EGG-02 + SRB-EGG-03) as well as in a sample from Tuzla – Divkoviči I (BiH-E-01) were below the EU MAC and are not considered as high, however the level of PCDD/Fs expressed in the WHO-TEQ from Tuzla exceeded very slightly the EU MAC set just for PCDD/Fs. The samples from Zenica and Obrenovac belong to those with quite elevated levels of PCDD/Fs and DL PCBs in comparison with the collection of samples from IPEN´s The Egg Report from 2005, and comparable with samples from Bolshoy Trostenec, Belarus (waste dumpsite), Barangay Aguado, Philippines (medical waste incinerator), Santos, Mozambique (cement kiln) or Mossville, USA (petrochemical complex) (DiGangi and Petrlik 2005, IPEN Dioxin PCBs and Waste Working Group, Cavite Green Coalition et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Foundation for Realizaiton of Ideas et al. 2005, IPEN Dioxin PCBs and Waste Working Group, JA! Justiça Ambiental et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Mossville for Environmental Action Now et al. 2005). Putative sources of dioxin and dioxin-like PCBs contamination at selected Balkan hot spots are considered in the discussion section below.

5.4. Polychlorinated biphenyls (PCBs)

None of the thirteen free range chicken eggs samples from the hot spots in the three Balkan states exceeded the EU limit for 6 PCB indicator congeners in hen eggs. Elevated levels above 10 ng g^{-1} fat were observed in samples of eggs from Tuzla and Zenica. 6 PCB congeners in sample BiH-E-01 from Tuzla reached half of the EU limit (see the graph in Figure 7).

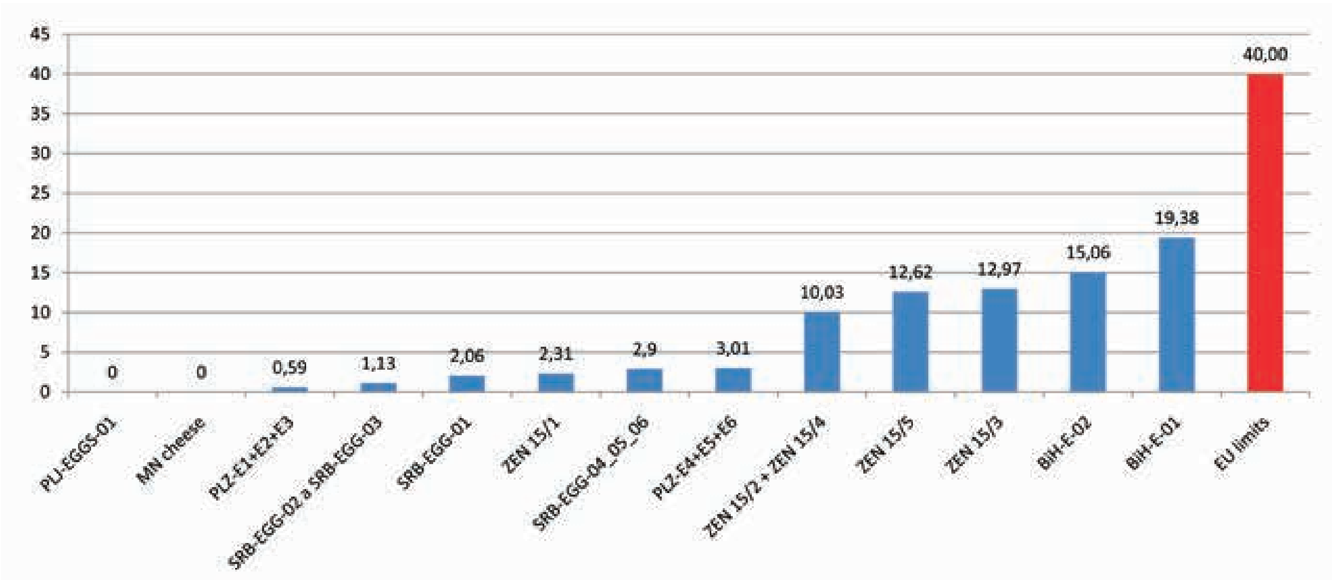


Figure 7: Graph comparing 6 PCB congener levels in different pooled chicken eggs samples from three Balkan states (full set of results is in Table 4).

5.5. Organochlorinated pesticides (OCPs)

EU limits for pesticide residues, including OCPs in chicken eggs, are set per fresh weight of egg. A comparison of DDT metabolites in twelve samples of chicken eggs and one cheese sample from Western Balkan states is in Table 6. The highest observed level of 4 DDT metabolites (145.44 ng g^{-1} f.w.) in eggs from Tuzla (BiH-E-02) was three times higher than the EU limit. DDT in eggs collected close to the steelworks in Zenica, Bosnia and Herzegovina was also very close to the limit value (47.71 ng g^{-1} f.w.). Significantly elevated levels of DDT were observed also in samples from the Obrenovac area, Serbia as well as from Zenica, Bosnia and Herzegovina (see Table 6).

The sum of α-HCH, γ-HCH, and β-HCH was within the range of 0.02 – 0.45 ng g^{-1} fresh weight. None of the samples exceeded EU limit values for individual congeners (10 – 20 ng g^{-1} fresh weight). The highest level of HCHs was measured in free range chicken eggs BiH-E-02 from Tuzla.

Table 6: Summarized results of analyses for DDT and its metabolites for twelve pooled free range chicken egg samples and one cheese sample from three Balkan states. There are also EU limit values (European Commission 2008) for comparison. These results are expressed in ng g-1 fresh weight because EU limits are set for fresh weight for OCPs.

Sample	ZEN 15/1	ZEN 15/2 + ZEN 15/4	ZEN 15/3	ZEN 15/5	BiH-E-01	BiH-E-02	PLZ-E1+E2+E3	PLZ-E4+E5+E6	PLJ-EGGS-01	SRB-EGG-01	SRB-EGG-02 + SRB-EGG-03	SRB-EGG-04 + 05 + 06	MN cheese
Sum of DDT	0.63	48.09	16.65	26.95	1.10	145.62	0.32	0.05	0.83	13.16	16.71	18.62	1.11
Sum of DDT (EU)	0.61	47.71	16.63	26.83	1.08	145.44	0.31	0.03	0.82	13.14	16.69	18.60	1.09

5.6. Mercury

The highest level of mercury (14 ng g^{-1} f.w.) was measured in the pooled eggs sample from Tuzla (BiH-E-01). This result complements findings by Šír (2015), that: *"Higher concentrations of heavy metals (nickel, chromium, cadmium, arsenic and mercury) in soils and sediments were found in the closer distance from the ash depositions …".* 14 ng g^{-1} is higher than the level of mercury measured in eggs from Rostovka close to the Nura river which is contaminated with mercury. Levels of mercury in other egg samples from Western Balkan states were much lower (see Table 4). The source of mercury contamination could be e.g. the chlor alkali plant in Tuzla or the coal-fired power plant.

6. DISCUSSION

6.1. Background levels of POPs in eggs

We did not analyse levels of unintentionally produced POPs in free range chicken eggs sample from Plužine, considered as a background location with regards to POPs, by using the GCMS – HRMS method[3] but there were low levels of dioxin, PCBs and HCB in eggs from the Pljevlja hot spot located in Montenegro. The levels of POPs in this sample were lower for PCDD/Fs and DL PCBs as well as for HCB, and NDL PCBs (DiGangi and Petrlík 2005), compared to those observed in the background samples from other studies of POPs in chicken eggs, although it does not come from a non-industrialized remote area. A comparable low level of PCDD/Fs + DL PCBs was measured for example in commercial eggs from Turkey (Aslan, Kemal Korucu et al. 2010), while a higher level of 0.90 pg WHO-TEQ g^{-1} of fat was observed in eggs from a supermarket obtained in Karaganda, Kazakhstan (Petrlík, Kalmykov et al. 2015). So we suggest considering levels of U-POPs observed in free range chicken eggs in Pljevlja as background levels for the region, while considering the levels of DDT 0; 1.83 ng g^{-1} of fat) and HCHs (0; 0.53 ng g^{-1} of fat) observed in two free range chicken eggs samples from Plužine as background levels for the region. HCB concentrations (1.36; 2.27 ng g^{-1} of fat) in the eggs from Plužine – Orah were higher, in comparison with sample from Pljevlja (0.43 ng g^{-1} of fat). Levels of PCDD/Fs and DL PCBs in eggs from Plužine (see chapter 3.1.) which were analysed only by using the DR CALUX method were comparable to the egg sample from the supermarket in Karaganda mentioned above.

