High levels of PCDD/Fs around sites with waste containing POPs demonstrate the need to review current standards

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Introduction: The case of use of mixed fly ash and bottom ash from the Byker waste incinerator (WI) for paving footpaths between allotments in Newcastle, UK between 1994 and 1999 led to serious contamination of free range poultry by PCDD/Fs [1,2]. It also raised awareness about use of WI residues contaminated by PCDD/Fs. Similar cases of "Kieselrot" in Germany led to the establishment of the first standards for PCDD/Fs limits in soil [3]. Both cases demonstrate impacts of uncontrolled use of waste containing significant levels of PCDD/Fs in scenarios with sensitive uses. It is now broadly assumed that tighter regulatory controls over wastes since that time would prevent any repeat of such incidents. However, recently obtained information about transfers of WI residues challenges this assumption. So, we asked the question, are current legislative and regulatory measures to control movement of PCDD/Fs via waste transfers effective in preventing contamination incidents?

Information about transfers of WI residues across the Czech Republic was collected by Arnika in 2004. This data indicated two major facilities were mixing WI fly ash with other waste which was then used as a remediation material at abandoned mining and ore processing sites, either above or below ground. The mixture was either disposed of at the remediation site (site I) or transported to other locations (site II). PCDD/Fs and other toxic chemicals contained in the WI fly ash can leach constantly from the residue contaminating the environment around the reprocessing and disposal sites. In Thailand and China we also observed that WI fly ash was stored next to municipal waste incineration (MWI) plants for long periods and that wind and water mobilised small ash particles contaminating the local environment.

Materials and Methods: Sampling of soil, dust, sediments, fish, shellfish, crabs and/or free-range chicken eggs at and around selected sites where WI fly ash was handled and/or stored for extended periods was conducted in order to assess contamination by PCDD/Fs and dioxin-like PCBs (dl-PCBs) using bioassay or instrumental analysis.

Bioassay: All samples collected between 2005 and 2012 were analyzed at BDS for dioxin-like (dl) activity according to the standard procedures of the DR CALUX® [4], which has been described in detail elsewhere [5]. 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 (37ºC, 5% CO2, 100% humidity). Cells were exposed in triplicate on 96-well microtiterplates containing the standard 2,3,7,8-TCDD calibration range, a DMSO blank. Following a 24-hour incubation period, cells were lysed. A luciferine containing solution was added and the luminescence was measured using a luminometer (Berthold Centro XS3). Results are expressed in bioanalytical toxic equivalents (BEQs).

Instrumental analysis: All samples from site I collected in year 2004 and from all sites in this study collected after the year 2012 were analyzed by GC/HRMS in ISO 17025 accredited laboratories with a resolution > 10,000 using ^{13}C isotope labelled standards. PCDD/F and dl-PCB analysis. PCDD/F and dl-PCB analysis followed the European Union's methods of analysis for the control of levels of PCDD/Fs and dl-PCBs for levels in certain foodstuffs in Commission Regulation (EC) No 252/2012 [6].

Results and Discussion: UK, Bishop's Cleeve: There is a monofill hazardous waste landfill at Bishop's Cleeve where WI air pollution control (APC) ashes are 'treated' on site by mixing with leachate and disposed of to open cells. Off-site exposure may occur through inhalation of airborne APC residues or through indirect exposure at some point distant from the site of disposal. Three pooled samples of free range chicken and duck eggs were taken in 2010 and 2011 in the Wingmoor Farm area. In two of them significantly high levels of 21 and 55 BEQs respectively were measured, exceeding the EU standard for PCDD/Fs + dl-PCBs by four- and eleven-times respectively. The third sample was below the EU

standard with a level of 1.8 BEQs. These results have proven contamination of the area surrounding the facility treating WI APC residues from across the UK. The levels of PCDD/Fs in airborne dust measured between 2 – 2,335 pg TEQ /g dm at Wingmoor Farm, Bishop's Cleeve in October – November 2010, based on Environment Agency Analytical Report [7].

Czech Republic, waste reprocessing and products from mixed waste disposal site I: Sediment samples were taken around the old underground mining area where the facility for mixing of wastes is co-located. Samples were taken upstream and downstream from the area in 2004. PCDD/Fs in the upstream sample measured 2.8 pg I-TEQ/g dm while a downstream sample and a mine outflow sample measured 10 and 4.2 pg I-TEQ/g dm PCDD/Fs respectively. Bioassay screening for dl-toxicity conducted for sediment samples from the tailing pond and outlet from the remediated underground mine in 2011 have shown levels of 21 and 29 BEQs respectively. For comparison: In sediment from an industrial area of the Czech Republic, the level of 5.6 BEQs was measured. The results of analyzed samples from site I show increased dioxin in the local environment due to waste processing. PCDD/Fs were measured in the waste mixture from the facility at a level of 391 pg I-TEQ/g dm [8].

