



TOXIC ASH POISONS OUR FOOD CHAIN



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IPEN

April 2017





a toxics-free future

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IPEN in cooperation with Arnika Association (Czech Republic) and National Toxics Network (Australia).

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Established in 1998, IPEN is currently comprised of over 500 Participating Organizations in 116 countries, primarily developing and transition countries. IPEN brings together leading environmental and public health groups around the world to establish and implement safe chemicals policies and practices that protect human health and the environment. IPEN's mission is a toxics-free future for all.

ACKNOWLEDGMENTS

IPEN, Arnika and NTN gratefully acknowledge the financial support provided by the Government of Sweden, Global Greengrants Fund, and other donors, which make the production of this document possible. The views herein shall not necessarily be taken to reflect the official opinion of any of the institutions providing financial support.

We also thank to all participating organizations of IPEN which helped to collect information and/or conduct sampling at selected locations, and to Center of Environmental Solutions – CES (Belarus), Nature University (China), EARTH (Thailand), Taiwan Watch Institute (Taiwan), and Public Interest Consultants (UK) in particular.

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1. EXECUTIVE SUMMARY

This report was prepared by IPEN to address a major source of POPs contamination of the environment that is often overlooked, underestimated or incorrectly classified in risk assessments, exposure scenarios and regulatory controls on waste. Ash and other residues from waste incineration contain dioxins, furans (PCDD/Fs) and a range of other highly toxic POPs at levels which are a threat to human health and the environment. Current management practices and regulatory threshold levels for POPs that contaminate incinerator residues are not preventing releases of POPs into agricultural settings, the food chain and the broader environment.

Waste incineration is often proposed by industries as a “solution” to waste management problems and a superior alternative to landfill. However, burning waste creates large amounts of toxic ash and other residues (approximately 30% by weight of the original waste volume) which are either dumped in landfill, on open ground and in some countries deep in underground voids. In some jurisdictions ash is incorrectly thought to be benign resulting in its use in agricultural settings and construction leading to significant POPs exposure potential. Municipal waste incineration destroys valuable resources and converts non-toxic material into toxic ash. Hazardous and medical waste incineration generates significant quantities of toxic ash when there are a range of non-incineration alternatives available to treat these wastes without creating POPs contaminated residues.

However, there are currently hundreds of waste incinerators around the world generating millions of tons of toxic ash every year, releasing POPs to the environment either from waste disposal practices or under the guise of valorized “products” such as construction materials, agricultural soil amendment and road base. This report examines POPs pollution that is occurring as a result of these practices, citing relevant scientific literature, case studies and the inadequacies of the regulatory regime to address the problem. A key focus of this report is the need for global adoption of strict “Low POPs Content Levels” which define POPs wastes and require them to be treated as hazardous waste where its POPs content must be destroyed. This report shows how the current weak Low POPs Content Level for dioxin is resulting in poor management of waste incineration ash, allowing transboundary movement of wastes and contamination of food products such as eggs which exceed EU standards and tolerable daily intakes for humans.

This report provides extensive data on the scale of the toxic ash problem, POPs in waste incinerator ash, modes of release to the environment, inadequate management practices, exposure scenarios for human receptors and their consequences. The Stockholm Convention on POPs requires that parties take measures to reduce and eliminate POPs from the environment yet waste incineration continues to undermine the Convention by creating millions of tons of POPs contaminated residues every year. Article 10 of the Stockholm Convention requires that the public be given full access to information on POPs sources and how they are impacted by them. Until now, information on the growing POPs contamination events caused incinerator residues has not been easily accessible to the public.

This report publicly exposes the reality of incineration ash contamination and raises strong arguments for the phase out of waste incineration in favour of non-combustion techniques for waste treatment and sustainable techniques for waste management. It also makes clear the need for the establishment, at global environmental conventions, of strict Low POPs Content Levels to prevent transboundary movement of toxic wastes to low income countries and environmentally harmful distribution of waste incineration residues in all countries.

1.1 KEY FINDINGS OF THE REPORT

- The amount of **dioxins released** (contained) **in waste incineration fly ash is highly underestimated** (its content is 3 – 10-times as much as previously estimated) – the scope of the problem is bigger than previously thought.
- **Fly ash is reused for different purposes on a broad scale**, and is getting **out of control**. This is especially due to its high dioxin content and the manner in which it is disposed of, which does not lead to destruction or irreversible transformation of POPs content in ash – **POPs recycling is occurring on a large scale through ash distribution**.
- Among the most critical and difficult to control uses is as a **food additive for poultry** (see the Toxic Egg Scandal in Taiwan; chapter 10.1.4), **fertilizer** or as an **amendment to soil** for agricultural use, use for **roads and as pathway pavement in areas with locally grown food** (Newcastle case).
- Efforts to prevent the formation of dioxin contained in fly ash is minimal – it is not easy material to handle and **it would be easier to manage less chemically difficult wastes than fly ash** instead of trying to find technically complicated solutions to fix heavy metals and

other forms of stabilization. Why do we need to destroy dioxins when we don't have to create them?