3 PCDD/Fs and DL PCBs were measured by DR CALUX bisoassay method in eggs from Plužine (see chapter 3.1).

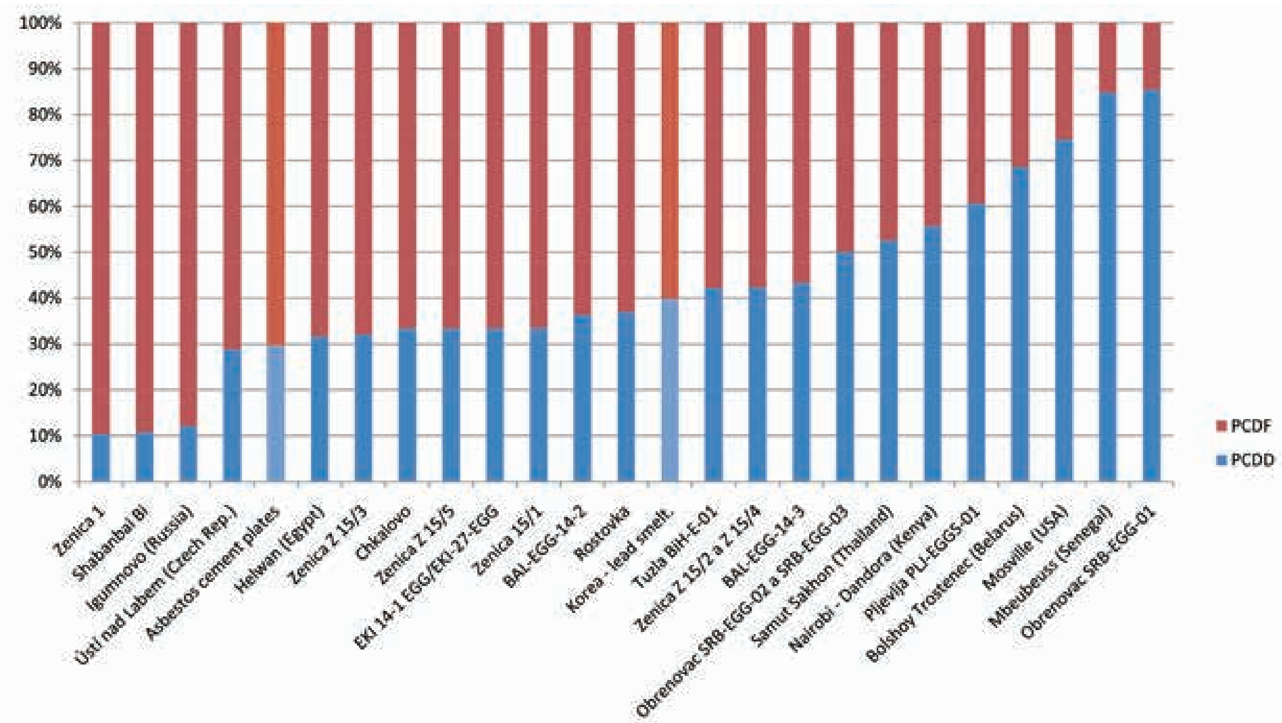
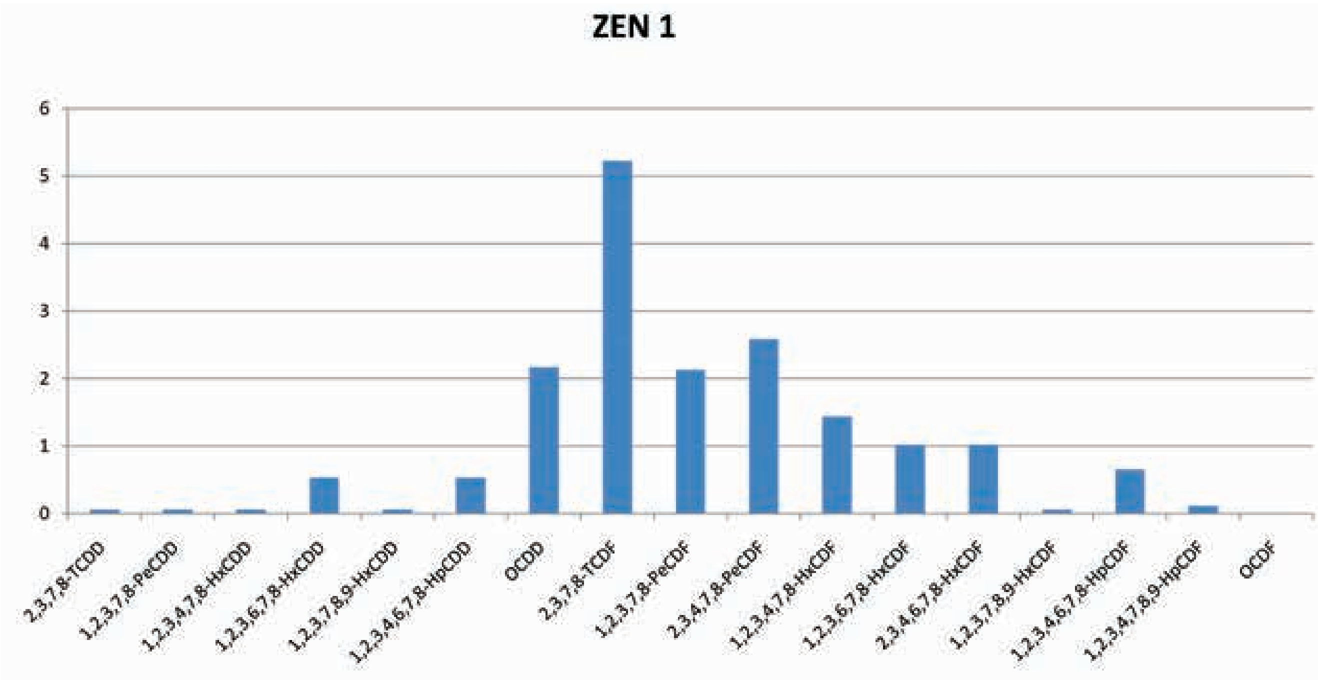
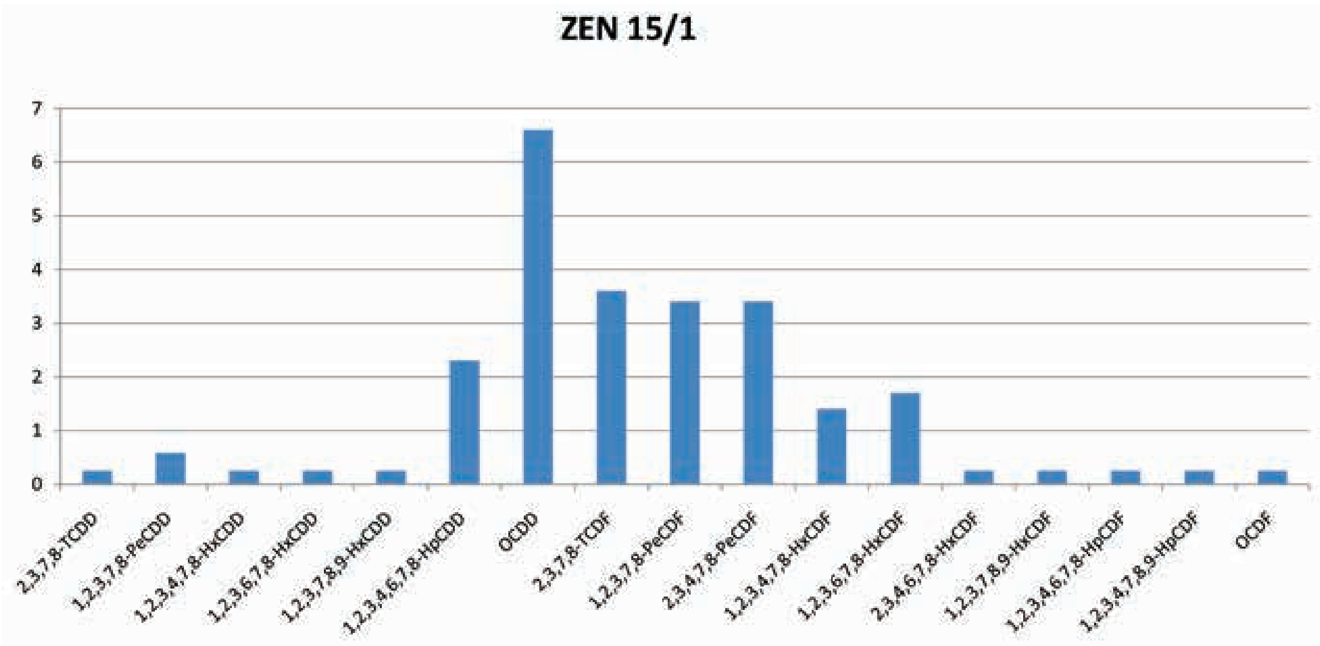