Czech Republic, waste reprocessing site II: At this location there is a reprocessing plant managing different solid wastes and sludge, including fly ash, from several waste incinerators. Sediment samples were taken in adjacent to the facility repeatedly in 2015 and 2016. Results of their analyses for PCDD/Fs + dl-PCBs are summarized in Table 1. Sediment results demonstrate influence of the reprocessing of wastes containing high volumes of PCDD/Fs on the surrounding environment. The samples closest to the site have the highest contamination while levels in sediments of the creek downstream are more than 10-times higher than those observed at clean reference site in the Czech Republic.

Table 1. PCDD/Fs and dl-PCBs measured in sediments in surroundings of site II in pg WHO-TEQ/g dm*

Sampling site	Pond and wetland influenced by plant	Downstreem creek	Creek (no direct connection with retention pond)	Background levels (Czech Rep.)[9]
PCDD/Fs	259 - 289	19 - 48	4 - 13	1.4
PCDD/Fs + dl-PCBs	279 - 301	33 - 61	5 - 17	1.6

Notes: *If not noted otherwise, levels of bothPCDD/Fs and dl-PCBs in this article are expressed in WHO_{2005} TEQ shorten to TEQ

Thailand, Phuket waste incinerator: Fly ash from t WHO-TEQhis municipal WI was stored in the area between the building and an adjacent mangrove forest zone for a long time before 2011. The site was investigated by the Swedish EPA[10] and Arnika/EARTH team [11]. PCDD/Fs + dl-PCBs in fly ash were measured at levels of 3,300 – 8,300 pg TEQ/g dm. The level of PCDD/Fs + dl-PCBs observed in sediment in the lake with ash deposits was 2,800 pg TEQ/g dm. Bioassay analysis of sediment from mangrove forest has shown a level of 24 pg BEQs/g dm, which is six times higher than maximum concentration in sediments from Tha Tum industrial area. In Tha Tum levels of 0.27 – 3.8 pg TEQ/g dm were found recently [12].

The fish samples from the incinerator area contained 1.2 to 5.6 pg TEQ/g fat [10], while the bioassay analysis of fish from mangrove forest area resulted in 42.5 pg BEQ/g fat. Mud crab, oyster and shellfish from the mangrove forest were also analyzed by bioassay and levels of 43.6, 34.6 respective 3.0 pg BEQ/g fat were observed. PCDD/Fs + dl-PCBs in fish from the Chanthaburi locality were < LOD - 0.01 pg TEQ/g fat. Eggs of passerine birds collected near the waste incinerator site measured 6.1 pg BEQ/g fat, exceeding the EU 5 pg TEQ/g fat limit value for eggs, and reference level of 0.08 pg TEQ/g fat[13] for Thai eggs respectively.

Levels of PCDD/Fs + dl-PCBs observed in biota and sediments around fly ash storage in Phuket show significantly higher levels than those observed at background or even industrial sites in Thailand.

China, municipal waste incinerator in Wuhan: Eggs were sampled from two private chicken farms in the vicinity of an incinerator at Guoding Shan in Wuhan. The first (site A) was 0.3 km southwest of the incinerator and the second (site B) was 1 km northwest of the incinerator. The bioassay test in eggs from site B was 8.8 pg BEQ/g fat. Instrumental analysis of the same sample showed levels of 13.3 pg TEQ/g fat for the sum of PCDD/F and dl-PCB with major contribution coming from PCDD/F with 8.6 pg TEQ/g fat in eggs from site B. The BEQ in eggs from site A was 35 pg BEQ/g fat and instrumental analysis reported 16 pg TEQ/g fat for the sum of PCDD/F and dl-PCB with major contributions coming from PCDD/F with 12.2 pg TEQ/g fat. The PBDD/Fs were also found in these eggs at high level of 29 pg TEQ/g fat. Fly ash stored for a long time in the area of MWI[14] could significantly contribute to the contamination of eggs by both chlorinated as well brominated dioxins. A level of 779 pg TEQ/g dm. PCDD/Fs was measured in a sample of fly ash from Wuhan MWI in 2015.

Information from studied sites is important for establishing potential exposure to PCDD/Fs and dl-PCBs from wastes containing these chemicals at certain levels and for a definition of effective limits for their content in wastes. Limiting POPs in wastes and their subsequent management are key objectives of both the Stockholm and Basel Conventions. Potential exposure routes of *wastes contaminated by POPs (PCDD/Fs, DL PCB) - dust/soil/sediment - biota (poultry, birds, fish)* is clearly demonstrated in the cases described here. We collected some similar case studies described in literature and summarized them in Table 2 in addition to those analysed and described in this study.