- **Waste incineration fly ash and other industrial wastes containing dioxins are the subject of waste traffic** – its **transboundary movement** makes control of dioxin releases even harder.
- By using fly ash for backfilling, embankment and remediation of contaminated sites, **new contaminated sites are being created** (to clean sites contaminated with dioxin containing fly ash may cost in excess of 80 million USD).
- Applying **fly ash** and other wastes **containing levels of dioxin over 0.05 ppb in agriculture** (and other land based application) **can lead to contamination of the local food chain**, and free range poultry eggs in particular at **critical levels over currently used safety limits** (2.5 pg WHO-TEQ g⁻¹ fat) **by several fold**, with some cases revealing a 10 fold exceedance. Locally produced food is of great importance in developing countries and rural locations in developed countries in particular.
- **Fly ash leachate is mostly tested for heavy metals under “model” conditions** that do not represent reality. **Real waste and real condition scenarios are rarely used.** Testing for leaching of dioxins in specific conditions (e.g. in radioactive water of remediated contaminated sites or in salty brackish waters) is either not happening or is very rare.
- Even the most strict proposal by consultants of the EU for a Low POPs Content Level (1 ppb) is underestimating the true risk as it does not include DL PCBs in the modelling and ignores the fact that lower levels of dioxin in soil (4 – 75 pg TEQ g⁻¹) can lead to serious exceedances of the EU standard for eggs.
- The range of observed dioxin levels in fly ash is from below the level of quantification (virtual zero) to 96,000 ppb.
- **Fly ash contains a wide range of other POPs** including undestroyed POPs treated by waste incinerators.
- There is wide range of **alternative waste management practices and waste disposal (use) technologies** and techniques that **can prevent formation of dioxin** as occurs in waste incineration.
- There are a **range of alternative technologies** which are **capable for effective destruction of PCDD/Fs** and other POPs in waste incineration fly ash however they are not used.
- **Far more stringent levels for PCDD/Fs control in waste and/or contaminated soil exist** which are below the current provisional LPCL value of 15 ppb, e.g. **1 ppb or 3 ppb**. Research on dioxin leach-

ate seems to be more advanced in countries with these limits for PCDD/Fs in wastes and/or contaminated soils.

1.2 RECOMMENDATIONS

Based on these findings and in agreement with some other studies like for example Paustenbach, Fehling et al. (2006) or Swedish EPA (2011) we suggest to Parties to the Stockholm Convention and Parties to the Basel Convention to adopt the more stringent value for Low POP Content Level for dioxin of 1 ppb¹. An additional suggestion is to ban the use/application of wastes to soil or on terrain surface (without stabilization) with a level of PCDD/Fs and DL PCBs above 0.05 and/or at least 0.1 ppb. We also suggest to incorporate DL PCBs into the evaluation of LPCL, so the level of 1 ppb will be applicable for both PCDD/Fs and DL PCBs as a total expressed in WHO-TEQ.

We also encourage decision makers and bodies of both Conventions to promote and use practical technologies for real destruction of dioxins in waste incineration fly ash above 1 ppb with DE above 99.999% measured as total TEQ level. BAT and BEP Guidelines for the use of these technologies should be developed and a list of ESM technologies in Basel Technical Guidelines on POPs Wastes should be enlarged by listing technologies that are clearly available but have not yet been included.

We also recommend an inventory of PCDD/Fs and other U-POPs in WI residues should be conducted more precisely than is currently the case.

1 "Various possible soil guidelines based on cancer and non-cancer risks are presented and discussed. In the main, the current toxicology, epidemiology, and exposure assessment data indicate that the historical 1 ppb TEQ soil guidance value remains a reasonable screening value for most residential sites. This analysis provides risk managers with a thorough and transparent methodology, as well as a comprehensive information base, for making informed decisions about selecting soil cleanup values for PCDD/Fs" Paustenbach, D., K. Fehling, P. Scott, M. Harris and B. Kerger (2006). *Identifying soil cleanup criteria for dioxins in urban residential soils: how have 20 years of research and risk assessment experience affected the analysis?* J Toxicol Environ Health B Crit Rev 9(2): 87-145.

2. PREFACE

This year, for the first time, The Stockholm Convention will evaluate its effectiveness having now been in force for a decade. On this occasion, a larger number of experts focused on partial evaluation of different aspects of the convention. While some seem to be successes such as the fact that the Convention now covers a broader scale of Persistent Organic Pollutants (POPs) than it did in its initial phase, there are also some concerns that Convention did not meet expectations and does not prevent POPs pollution of different parts and spheres of planet Earth. One group of scientists looking mainly at POPs levels in ambient air concluded that “... *a decade of air monitoring data has not been sufficient for detecting general and statistically significant effects of the Stockholm Convention. Based on these lessons, we present recommendations for the future operation of existing monitoring programs and advocate for a stricter enforcement of the provisions of the Stockholm Convention, in the current absence of proof for its effectiveness*” (Wöhrnschimmel, Scheringer et al. 2016). This statement applies to dioxins in particular.

There are areas where we have even less information and where we can say that this gap was created by the poor establishment of a starting point by the Convention itself. The large gap is the issue of generation of unintentional POPs and their releases in wastes. Although one can suggest that waste is not released directly into the environment and therefore it is incorrect to use term “release” in connection with waste, the argument is more complex. This might be true for a part of the waste however a bigger portion of wastes move without significant controls and are a source of various toxic chemicals including dioxins. By the “poor establishment of starting point” by the Convention we mean the definition of the Low POPs Content Levels which are crucial for waste management of POPs wastes in many ways. This study shines some light on this rather dark side of the Stockholm Convention.

3. WASTE INCINERATION ASH POISONS THE FOOD CHAIN

The objective of the Stockholm Convention on Persistent Organic Pollutants (POPs) is: “*to protect human health and the environment from persistent organic pollutants*” (Stockholm Convention 2010). One of the advantages of this Convention in comparison with similar Multilateral Environmental Agreements (MEAs) is that it takes into account releases of chemicals into all environmental media (compartments) including water and land as well as wastes. These pathways of potential pollution of the environment are as important as air emissions. Let’s look at one type of waste and its impact on one of these compartments in practice with a focus on two groups of chemicals listed under Stockholm Convention: polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), commonly called dioxins.