Figure 8: Share of PCDD and PCDF congeners on total WHO-TEQ values in different free range chicken eggs (in darker colours) and two other matrix samples (bars in less intense colour). Sources of information: for data on eggs (IPEN Dioxin PCBs and Waste Working Group, Eco-SPES et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Envilead et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Foundation for Realizaiton of Ideas et al. 2005, IPEN Dioxin PCBs and Waste Working Group, Periyar Malineekarana Virudha Samithi – PMVS et al. 2005); for other than egg samples data (Sam-Cwan 2003, Winkler 2015).

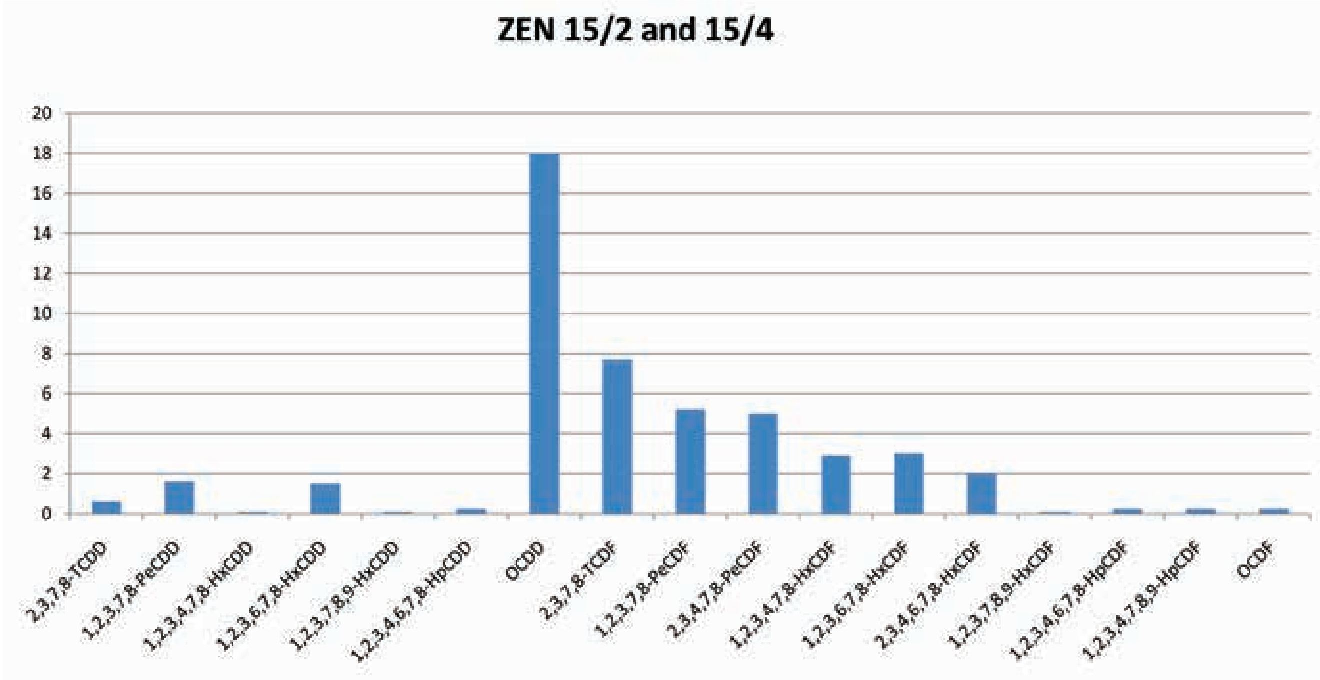
6.2. Dioxin congener patterns and putative sources of pollution

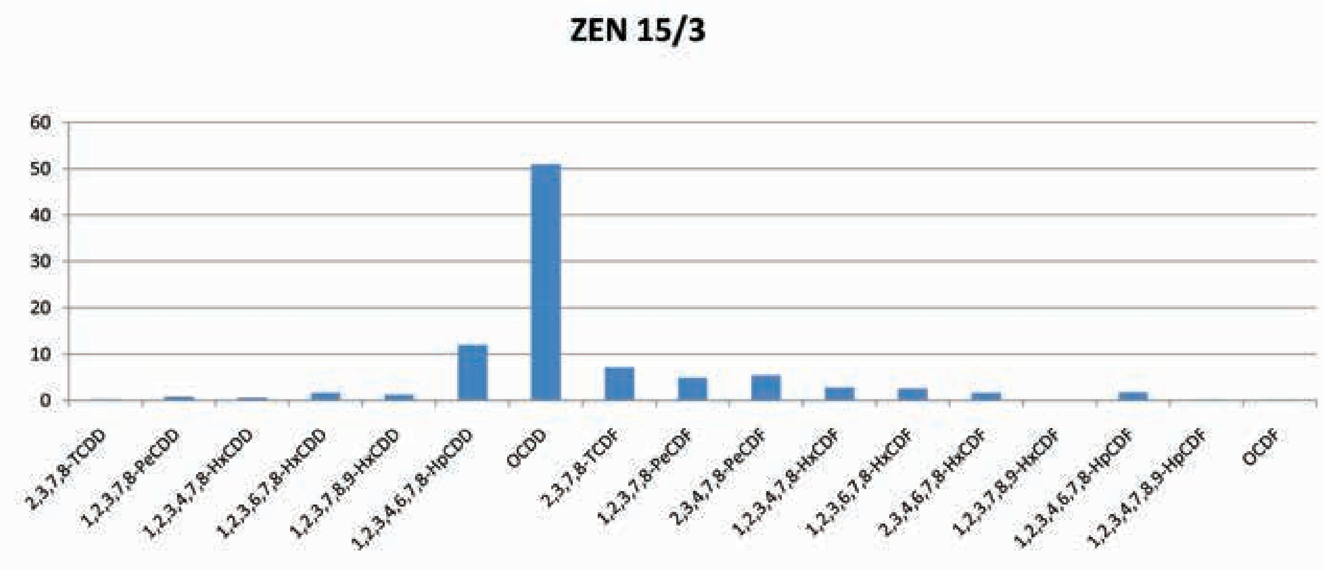
We can compare dioxin congener patterns in free range chicken eggs with their typical patterns for certain types of pollution sources in order to get closer to discovery of their sources at the studied sites. The graph in Figure 8 shows the share of PCDD and PCDF congeners against total WHO-TEQ levels of PCDD/Fs in egg samples and two non-egg samples (air emissions from a lead smelter or the content of PCDD/Fs in asbestos cement fibre plates). There are egg samples from a previous IPEN report where the most likely dioxin sources were identified. The division between PCDD and PCDF congeners in toxic equivalents is used as one of the criteria for a basic classification of potential sources (Sam-Cwan 2003, Yoon-Seok 2003). However, it can be only used as basic information; further analysis of the dioxin congener pattern is needed.