Table 2. Summary of levels of PCDD/Fs and/or BEQs observed at different sites influenced by fly ash and other waste contaminated by PCDD/Fs described in this study or in literature

	Year(s) of sampling	Fly ashes (waste)	Soil/sediment direct impact	Soil/sed. reference	Eggs	Eggs – reference[1
Units		pg TEQ/g dm			pg TEQ/g fat	
Thailand (WI Phuket)	2010 - 2011	3,200 - 8,000	2,700**	na	6.1*	0.08[13
China (WI Wuhan)	2014 - 2015	779	na	na	12.2	0.2 [15
UK (Bishops Cleeve)	2010 - 2011	2,500	6.5 – 11*	0.05 - 1.2	1.8; 21; 55*	0.2[1
UK (Newcastle) [1,2	2000	20 - 9,500	7 – 292	na	0.4 – 56	0.2[1
Peru (Zapallal) [10	2010	50 - 12,000	5 – 11	0.05 - 1.2	3.4 - 4.4	0.12[10
Taiwan (eggs event) [16	2005	Na	na	na	32.6	0.274[17
Poland (henhouse) [18	2015	3,922	16 – 47	0.1 - 0.8	12.5 - 29.3	0.44[18

Notes: *BEQs (total dioxin-like toxicity), ** sediment, na – not available

In several demonstrated cases processing/disposal of waste containing PCDD/Fs between 20 and 12,000 pg TEQ/g led to contamination of the food chain (eggs or poultry meat) up to levels >20-times higher than the suggested EU limit for PCDD/Fs in food (2.5 pg TEQ/g fat) [19. Levels from reference sites (background levels) in free range chicken eggs was exceeded up to 280-times.

A Swedish EPA study demonstrated that PCDD/Fs levels of 30 pg TEQ/g fat in an egg will be exceeded at soil concentrations of approximately 4 to 75 ng TEQ/kg dm. Therefore, the European maximum level of 2.5 pg TEQ/g PCDD/F in fat[19 can be exceeded at levels that are ten times lower (i.e., 0.4 and 7 ng TEQ/kg dm). Based on the upper level of the range given in the Swedish EPA study and examples of a scenario with contaminated wood waste [10, it can be concluded that application of fly ash and other wastes containing levels of dioxin over 0.05 ppb in land based application can lead to unacceptable contamination of the local food chain. In some other studies, even lower levels of dioxins in soils led to contamination of free range chicken eggs exceeding the EU standard for food [20,21. Free range eggs can be impacted at critical levels, and in some cases revealing a more than 20-fold exceedance of current EU limits. Locally produced food is of great importance in developing countries and rural locations in developed countries therefore this exposure scenario is of particular concern. In addition, last major dioxin contamination incident in Germany was caused by uncontrolled use of waste from biodiesel production containing 123 pg TEQ/g PCDD/Fs[22 for feed production which clearly shows the existing legislative limits for PCDD/Fs content in wastes are not strict enough.

Scope of the problem: The case studies described above demonstrate the situation at several sites in different countries, however from the global (Stockholm Convention) point of view it is important to examine how the major portion of total PCDD/Fs releases/transfers can be addressed by improved management of WI residues.

We were able to estimate the total amount of PCDD/Fs in the wastes accepted for a facility at one of the sites in the Czech Republic as we have statistics for this site for 2014 - 2015. For the period of these two years, the estimated amounts of PCDD/F inputs into the facility were approximately 33 g TEQ (in waste incineration fly ash and dust from the metallurgical industry). A values of 74 and 51 g TEQ were reported into Czech PRTR as releases (transfers) to waste transfers from which approximately 25 g TEQ/year was in WI residues [23]. This comparison demonstrates reliability of data in Czech PRTR system which requires companies to report chemically specific details about waste transfers.

Total global dioxin releases were recently calculated at level of 100 kg TEQ/year [24]. This estimate incorporates an earlier calculation for 86 countries[25] based on their inventories. The inventories were demonstrated to be incomplete due to missing data about their releases of PCDD/Fs into wastes including countries with large capacities of WI (e.g., China, Germany, Japan). Estimation of annual PCDD/Fs releases into WI residues is in the range of 7 – 10 kg TEQ/year [26]. We can see that addressing the PCDD/Fs in WI residues, APC residues, in particular, helps to address a significant flow of PCDD/Fs globally based on these estimations.

Conclusions and Recommendations: All described cases demonstrate that waste containing PCDD/Fs below the currently established provisional POPs limit (LPCL) of 15 ppb (15,000 pg TEQ/g) can lead to significant contamination around sites where the waste is reprocessed or disposed of in a way that doesn't destroy or irreversibly transforms PCDD/Fs or dl-PCBs contained in the waste as required by Article 6 of the Stockholm Convention. Even waste above ~ 0.02 / 0.05 ppb can contaminate soil if used on surface without any treatment. Based on the findings of this and other studies, we recommend the establishment of a new limit (LPCL) for PCDD/Fs in wastes at 1 ppb, and to limit use of wastes containing PCDD/Fs + dl-PCBs above 0.05 ppb on surface soils without pre-treatment.

During the collection of data for calculation of total volume of PCDD/Fs contained in concerned wastes (fly ash and APC residues from WI in particular) we found that this information is not available in many countries or monitored in any way. We also noted that chemically specific reporting about POPs (PCDD/Fs in our case) in wastes into PRTR is a highly appropriate tool to fill this gap. The best solution is to prevent formation of PCDD/Fs in wastes is by substitution of materials and changing technological processes and waste management practices by promoting technologies that do not create U-POPs as suggested in Article 5 of and Annex C to the Stockholm Convention.

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