Did the Stockholm Convention successfully address the problem of wastes containing PCDD/Fs as unintentionally produced by-products? As we see from the construction of Article 6 of the Stockholm Convention (see Article 6 in the box) the **definition of “Low POPs Content Level” (LPCL)** is crucial for defining wastes to be designated as “POPs wastes”. In the absence of any other limit value for the definition of hazardous waste according to its POPs content, Low POPs Content Level is crucial for controlling transboundary movement of hazardous wastes according to the Basel Convention (Basel Convention 2014).²

In order to prevent releases of POPs from wastes the first step needed to be taken is identification of POPs wastes and the second step is the identification of proper environmentally sound management methods for such wastes. Has this happened in the case of PCDD/Fs? We tried to look at this issue in the case of waste incineration residues, which seems to be better documented than other types of wastes.

² This applies to waste incineration residues in particular as they are listed in Annex II to Basel Convention as wastes considered to be “other waste”, although they might contain PCDD/Fs which are listed under substances in Annex I, however waste incineration residues are often declared to be non-hazardous including fly ash and Air Pollution Control (APC) residues as their content of dioxins is not taken into account during the evaluation of their hazardous properties unless there is specific limit for these substances included in national legislation. Therefore, in this case, LPCL is also an important definition for transboundary movement of wastes.



ARTICLE 6 - STOCKHOLM CONVENTION

Measures to reduce or eliminate releases from stockpiles and wastes

1. In order to ensure that stockpiles consisting of or containing chemicals listed either in Annex A or Annex B and wastes, including products and articles upon becoming wastes, consisting of, containing or contaminated with a chemical listed in Annex A, B or C, are managed in a manner protective of human health and the environment, each Party shall:
 - (a) Develop appropriate strategies for identifying:
 - (i) Stockpiles consisting of or containing chemicals listed either in Annex A or Annex B; and
 - (ii) Products and articles in use and wastes consisting of, containing or contaminated with a chemical listed in Annex A, B or C;
 - (b) Identify, to the extent practicable, stockpiles consisting of or containing chemicals listed either in Annex A or Annex B on the basis of the strategies referred to in subparagraph (a);

Article 6 - Stockholm Convention (continued)

- (c) Manage stockpiles, as appropriate, in a safe, efficient and environmentally sound manner. Stockpiles of chemicals listed either in Annex A or Annex B, after they are no longer allowed to be used according to any specific exemption specified in Annex A or any specific exemption or acceptable purpose specified in Annex B, except stockpiles which are allowed to be exported according to paragraph 2 of Article 3, shall be deemed to be waste and shall be managed in accordance with subparagraph (d);
 - (d) Take appropriate measures so that such wastes, including products and articles upon becoming wastes, are:
 - (i) Handled, collected, transported and stored in an environmentally sound manner;
 - (ii) Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option or the persistent organic pollutant content is low, taking into account international rules, standards, and guidelines, including those that may be developed pursuant to paragraph 2, and relevant global and regional regimes governing the management of hazardous wastes;
 - (iii) Not permitted to be subjected to disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants; and
 - (iv) Not transported across international boundaries without taking into account relevant international rules, standards and guidelines;
 - (e) Endeavour to develop appropriate strategies for identifying sites contaminated by chemicals listed in Annex A, B or C; if remediation of those sites is undertaken it shall be performed in an environmentally sound manner.
2. The Conference of the Parties shall cooperate closely with the appropriate bodies of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal to, inter alia:
- (a) Establish levels of destruction and irreversible transformation necessary to ensure that the characteristics of persistent organic pollutants as specified in paragraph 1 of Annex D are not exhibited;

Article 6 - Stockholm Convention (continued)

- (b) Determine what they consider to be the methods that constitute environmentally sound disposal referred to above; and
- (c) **Work to establish, as appropriate, the concentration levels of the chemicals listed in Annexes A, B and C in order to define the low persistent organic pollutant content referred to in paragraph 1 (d)(ii). (Stockholm Convention 2010).**

4. WASTE INCINERATION RESIDUES: THE SCALE OF THE PROBLEM

“Today solid residues from modern Waste-to-Energy facilities constitute the primary emission route to the surrounding environment. Although bottom ashes are generated in larger quantities, the main pollution potential is found in the air-pollution control (APC) residues originating from cleaning the flue gases before emission to air. While a range of different types of APC residues exists the overall properties and environmental concerns are the same, regardless of the incinerator and country of origin.” (Astrup 2008)

Incineration of solid waste ends up with a certain amount of residues in different forms. In total the residues are estimated to be between 25% and 35% (in some cases up to 40%) of the original weight of waste input (EA 2002, Petrlik and Ryder 2005). The larger volume is bottom ash, which can reach 20 – 30%³ by mass of the original waste on a wet basis. The fly ash component from APC residues are in the order of 1–3% and total APC residues account for 2 – 5% of the waste input mass on a wet basis (Sabas, Poletini et al. 2003). Fly ash and APC residues contain, in general, higher concentrations of toxic chemicals, including PCDD/Fs, than bottom ash.