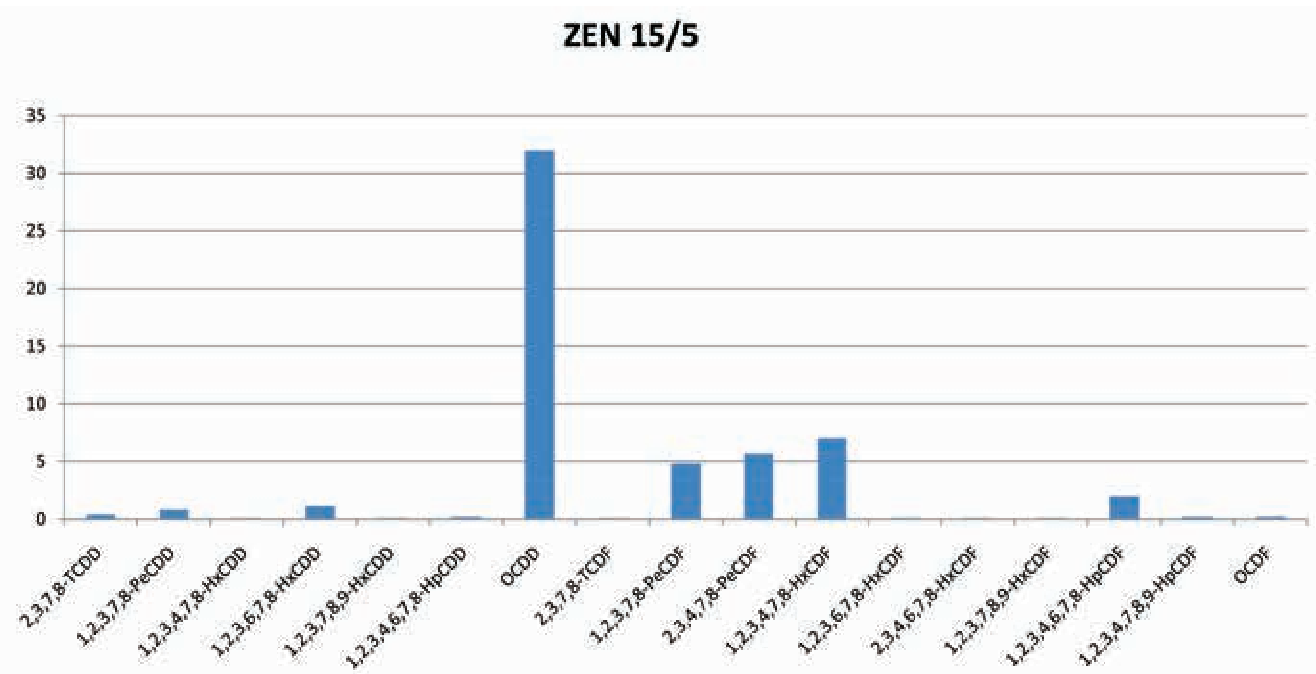




Figures 9–13: Dioxin congener patterns for free range chicken samples from the broader Zenica area.







Figures 9 – 13: Dioxin congener patterns for free range chicken samples from the broader Zenica area.

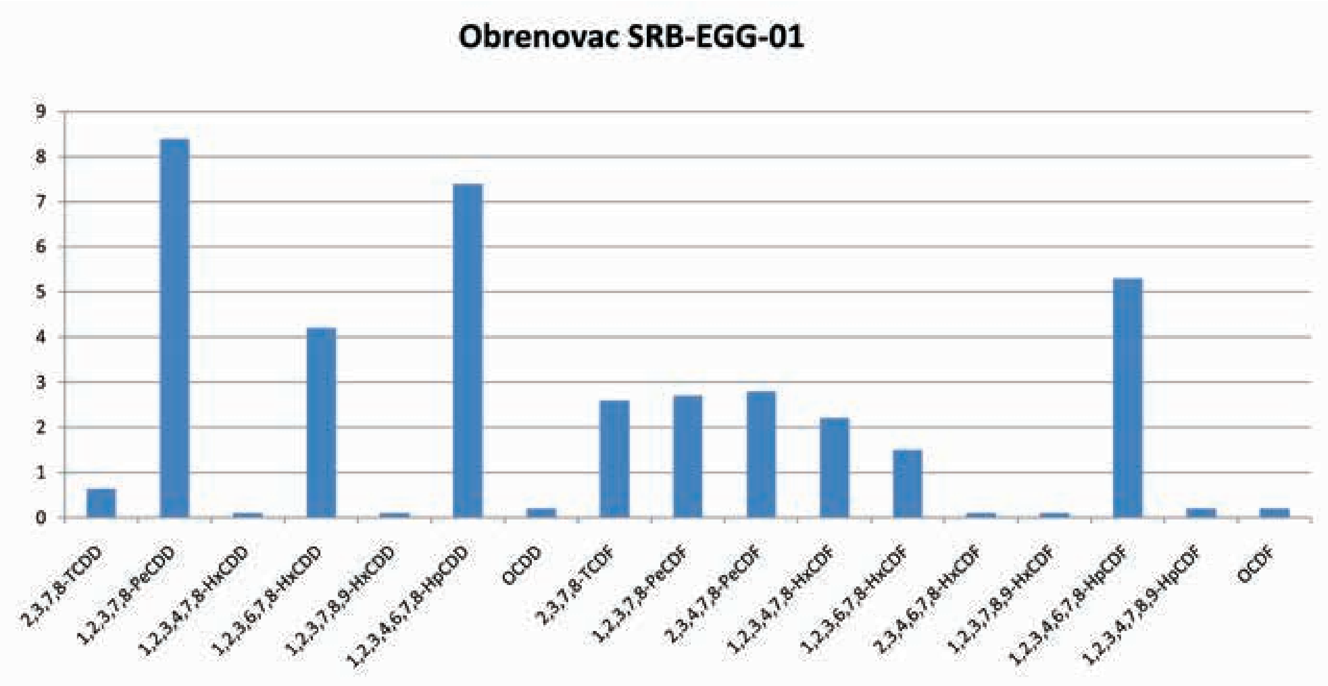
ArcelorMittal is one of the major polluters in Bosnia and Herzegovina. While the steelworks is located in the deep valley, villages occupy hills all around smoking chimneys. *Photo: Adéla Turková / Arnika*

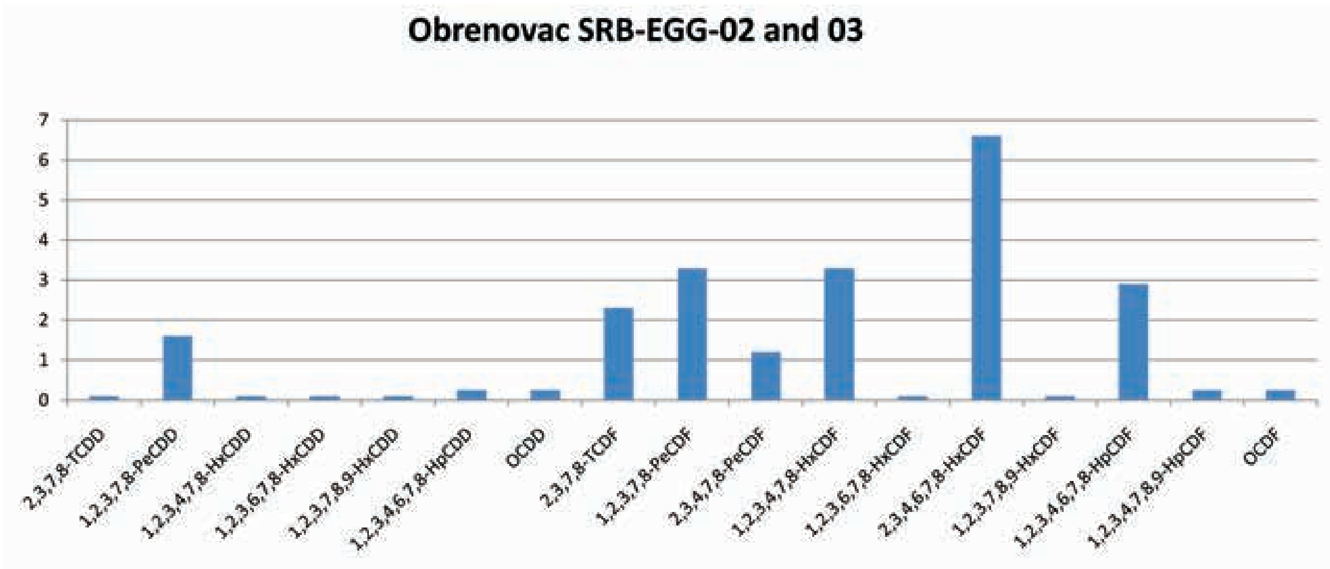
6.2.1. Zenica

The even balance between PCDD/Fs and PCBs congeners against total WHO-TEQ levels within samples from Zenica show that putative sources of pollution can vary in different parts of the valley/households. It is clear that there is not only one single source of contamination of free range chicken eggs in Zenica area when we compare dioxin congener patterns for these samples (see graphs in Pictures 9 – 13). Only three of them, ZEN 15/2 + 4, ZEN 15/3, and ZEN 15/5 are closer each to other and show similarities to some extent. OCDD dominates those patterns. This congener is dominant also in sample ZEN 15/1, however that sample has a very different share of PCDD and PCDF against total WHO-TEQ level in comparison with other samples from the Zenica area (see Figure 8). The prevalence of PCDFs shows some combustion sources of pollution by dioxins (Everaert and Baeyens 2002). They can vary from open burning of waste to metallurgy. Most likely there will be multiple sources of pollution by PCDD/Fs however the decreasing level of WHO-TEQ in free range chicken eggs in a side valley could mean that the steelworks are a significant source of dioxin contamination, although they are probably not the only source of dioxin pollution.

6.2.2. Obrenovac

Dioxin congener patterns for two samples from Obrenovac (see Figures 14 – 15) are specific and differ even more than the samples from Zenica. A higher level of total WHO-TEQ was observed in sample SRB-EGG-01, from the localition on south east of the Nikola Tesla power plant and its ash pond (see map at Figure 2). It is in the opposite direction of the prevailing winds. Also the prevalence of PCDD congeners over PCDF congeners in sample rather points to chemical production as a potential source of contamination of eggs (see graph on Figure 8) like for example in eggs from Mbeeubeus, Senegal (IPEN Dioxin PCBs and Waste Working Group, Pesticide Action Network (PAN) Africa et al. 2005) or Mossville, USA (IPEN Dioxin PCBs and Waste





Figures 14 – 15: Dioxin congener pattern for two pooled free range chicken eggs samples from the Obrenovac area, Serbia.

Working Group, Mossville for Environmental Action Now et al. 2005). We didn't find a specific dioxin pattern close to that one for sample from Grabovac (SRB-EGG-01) and we are not aware of any location with obsolete chemicals close to this place. The chicken owner doesn't buy additional food for the chickens and the chicken house is not painted. We can exclude these pathways as potential source of contamination of eggs. One of the options might be residual contamination in soil after floods brought from other distant place and/or residual contamination after the Kosovo conflict (UNEP and UNCHS 1999). The other sample from nearby (SRB-EGG-02 + 03) has a prevalence of PCDFs, which rather points to combustion sources of dioxin pollution (Everaert and Baeyens 2002) and also the level of PCDD/Fs in the egg sample was lower (see chapter 3.1).

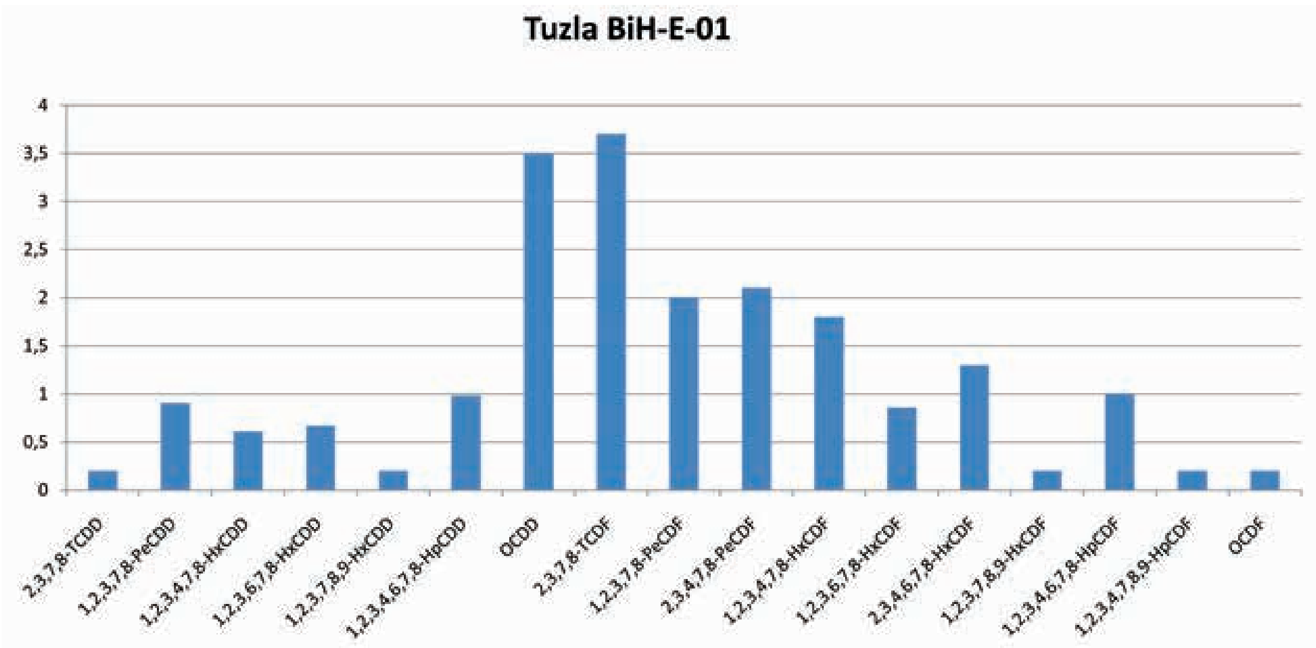


Figure 16: Dioxin congener pattern for free range chicken eggs sample from Tuzla.

6.2.3. Tuzla

The dioxin congener pattern in egg samples from Tuzla (see Figure 16) is similar to those from Balkhash – Rembaza (Petrlík, Kalmykov et al. 2015) (see Figures 17 – 18) to some extent, however they are not identical. The prevalence of PCDF congeners and OCDD points to large combustion sources of potential pollution by dioxins in these cases (Everaert and Baeyens 2002, Petrlík, Kalmykov et al. 2015), however most likely there are multiple sources of pollution by dioxins in Tuzla, including large combustion plants, and potential burning of wastes in households. Also the nearby chlorine chemical plant cannot be excluded.