The total volume of fly ash⁴ produced by waste incinerators globally is not easy to calculate as basic data is unavailable. In 2013, there were more than 1600 waste to energy (W-t-E) plants (as modern waste incinerators producing energy are called) globally. Their total capacity was more than 228.24 million tons per year (Coenrady 2013). If we calculate that 3% of fly ash is created from the total weight of burnt waste, the result is the production of 6.85 million tons of fly ash per year, however the capacity of municipal solid waste incinerators (MSWI) is not always fully utilized, so fly ash production is most likely less than this estimate. On the other hand, some MSWI are operated without energy outputs and are therefore not included in this capacity estimate. In addition, there are many hazardous waste (HazWI) and medical waste incinerators (MedWI) not included

³ For some waste incinerators based in UK this amount was up to 39% according data collected by Environment Agency. Source: EA (2002). Solid Residues from Municipal Waste Incinerators in England and Wales A report on an investigation by the Environment Agency, Environment Agency: 72.

⁴ We will use this term in order to simplify the text but the meaning is APC residues including fly ash.

in this capacity estimate. Large hazardous waste incinerators are mostly operated only in developed countries while in developing countries medical waste incinerators are quite often used with small annual capacity up to several thousand tons. When talking about management of fly ash from waste incineration we are probably talking about several millions tons of residues that must be disposed of every year.

There are estimates about total content of dioxins in waste incineration residues (mainly fly ash) derived from country reports and in National Implementation Plans (NIPs) for the Stockholm Convention both of which are submitted to the Secretariat of the Stockholm Convention from 86 countries.⁵ Based on this information PCDD/Fs releases in waste incineration residues are almost 800 g I-TEQ per annum (EEC of SC 2016), however, when we look closer we can see that countries with the highest capacity of waste incineration (e.g. Germany, China, Japan) did not report any dioxins in waste incineration residues and some others were not included, such as Ukraine which reported PCDD/Fs releases in residues of 156.5 g I-TEQ/annum for 2002 (MEPU 2007). For the total capacity of W-t-E plants we can also calculate total releases of PCDD/Fs in fly ash using the emission factors for waste incineration residues in the Dioxin Toolkit which was updated in 2013 (UNEP and Stockholm Convention 2013). This calculation leads us to estimates of 3.4 kg I-TEQ and 45.6 kg I-TEQ dioxin releases per year (in fly ash wastes) for class 3 and class 4 municipal waste incinerators⁶ respectively. This estimate assumes that W-t-E plants use 100% of their installed capacity which is mostly not the case but there is no data about the actual capacity used every year by W-t-E plants. Let us assume that between 85 to 90% of their capacity is used per annum. The total amount of dioxin released in WI residues should be adjusted from the previously quoted estimates using this percentage.

We are not able to conduct the same calculation for hazardous and medical waste incinerators as information on their global capacity is not available. There are some indications of the scale of dioxin releases in fly ash from these waste incinerators in the NIPs from a few countries, and there is additional data from other information sources. They are either summarized in Table 1 or explained further in this study.

5 NIPs can be found at: <http://chm.pops.int/Implementation/NationalImplementationPlans/NIPTransmission/tabid/253/Default.aspx> and country reports at <http://chm.pops.int/Countries/Reporting/NationalReports/tabid/3668/Default.aspx>

6 We can look at the situation in the Czech Republic in order to get better idea which of these two figures may be closer to reality: There are 3 MSWI in this EU country. All three should be designated class 4 waste incinerators according Dioxin Toolkit classification. Their capacity is 680,000 tons of waste/year and by using emission factors from Toolkit we calculate 10.2 g I-TEQ as an estimate of total dioxin releases in wastes from these three facilities. Comparing with real figures from the Czech Pollution Release and Transfer Register (PRTR) system we note that 26 g I-TEQ PCDD/Fs was reported for year 2011, the only year when all 3 MSWI had to report their PCDD/Fs transfers in waste.

TABLE 1: PCDD/Fs RELEASES IN g TEQ/ANNUM.

Country	Haz. waste incin.	Med. waste incin.	Year	Sources	Notes
Albania	0	0.07	2004	MEFWA 2006	
Argentina	27	-	2006	República Argentina 2007	
Brazil	20.72	-	2014	Federative Republic of Brazil 2015	
China	186	748.9	2004	The People's Republic of China 2007	
Czech Republic	17.8	9	2015	MŽP 2016, Mach 2017	
EU	61.8	29.1	2005	BiPRO 2005	MedWI calculated for 10 EU member states only
EU Switzerland Norway	25	100	1999	Wenborn, King et al. 1999	Industrial waste and sewage sludge incineration
Hungary	11.53	-	2006	Ministry of Environment and Water 2009	Calculated from data in Annex 6
India	3,965.8	-	2010	Government of India 2011	This figure is for all waste incineration plants in India (including MedWI), however there was only one W-t-E plant in operation in India with capacity 54,000 tons/annum, according the database of more than 1600 facilities . Nearly 4.4 million tons of hazardous waste is generated every year in India.
Indonesia	58	-	2001	The Republic of Indonesia 2008	Not very clear whether all comes from hazardous waste incinerators
Kenya	10.15	-	2006	MENR 2006, EEC of SC 2016	Calculation for both hazardous and medical waste incinerators together (HazWI 18%, MedWI 82%)
Lithuania	0.64	0.5	2004	MoE Republic of Lithuania 2006	

Country	Haz. waste incin.	Med. waste incin.	Year	Sources	Notes
Macedonia	0	0.11	2003	MEPP 2004	
Nigeria	0	15.851	2004	Federal Ministry of Environment 2009	
Turkey	0.9	0.352	2006	MEF 2010	

A collective inventory for 13 EU candidate countries calculated total releases in waste incineration residues⁷ from hazardous and medical waste incineration to be 5 g I-TEQ and 28 g I-TEQ respectively per year (Pulles, Quass et al. 2004). These figures seem to significantly underestimate the real releases as the three medical waste incinerators in the Czech Republic (of total capacity 8,400 tons/annum) released into fly ash more than 9 g I-TEQ dioxins in 2015 (MŽP 2016, Mach 2017) and two hazardous waste incinerators of a capacity of 37,200 tons/year released 17.8 g I-TEQ PCDD/Fs according to their reports into the Czech PRTR system for the year 2015 (MŽP 2016). In 2006 the Hungarian hazardous waste incinerators released PCDD/Fs into waste residues of more than 11.5 g I-TEQ/annum (Ministry of Environment and Water 2009). So just 2 of 13 former EU candidate states count for at least 9 g I-TEQ and 29.3 g I-TEQ total releases in WI residues per annum from medical and hazardous waste incinerators respectively.

The BiPRO study for the European Commission (BiPRO 2006) estimated 1,900 g TEQ/year of PCDD/Fs in waste incineration residues for EU countries however this report did not include solid residues from hazardous waste incineration into the PCDD/Fs inventory for wastes. This figure for all residues is more closely specified in a previous BiPRO report (BiPRO 2005), where fly ash and APC residues from MSWI account for 1,530 g TEQ/year, HazWI accounts for 61.8 g TEQ/year in fly ash and APC residues and MedWI for 29.1 g TEQ/year in fly ash and other APC residues. The estimates for the hazardous and medical waste incineration share seems to be underestimated in light of data from two countries with rather small HazWI and MedWI capacity, namely the Czech Republic and Hungary as shown above (Ministry of Environment and Water 2009, MŽP 2016, Mach 2017).

⁷ The dioxin inventory for new EU candidate countries used the term “releases to land” meaningful releases in wastes according UNEP’s Dioxin Toolkit.

Based on available data, the overall calculation for PCDD/Fs in fly ash and other APC residues produced by HazWI and MedWI globally, might be within a similar scope as they are for MSWI when calculated according to the Dioxin Toolkit emission factors. It means that in total the releases could amount to approximately 7 kg I-TEQ of dioxins released into waste incineration residues annually (at a minimum), although the final figure is more likely closer to or over 10 kg TEQ/year of PCDD/Fs,⁸ taking into account that not all MSWI are in category 4 of the Dioxin Toolkit classes (see above). This seems to be a bigger share of total PCDD/Fs releases into the environment than estimated from inventories obtained by Stockholm Convention Secretariat from individual countries (EEC of SC 2016). So, we believe that waste incineration fly ash and other APC residues cannot be underestimated in terms of PCDD/Fs content, and appropriate measures should be undertaken to address this source of environmental contamination. Given the identification of this major source of POPs pollution, the proposed **Low POPs Content Levels represent a crucial addition to the set of control measures for POPs waste to be established at a global level.**

We reviewed almost 300 major studies and articles focused on WI residues, and fly ash including APC residues in particular. We searched for the following information about WI in these studies:

- Management practices (use) of WI residues in relation to potential contamination of the environment by toxic chemicals and POPs in general, and PCDD/Fs in particular
- Data about observed levels of dioxins and other POPs in these wastes, and their potential to leak into environment
- Technologies used to destroy or irreversibly transform POPs properties, in fly ash in particular
- Policy measures leading to prevention of POPs releases into environment.

⁸ Just for indication of the scope: Total amount of PCDD/Fs releases was calculated at level of almost 71 kg TEQ/year, based on data for 86 countries. Fiedler, H. (2016). *Release Inventories of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans*. Dioxin and Related Compounds: Special Volume in Honor of Otto Hutzinger. M. Alae. Cham, Springer International Publishing: 1-27.

5. THE FATE OF FLY ASH AND APC RESIDUES FROM WASTE INCINERATORS IN THE ENVIRONMENT

5.1 THE WIDE RANGE OF USES OF WASTE INCINERATION FLY ASH AND OTHER AIR POLLUTION CONTROL RESIDUES (APC)

Currently, no general consensus appears to exist regarding residue disposal and use solutions on a worldwide level, although the **BAT/BEP Guidelines** of the Stockholm Convention contain advice on how to avoid POPs releases due to improper handling of APC residues. *“Fly ash from electrostatic precipitators and residues from air pollution equipment almost certainly contain significant amounts of chemicals listed in Annex C of the Convention, so these wastes have to be **disposed of in a controlled way**. Fly ashes should never be used as soil amendment in agricultural or similar applications. ... This includes the separate management of bottom ash from fly ash and other flue gas treatment residues in order to avoid contamination of the bottom ash ...,”* are some of the suggestions of the BAT/BEP Guidelines (Stockholm Convention on POPs 2008), and they are widely ignored as will be demonstrated below. We believe that this problem occurs due to the very weak **Low POPs Content Level** which does not require all stakeholders to pay attention to the fate of PCDD/Fs and other POPs during WI residues management.

There were several reviews conducted of different uses of WI fly ash (Ferreira, Ribeiro et al. 2003, Astrup 2008, Lam, Ip et al. 2010, Lichtfouse, Schwarzbauer et al. 2013, Sun, Li et al. 2016) or its treatment technologies and disposal (Ecke, Sakanakura et al. 2000, Sabbas, Poletti et al. 2003, Amutha Rani, Boccaccini et al. 2008, Astrup 2008, Kulkarni, Crespo et al. 2008, Quina, Bordado et al. 2008, Lam, Ip et al. 2010, Lichtfouse, Schwarzbauer et al. 2013, Zacco, Borgese et al. 2014, Sun, Li et al. 2016) including those uses and treatments not suggested by BAT/BEP Guidelines.