6.3. Large coal combustion plants as potential sources of dioxin pollution

Both the metallurgic industry and coal fired power plants are signicant sources of dioxin, and other unintentionally produced POPs, and are listed as such also in Annex C to the Stockholm Convention [4] (Stockholm Convention 2010). They are also listed in the Dioxin Toolkit (UNEP and Stockholm Convention 2013) as such, and accompanied with specific emission factors for PCDD/Fs released to all environment compartments.

Fernández-Martínez et al. Fernández-Martínez, López-Vilariño et al. 2004) studied PCDD/Fs releases from power plants in Spain with the following result: *"A total of five plants were selected for the study located at different provinces in Spain. In all the cases, the results revealed very low levels, in the range of 0.41 pg I-TEQ m^{-3}. The profile indicated in the majority of the cases predominance of highly chlorinated congeners being OCDD the most important contributor. The findings were also used to estimate contribution of PCDDs/PCDFs emitted from coal-fired power plants in Spain. Individual plant results revealed values below 0.02 g I-TEQ per year and plant. Nevertheless, considering the total coal consumption in Spain in 1997, the values are comparable to those reported in other countries in the range of 0.6–0.7 g I-TEQ per year."* Data in Czech PRTR system reported for 2014 show values up to 0.55 g I-TEQ per year per one coal-fired power plant (IRZ 2015).

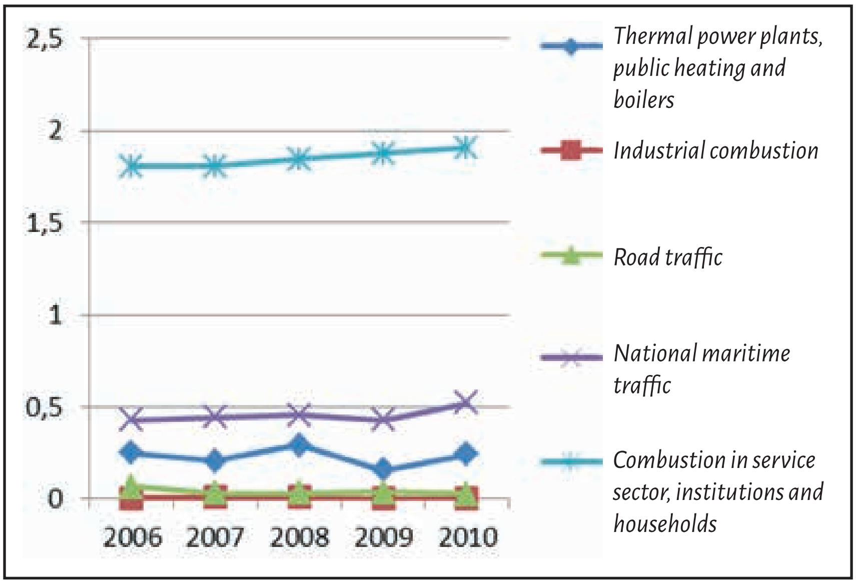


Figure 17: Graph showing development of PCDD/Fs emissions from combustion sources in Montenegro for the period 2006–2010, calculated by using CLRTAP emission factors. Source: (Ministry of Sustainable Development and Tourism 2013). Graph is indicated in g I-TEQ per year.

Another report from Poland focused on monitoring of dioxins in pine needles concluded that: *„The CDD/F homologue groups and congeners profiles of pine needles with highly dominant HpCDD/F and OCDD/F found in this survey suggest on lack of significant other than coal/lignite/wood combustiont sources of PCDD/Fs diffusion to ambient air in Poland."* (Bochentin, Hanari et al. 2007).

With regards to DL PCBs, one study done in the UK observed that: *„Levels of dioxin-like PCB reported in the literature and measured in UK plant tests showed that well-controlled modern combustion plants with comprehensive pollution controls gave low emissions, typically about 5-10% of the toxic equivalent of the emissions of polychlorinated dibenzodioxins and dibenzofurans at the same plants and below the widely used standard of 0.1 ng TEQ m^{-3}."* (Dyke, Foan et al. 2003).

Specific measurements of PCDD/Fs releases from coal burning power plants in any of the three studied Western Balkan states are virtually non-existent. The Serbian National Implementation Plan for the Stockholm Convention (Ministry of Environment and Spatial Planning of the Republic of Serbia 2010) doesn't mention coal-fired power plants in its dioxin releases inventory despite the fact that it is listed among significant sources of pollution by PCDD/Fs. Čudić, Kisić et al (2007) looked at levels of different contaminants in fly ash from the Obrenovac (Nikola Tesla) power plant and found content of PCDD/Fs less than 5 pg TEQ g^{-1} of dry mass. The analysis of the deposited fly ash done for this study didn't find level of PCDD/Fs above LOQ (LOQ = 0.9 pg TEQ g^{-1}).

4 Stockholm Convention Annex C, Part II and Part III

Dumpsite of the power plant in Plevlja, Montenegro, looks like moonscape and stretches for kilometers.

Photo: Jitka Straková, Arnika

The National Implementation Plan for Stockholm Convention for Montenegro calculates total emissions of PCDD/Fs from combustion sources as is shown on graph in Figure 19. This calculation is based on default emission factors developed within the framework of the Convention on Long Range Transboundary Air Pollution (CLRTAP).

In the light of the above mentioned reports we come to the conclusion that also in the cases of free range chicken eggs from both the Obrenovac and Tuzla broader areas which contained significant levels of PCDD/Fs and DL PCBs, the local coal fired power plants and their ash deposits should be considered as one of contributing sources to this contamination, however further investigation is needed to discover all major dioxin pollution sources in these areas.

Formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) can be accompanied by formation of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) or polyhalogenated dibenzo-p-dioxins and dibenzofurans, depending on the presence and balance of chlorine and bromine in the coal or the combustion process (Lemieux and Ryan 1998, Lemieux, Stewart et al. 2002). While chlorine or bromine content in the coal enhances formation of dioxins, sulfur inhibits it (Pandelova, Lenoir et al. 2005), so the content of different elements in coal is important information with regards to the evaluation of the potential of burning certain coal typed for leading to halogenated dioxin formation. We did not have the information about the full set of elements contained in coals burned in power plants in Pljevlja, Obrenovac and Tuzla.

A huge fly ash dumpsite in the vicinity of the Nikola Tesla thermal power plant in Obrenovac, Serbia. *Photo: Jitka Straková, Arnika*

"Resettle us or the power plant" – citizens of Tuzla, Bosnia and Herzegovina, demanded in 2013 in reaction to the catastrophic air pollution.

Photo: Centar za Ekologiju i Energiju Tuzla (www.ekologija.ba)

7. CONCLUSIONS AND RECOMMENDATIONS

POPs contamination in some free range chicken eggs from Bosnian and Serbian hot spots shows that there are significant sources of pollution by dioxins and dioxin like PCBs as well as significant levels of DDT in the environment at some places in Tuzla, Zenica, and the Obrenovac area in particular. High levels of PCDD/Fs and DL PCBs were found in free range chicken egg samples from the Obrenvac and Zenica areas. More than half of the samples exceeded the EU MAC for PCDD/Fs and DL PCBs in chicken eggs. More regular monitoring of dioxins and DL PCBs in food samples should be undertaken by the national authorities.

Identical Bosnian and EU MAC for PCDD/Fs and DL PCBs for chicken eggs used in this study were exceeded more often than those for OCPs. None of the egg samples exceeded MAC for 6 PCB congeners. High levels of dioxins and dioxin-like PCBs in free range chicken eggs from Tuzla confirm serious contamination of the city by these pollutants at least in some areas.

Apart the eggs collected in Pljevlja, where the value of PCDD/Fs and DL PCBs was at a concentration considered as background level in general (DiGangi and Petrlík 2005, Petrlík, Kalmykov et al. 2015), all other locations showed considerably high levels of dioxins and dioxin-like PCBs and their consumption should be minimized. Most critical is the situation in Grabovac and Zenica. Dioxin-like compounds in free range chicken eggs in the sample from Grabovac allow consumption of only three quarters of an egg per day for adults and one third of an egg per day for 10-year-old children.