A study published in 2000 listed melting, cementitious S/S (stabilization and solidification), stabilization with a chemical agent and acid extraction as accepted treatment techniques in Japan (Ecke, Sakanakura et al. 2000). Thermal methods (e.g. waste incineration) or inertization based on the use of colloidal silica as metal stabilizer were added onto that list by later studies (Lam, Ip et al. 2010, Zacco, Borgese et al. 2014, Sun, Li et al. 2016). This is not an exhaustive list as there are missing technologies which are focused on chemical or physical-chemical destruction of dioxins (Mino and Moriyama 2001, Mitoma, Uda et al. 2004, Government of Japan 2006, Kulkarni, Crespo et al. 2008, Ocelka, Pekárek et al. 2010, Hallett 2016).

Nine possible applications of WI fly ash were identified by Ferreira, Ribeiro et al. (2003) and grouped into four main categories: construction materials (cement, concrete, ceramics, glass and glass-ceramics); geotechnical applications (road pavement, embankments); “agriculture” (soil amendment); and, miscellaneous (sorbent, sludge conditioning). Each application was analyzed in detail. Since that study was completed it has been cited that fly ash is also used as a material for metals reclamation (Ferreira, Jensen et al. 2005). In another review of APC residue management for W-t-E plants for the International Solid Waste Association (ISWA), the only additional use described was the use of residues for neutralization of acidic solutions (Astrup 2008). It also contains an overview of uses of fly ash by countries of origin of major members of ISWA and disposal methods used to treat APC residues.

In some countries, residues are treated to minimize future release of contaminants (mainly salts and heavy metals, but in most cases not dioxins) and then landfilled under varying conditions (either traditional surface level landfills with leachate collection and top covers, or subsurface disposal sites such as old salt mines). Although the ISWA report suggested “*It cannot be recommended that APC residues are landfilled without prior treatment,*” (Astrup 2008), this guidance is not always followed. There is also wide range of pre-treatment methods which cannot be described as anything other than dilution of the fly ash and of the concentrations of toxic substances in it. Even pre-treated mixed material was documented to be carried by the wind and dust containing dioxins dispersed in surrounding areas (Wang, Wang et al. 2006, Mach 2017).

Fly ash and other APC residues contain high levels of PCDD/Fs and may also contain significant levels of other POPs (see chapter 8). The BAT/BEP Guidelines state they are “*to be disposed of in a controlled way*”. The current disposal methods and use for applications where it is hardly possible to achieve the control of releases of dioxins amounts to failure of the Stockholm Convention objective “*to protect human health and*

the environment from persistent organic pollutants.” Unfortunately this **failure is already happening as there are clear indications that fly ash with PCDD/Fs levels below 15 ppb is believed to be safe for any use or disposal.** The 15 ppb level was picked from different options by the EU as lowest economic burden, and they forced its adoption at international level as a provisional Low POPs Content Level under the Basel Convention General Technical Guidelines (Basel Convention 2015). However, EU consultants defined **levels above 1 ppb as the “worst case scenario for human health risks”** (see also chapter 11 Discussion about exposure scenarios and suggestions for a definition of Low POPs Content Level for PCDD/Fs); (BiPRO 2005).

5.2 AGRICULTURE

5.2.1 Soil amendment

According to the scientific literature fly ash is suggested for use in agriculture as a soil amendment in several different countries (Rosen, Bierman et al. 1994, Ferreira, Ribeiro et al. 2003, Jala and Goyal 2006, Wang, Liu et al. 2008, Pandey and Singh 2010, Mikalonis 2014), although the case of dioxin contamination in the Newcastle allotments (Pless-Mulloli, Edwards et al. 2000, Pless-Mulloli, Edwards et al. 2001, Watson 2001, Pless-Mulloli 2003) has clearly shown that uncontrolled use of WI residues can lead to gross pollution of the food chain through which it can be harmful for human health. A study from 1986 shows that Newcastle was not necessarily the first case in the UK, however “only” heavy metal uptake by plants grown on soil amended with WI fly ash was studied at that time (Wadge and Hutton 1986).

Wang, Liu and others in their study from 2008 suggest the addition of MSWI fly ash to the soil should not be excessive, and less than 5-10% is an advisable addition level depending on the acidity of the soil and the plants growing on it (Wang, Liu et al. 2008). Even such a small amount of WI fly ash can lead to serious contamination of the soil. In a controlled experiment, chickens were fed fly ash (containing 201 ng TEQ kg⁻¹) at 0.3 and 0.6 weight % of the commercial feed. The eggs reached maximum levels of 2.2 and 3.7 pg WHO-TEQ g⁻¹ fat during the feeding trials, while the maximum levels of the control group were 1.4 pg WHO-TEQ g⁻¹ fat, (Shih, Wang et al. 2009).

In another example scientists discovered that people in some parts of Taiwan intentionally add fly ash from industrial processes into duck feed in order to make the yolk more orange. They found this was most likely source of contamination of chicken eggs during so called “Toxic Egg

Event” (Lee, Shih et al. 2009). Levels of dioxins up to 32.6 pg TEQ g⁻¹ fat were found in Changhua County in 2005 during this food incident (The Epoch Times 2005).

In this study, we summarize some cases around the world with similar potential for pollution by PCDD/Fs as was demonstrated in Newcastle or Changhua County. They might be not visible in developing countries as there are less measurements of dioxins and other POPs due to lack of laboratory capacities.

5.3 GEOTECHNICAL USE OF APC RESIDUES

5.3.1 Embankments

Fly ash is widely used for embankment construction (Goh and Tay 1993, Ferreira, Ribeiro et al. 2003, Zhang, Soleimanbeigi et al. 2016). In Pakistan foundry sands are also used for embankments (Ansari 2014). Embankments are constructed from earth (soil) or stone materials and are used to hold back water (retaining walls, land reclamation, etc.), which means that ash can be in direct contact with river or even saline sea water and the potential leakage of chemicals from the ash moves directly to the river or to the sea respectively. Goh and Tay (1993) report that initial leaching of cadmium and chromium from non-stabilized fly ash exceeded drinking water standards and that stabilized fly ash presented lower values, which is not surprising. However, they limited their study to leaching from fly ash and did not look into what happened for the soil/fly ash system, which could give a more precise indication of the leaching behavior from embankments constructed with these materials. No tests for dioxin leaching in the case of this use of WI fly ash were found in the literature.

5.3.2 Road construction and pavement

Agricultural use of fly ash is probably most direct way of contamination of the food chain by toxic pollutants however, other uses of APC residues can lead to significant PCDD/Fs releases into the environment and contamination of the food chain too. The Newcastle/Byker case in the UK was caused by the use of WI residues as road/path construction material. This is widely used in the Netherlands where 30% of APC residues from W-t-E plants was used for asphalt filling according to the ISWA report from 2008 (Astrup 2008), while the Netherlands NIP from 2006 states that more than 65% of fly ash from W-t-E plants was used as raw material, which means “reused”. The same practice was observed in other EU countries (e.g. Belgium, Czech Republic, Denmark, France, Spain, UK), USA



Figure 1: Waste incinerator in Copenhagen with pile of bottom ash; Source: (Borking 2011). In many EU countries is bottom ash used for roads construction and pavement. In some cases it also includes fly ash.

(Van der Sloot and Kosson 2003, Mikalonis 2014, Zhang, Soleimanbeigi et al. 2016) and Asian countries (Wang, Chen et al. 2010, Ansari 2014).

In countries with a lot of snowfall during winter or ice on the roads salt is used to prevent icy roads and/or sidewalks. If fly ash was used for construction of such roads or sidewalks what does it mean for leaking of dioxins and other POPs contaminants from the fly ash? We are not aware of any leakage tests trying to address this issue in specific conditions of road applications.⁹

Another potential route of contamination that has been subject to minimal research is particle erosion from roads, (either by wind, water or abrasion) paved with a mixture including fly ash. The BiPRO report on use of WI residues in roads commented: “*it has to be noted that uncertainty remains with respect to superficial mechanical abrasion*” (BiPRO 2005). There are also related questions on the potential contribution to contami-

⁹ The only comparable leaching test was published by Takeshita, R. and Y. Akimoto (1991). “Leaching of polychlorinated dibenzo-p-dioxins and dibenzofurans in fly ash from municipal solid waste incinerators to a water system.” Archives of Environmental Contamination and Toxicology 21(2): 245-252. See also chapter 7, where the leaching tests are discussed.

nation of free range chicken eggs in Menen, Belgium (Nouwen, Provoost et al. 2004) related to this exposure.

5.3.3 Cover layer at landfills

WI residues are often used as a cover layer at landfills in developed countries for financial reasons because this disposal method is often exempted from a disposal fee. In some cases, the ash is added in a layer at the end of each working day of the landfill to cover newly deposited waste at the “working face” of the landfill. This use of fly ash is not without problems, although it might look like a non-problematic use. Fly ash is exposed to weathering on the surface of the landfill and can become a source of fine dust released into surroundings (see case studies). If the ash is added as a daily management cover it can become windborne overnight until work recommences. The use of heavy vehicles to move waste onto the surface of the landfill can release further amounts of contaminated ash in fine particulate form. It is also then exposed to the influence of precipitation and



Figure 2: This location is close to the Czech/Polish borders, where mixed fly and bottom ash from MWI was used for the cover layer of landfill (on the top of hill at this photo) and also to fill in the drainage line down the hill through the cattle pasture ending in a nearby creek. Levels of PCDD/Fs measured in the material were up to 0.08 ng TEQ g⁻¹ d.m. Photo: Jan Losenický, Arnika, November 2011.

if mixed with waste containing materials that enhance leaching of dioxins, can release them into waste surface waters and via leachate to groundwater (see chapter 7). Mostly waste mixtures used for cover layers of landfill undergo leachate tests, however these are not focused on PCDD/Fs leaching because there is no regulatory pressure to consider PCDD/Fs concentrations due to very flexible or non-existing limits for their content. Reuse of fly ash for cover layer at landfills is in some way similar to its use in construction of roads and can lead to similar problems of release into the environment.

5.4 USE OF APC RESIDUES AS CONSTRUCTION MATERIALS

Apart from use in road construction or by maintaining landfill covers, direct use in building construction is promoted and practiced for waste incineration residues. In addition the World Energy Council promotes the reuse some of waste incineration residues in applications such as fill in the building and construction industries. (WEC 2013) More specific examples of these uses are given in following subchapters.