It is clear that contamination of eggs in Zenica by PCDD/Fs and DL PCBs is higher in the valley where the steelworks are located while the side of the valley has somewhat lower levels of dioxin like compounds in free range chicken eggs; however there may be several sources of pollution by dioxins.

In the light of the studies mentioned in the discussion part of this study we come to the conclusion that also in the cases of free range chicken eggs from both the Obrenovac and Tuzla broader areas which contained significant levels of PCDD/Fs, local coal fired power plants and their ash deposits should be considered as one of the contributing sources to this contamination, however further investigation is needed to discover all major dioxin pollution sources in these areas.

Inhabitants at all selected hot spots should be warned before burning wastes in their household stoves and/or its open burning as it can be a serious source of pollution of the environment by POPs.

National plans for addressing sources PCDD/Fs and DL PCBs releases should be developed. The BAT/BEP Guidelines of the Stockholm Convention (Stockholm Convention on POPs 2008) should be applied when permitting potential sources of pollution by U-POPs such as metallurgical, chemical, and large coal combustion plants in all three countries. Special attention should be paid to waste management.

The National Implementation Plan for the Stockholm Convention in Bosnia and Herzegovina has not yet been submitted to the Stockholm Convention Secretariat (Stockholm Convention 2015). Preparing a NIP with the cooperation of all stakeholders, and civil society in particular, is a crucial step to addressing POPs contamination in the country.

People are usually not aware of possible contamination of their food. Chicken fancier from Pljevlja, Montenegro, is raising his chicken just behind the edge of the fly ash dumpsite.

Photo: Jitka Straková, Arnika

Because chicken are generally kept in the gardens or yards, their eggs can contaminate from the soil polluted by the industry. Tuzla, Bosnia and Hercegovina. *Photo: Jitka Straková, Arnika*

8. REFERENCES

Arkenbout, A. (2014). "Biomonitoring of Dioxins/dl-PCBs in the north of the Netherlands; eggs of backyard chickens, cow and goat milk and soil as indicators of pollution." Organohalog Compd 76: 1407-1410.

Arnika – Center for Citizens' Support. (2015, 06/2015). " Arcelor Mittal Steelworks Zenica " Retrieved 20-12-2015, 2015, from http://english.arnika.org/bosnia-and-herzegovina/hot-spots/arcelor-mittal-steelworks.

Aslan, S., M. Kemal Korucu, A. Karademir and E. Durmusoglu (2010). "Levels of PCDD/Fs in local and non-local food samples collected from a highly polluted area in Turkey." Chemosphere 80(10): 1213–1219.

Besselink H, J. A., Pijnappels M, Swinkels A, Brouwer B (2004). "Validation of extraction, clean-up and DR CALUX® bioanalysis. Part II: foodstuff." Organohalog Compd 66: 677-681.

Bochentin, I., N. Hanari, A. Orlikowska, B. Wyrzykowska, Y. Horii, N. Yamashita and J. Falandysz (2007). "Polychlorinated dibenzo-p-dioxins (PCDDs) and –furans (PCDFs) in pine needles of Poland." Journal of Environmental Science and Health, Part A 42(13): 1969-1978.

Bosnia and Herzegovina (2014). Pravilnik o maksimalno dozvoljenim količinama za određene kontaminante u hrani 68-14. Službeni Glasnik, Sarajevo: 39-49.

Čudić, V., D. Kisić, D. Stojiljković and A. Jović (2007). "Ash from Thermal Power Plants as Secondary Raw Material." Arhiv za higijenu rada i toksikologiju 58(2): 233-238.

DiGangi, J. and J. Petrlik (2005). The Egg Report – Contamination of chicken eggs from 17 countries by dioxins, PCBs and hexachlorobenzene.

Dvorská, A. (2015). Persistent Organic Pollutants in Ekibastuz, Blalkhash and Temirtau. Final report on the results of environmental sampling conducted in Kazakhstan in 2013 and 2014 as a part of the project Empowering the civil society in Kazakhstan in improvement of chemical safety . Toxic Hot Spots in Kazakhstan. Monitoring Reports. Prague-Karaganda, Arnika – Toxics and Waste Programme.

Dyke, P., C. Foan and H. Fiedler (2003). "PCB and PAH releases from power stations and waste incineration processes in the UK." Chemosphere 50(4): 469-480.

European Commission (2008). Commission Regulation (EC) No 149/2008 of 29 January 2008 amending Regulation (EC) No 396/2005 of the European Parliament and of the Council by establishing Annexes II, III and IV setting maximum residue levels for products covered by Annex I thereto. Text with EEA relevance European Commission. Official Journal of the European Communities: L 58, 51.53.2008, p. 2001–2398.

European Commission (2011). Commission Regulation (EU) No 1259/2011 of 2 December 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non dioxin-like PCBs in foodstuffs (Text with EEA relevance). European Commission. Official Journal of the European Union. EC 1881/2006: 18-23.

European Commission (2012). Commission Regulation (EU) No 252/2012 of 21 March 2012 laying down methods of sampling and analysis for the official control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs and repealing Regulation (EC) No 1883/2006 Text with EEA relevance European Commission. Official Journal of the European Communities: L 84, 23.83.2012, p. 2011–2022.

Everaert, K. and J. Baeyens (2002). "The formation and emission of dioxins in large scale thermal processes." Chemosphere 46(3): 439-448.

Gasparini M, B. B., Schinetti M, Di Millo S, Tilola M, Maccabiani G, Menotta S, Losio MN, Ferretti E (2011). "Application of DR-CALUX to Milk and Egg Samples: Comparison Between HRGC-HRMS and Screening Data." Organohalogen Compounds 73: 2120-2123.

Hoogenboom, R., M. ten Dam, M. van Bruggen, M. Zeilmaker, S. Jeurissen, W. Traag and S. van Leeeuwen (2014). Dioxines en PCB´s in eieren van particuliere kippenhouders. Wageningen, RIKILT (University & Research centre): 25.

IPEN Dioxin PCBs and Waste Working Group, Cavite Green Coalition, EcoWaste Coalition, GAIA, HCWH and Arnika Association (2005). Contamination of chicken eggs from Barangay Aguado in Philippines by dioxins, PCBs and hexachloroben-

zene. Keep the Promise, Eliminate POPs Reports. Manila, Prague, IPEN, Arnika Association, EcoWaste Coalition: 30.
IPEN Dioxin PCBs and Waste Working Group, Eco-SPES, Eco-Accord and Arnika Association (2005). Contamination of chicken eggs from the Dzerzhinsk region, Russia by dioxins, PCBs and hexachlorobenzene. Keep the Promise, Eliminate POPs Reports. Dzerzhinsk, Moscow, Prague, IPEN, Arnika Association, Spolocnost priatelov Zeme: 30.
IPEN Dioxin PCBs and Waste Working Group, Envilead and Arnika Association (2005). Contamination of chicken eggs near the Dandora dumpsite in Kenya by dioxins, PCBs and hexachlorobenzene. Keep the Promise, Eliminate POPs Reports. Nairobi, Prague, IPEN, Arnika Association, Envilead: 22.
IPEN Dioxin PCBs and Waste Working Group, Foundation for Realizaiton of Ideas and Arnika Association (2005). Contamination of chicken eggs near the Bolshoi Trostenec dumpsite in Belarus by dioxins, PCBs and hexachlorobenzene. Keep the Promise, Eliminate POPs Reports. Minsk, Prague, IPEN, Arnika Association, Foundation for Realization of Ideas: 26.
IPEN Dioxin PCBs and Waste Working Group, JA! Justiça Ambiental and Arnika Association (2005). Contamination of chicken eggs from Matola, Mozambique by dioxins, PCBs and hexachlorobenzene. Keep the Promise, Eliminate POPs Reports. Maputo, Prague, IPEN, Arnika Association, JA!: 29.
IPEN Dioxin PCBs and Waste Working Group, Mossville for Environmental Action Now, Advocates for Environmental Human Rights and Arnika Association (2005). Contamination of chicken eggs from Mossville, Louisiana, USA by dioxins, PCBs and hexachlorobenzene. Keep the Promise, Eliminate POPs Reports. Mossville, Prague, IPEN, Arnika Association, MEAN, AEHR: 30.
IPEN Dioxin PCBs and Waste Working Group, Periyar Malineekarana Virudha Samithi – PMVS, Thanal and Arnika Association (2005). Contamination of chicken eggs from Eloor in Kerala, India, by dioxins, PCBs and hexachlorobenzene. Keep the Promise, Eliminate POPs Reports. Kochi, Prague, IPEN, Arnika Association, Thanal: 29.
IPEN Dioxin PCBs and Waste Working Group, Pesticide Action Network (PAN) Africa and Arnika Association (2005). Contamination of chicken eggs near the Mbeubeuss dumpsite in a suburb of Dakar, Senegal by dioxins, PCBs and hexachlorobenzene. Keep the Promise, Eliminate POPs Reports. Dakar, Prague, IPEN, Arnika Association, PAN Africa: 29.
IRZ. (2015, 30-09-2015). "Integrated Pollution Register Data about Releases and Transfers of Pollutants from the Enterprises Based in the Czech Republic for Period 2004 – 2014." from http://www.irz.cz.
Lemieux, P. and J. Ryan (1998). "Enhanced formation of dioxins and furans from combustion devices by addition of trace quantities of bromine." Waste Management 18(6-8): 361-370.
Lemieux, P. M., E. S. Stewart and J. V. Ryan (2002). "Pilot-scale studies on the effect of bromine addition on the emissions of chlorinated organic combustion by-products." Waste Management 22(4): 381-389.
Ministry of Environment and Spatial Planning of the Republic of Serbia (2010). National Implementation Plan for the Stockholm Convention. Belgrade: 295.
Ministry of Sustainable Development and Tourism (2013). National Implementation Plan for the Stockholm Convention 2014-2021. Podgorica: 70.
Pandelova, M., D. Lenoir, A. Kettrup and K. Schramm (2005). "Primary measures for reduction of PCDD/F in Co-combustion of lignite coal and waste: effect of various inhibitors." Environ Sci Technol 39(9): 3345-3350.
Petrlík, J., D. Kalmykov and P. Behnisch (2015). Persistent Organic Pollutants (POPs) in free range chicken eggs from hot spots in Central Kazakhstan. Final report on the results of environmental sampling conducted in Kazakhstan in 2013 and 2014 as a part of the project Empowering the civil society in Kazakhstan in improvement of chemical safety . Toxic Hot Spots in Kazakhstan. Monitoring Reports. Prague-Karaganda, Arnika – Toxics and Waste Programme.
Petrović, V., Ć. Jovanović, Marijana, S. Janković, L. Turubatović and B. Antonijević (2008). Average intake of dioxins and polychlorinated biphenyls among adult population in Serbia. 7th XenobioticMetabolism and Toxicity Workshop of Balkan Countries. Novi Sad, Serbia, 3-6 June 2008.

Pirard, C., J. Focant, A. Massart and E. De Pauw (2004). "Assessment of the impact of an old MSWI. Part 1: Level of PCDD/Fs and PCBs in surrounding soils and eggs." Organohalogen Compounds 66: 2085-2090.

Piskorska-Pliszczynska, J., S. Mikolajczyk, M. Warenik-Bany, S. Maszewski and P. Strucinski (2014). "Soil as a source of dioxin contamination in eggs from free-range hens on a Polish farm." Science of The Total Environment 466–467(0): 447-454.

Pless-Mulloli, T., B. Schilling, O. Paepke, N. Griffiths and R. Edwards (2001). "Transfer of PCDD/F and heavy metals from incinerator ash on footpaths in allotments into soil and eggs." Organohalogen Compounds 51: 48-52.

Sam-Cwan, K., Jin-Gyun, N., Sung-Hun, C., Jung-Hee, L., Yeon-Ho, K., Seung-Ryu, H., Chang-Han, J., Dong-Ho, M., Jae-Cheon, Y., Sang-Won, L., Sang-Eun, J. (2003). "PCDDs/PCDFs Emission from Nonferrous Metal Industry." Organohalog Compd 63: 81-85.

Shelepchikov, A., B. Revich, D. Feshin, S. Brodsky, V. Zilnikov and O. Sergeyev (2006). "Contamination of chicken eggs from different Russian regions by PCBs and chlorinated pesticides." Organohalogen Compounds 68: 1959-1962.

Stockholm Convention (2010). Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009. Text and Annexes. Geneva: 64.

Stockholm Convention. (2015). "NIPs Transmission." Retrieved 20-12-2015, 2015, from http://chm.pops.int/Implementation/NIPs/NIPTransmission/tabid/253/Default.aspx.

Stockholm Convention on POPs (2008). Guidelines on Best Available Techniques and Provisional Guidance on Best Environmental Practices Relevant to Article 5 and Annex C of the Stockholm Convention on Persistent Organic Pollutants. Geneva, Secretariat of the Stockholm Convention on POPs.

Šír, M. (2015). Impact of Balkan Power Plants on Inhabitants and the Environment Prague, Arnika – Toxics and Waste Programme: 45.

Šír, M. (2015). Results of environmental sampling in Kazakhstan: heavy metals in sediments and soils. (Final report). Toxic Hot Spots in Kazakhstan. Monitoring Reports. Prague-Karaganda, Arnika – Toxics and Waste Programme.

UNEP and Stockholm Convention (2013). Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional POPs under Article 5 of the Stockholm Convention. Geneva, United Nations Environment Programme & Stockholm Convention Secretariat: 445.

UNEP and UNCHS (1999). The Kosovo conflisct consequences for the environment and human settlements: 99.

Van den Berg, M., L. S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker and R. E. Peterson (2006). "The 2005 World Health Organization reevaluation of human and Mammalian toxic equivalency factors for dioxins and dioxin-like compounds." Toxicol Sci 93(2): 223-241.

Van Eijkeren, J., M. Zeilmaker, C. Kan, W. Traag and L. Hoogenboom (2006). "A toxicokinetic model for the carry-over of dioxins and PCBs from feed and soil to eggs." Food Additives & Contaminants: Part A 23(5): 509 – 517.

van Leeuwen, F. X. R., M. Feeley, D. Schrenk, J. Larsen, W. Farland and M. Younes (2000). "Dioxins: WHO's tolerable daily intake (TDI) revisited." Chemosphere 40(9-11): 1095-1101.

van Overmeire, I., J. van Loco, P. Roos, S. Carbonnelle and L. Goeyens (2004). "Interpretation of CALUX results in view of the EU maximal TEQ level in milk." Talanta 63: 1241-1247.

Wikipedia. (2015, 21-12-2015). "Pljevlja." Retrieved 21-12-2015, 2015, from https://en.wikipedia.org/wiki/Pljevlja.

Wikipedia. (2015a, 10-11-2015). "Obrenovac." Retrieved 21-12-2015, 2015, from https://en.wikipedia.org/wiki/Obrenovac.

Winkler, J. (2015). "High levels of dioxin-like PCBs found in organic-farmed eggs caused by coating materials of asbestos-cement fiber plates: A case study." Environment International 80: 72-78.

Yoon-Seok, C., Byeong-Woon, Y., Young-Hoon, M., Min-Kwan, K., Jong-Dai, K. (2003). "Inventory Study of PCDD/Fs for Metal Industries in South Korea." Organohalog Compd 63: 94-97.

ISBN: 978-80-87651-17-9

http://english.arnika.org

a toxics-free future