5.4.1 Cement

Fly ash is sometimes used as an additive to cement (Kikuchi 2001, Kerpert, Siddique et al. 2015) and some studies promote the replacement of cement by fly ash as it contains some quantities of typical cement minerals, although in less quantity than in cement clinker (Triano and Frantz 1992, Ferreira, Ribeiro et al. 2003). This is mainly due to the use of lime for air pollution control of flue gases in WI.

The Solvay Company has been working on the development of a physicochemical treatment for municipal solid waste incineration (MSWI) fly ashes: the Revasol process. According to the claims by the company, this process allows the use of ash in concrete and reduces the soluble fraction, fixing heavy metals and eliminating dioxins (Aubert, Husson et al. 2004). Authors also claimed that *“the leaching tests carried out on the concrete confirm that the process makes it possible to obtain materials without major risks for the environment”*, however no measurements of PCDD/Fs were demonstrated elsewhere in this process. Dioxins were probably not considered to be among *“major risks for the environment”*, although the process involves thermal treatment of fly ash as well so the generation of unintentional POPs (U-POPs) is very likely.

It is very common when it comes to discussion about environmental or health impact assessment of the use of WI fly ash in cement, that most studies just pay attention to leaking of heavy metals or fixing the chlorine

(Kikuchi 2001) and the salts. Although they mention potential problems with dioxins, leaching tests are not conducted. We discuss the PCDD/Fs leachate issue in one of later chapters in this study (see chapter 7).

Some studies suggest also use of WI residues for replacing the clay in production of bricks (Lin 2006), although it evolves thermal treatment and creation of U-POPs, including additional dioxins is very likely.

5.4.2 Glass and ceramics

A glass-like substance can be made of WI residues (both bottom ash and fly ash) by melting, at high temperatures (above 1300°C), which is also called vitrification. Some of the potential uses referred to for vitrified fly ash are: road base materials; embankments; blasting grit; partial sand replacement in concrete; in monolith blocks for coastal protection and, in the production of construction and decorative-materials, like water-permeable blocks, ceramic tiles, pavement bricks and decorative stones for gardens (Ferreira, Ribeiro et al. 2003, Amutha Rani, Boccaccini et al. 2008). Some suggest that microstructure materials coming out of vitrification of WI ash residues have potential to serve as a viable alternative for construction applications (Cheng, Chu et al. 2002). Wang, Yan et al. (2009) reported a decomposition rate (99.95%) of PCDD/Fs in TEQ in the produced slag by the vitrification process of MSWI fly ash. This is a lower destruction efficiency (DE)¹⁰ than for some other technologies (see chapters 14 and 15).

Application of MSW combined ash in the production of ceramic tiles was reported by GEC (1996). The tile contained 50% incinerator ash. The produced tiles were applied in outdoor and internal paving and on the exterior face of walls.

5.5 MISCELLANEOUS

5.5.1 Sludge conditioning

Wastewater contains small amounts of oil that make dewatering difficult. To overcome this problem the sludge can be conditioned by the addition of filter aids. The use of MSW fly ash as a chemical conditioner has been

¹⁰ Calculated on the basis of the mass of the POP content within the waste, minus the mass of the remaining POP content in the gaseous, liquid and solid residues, divided by the mass of the POP content within the waste, i.e., $DE = (\text{POP content within waste} - \text{POP content within gas, liquid and solid residual}) / \text{POP content within the waste}$. Basel Convention (2015). General technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants. Technical Guidelines. Geneva.

investigated (Hwa and Jeyaseelan 1997). In a pilot plant, with a capacity of 50 tons/day) 0.5 ton of incineration ash, 0.3 ton of dry sewage sludge and 0.3 ton of limestone were converted to 0.85 ton of cement clinker (Kikuchi 2001).

5.6 RECYCLING OF METALS

5.6.1 *Electrodialytic process.*

This process leads, to a certain extent, to extraction of heavy metals (Ferreira, Jensen et al. 2005), however it also ends with higher concentrations of PCDD/Fs in residues from the process.¹¹ Its proponents do not consider that as a significant issue, because it is below the current Low POPs Content Level.¹²

Residues from electric arc furnaces and ashes containing high levels of zinc are recycled in industrial processes, such as the Waelz process, to extract the metals. Since PCDD/Fs are regenerated in the process, the recycling may result in high emissions to air if the air pollution control devices are inefficient. Chi and coauthors demonstrated that 560 ng TEQ kg⁻¹ of recycled ash was emitted from one facility (Chi, Chang et al. 2006). This recycling option will therefore result in large emissions to air and highly contaminated solid waste residues are generated (Chi, Chang et al. 2006).¹³

5.7 FINAL REMARKS ABOUT REUSE OF WI FLY ASH (PCDD/FS CONTAINING WASTES)

The reuse of fly ash represents a significant environmental risk based on current global and national legislative and regulatory requirements that virtually ignore the potential releases of dioxin and other POPs from the residues into the environment. Even where leachate tests and stabilization are undertaken the tests and stabilization methods have been shown to be poorly suited to determining the fate of POPs in residues and controlling their release. Therefore, adopting and enforcing strict LPCL is a priority ensure that the release of POPs from this source is minimized. A far more effective approach would be to avoid the process of waste incineration altogether. There are numerous techniques and technologies available that

11 After the electro-dialytic treatment PCDD/Fs levels increased in the residues (between 1.4 and 2.0 times). This does not mean PCDD/Fs were synthesized, but that soluble materials dissolve, leaving behind the non-water soluble compounds, such as PCDD/Fs. Source: Dias-Ferreira, C., G. M. Kirke-lund and P. E. Jensen (2016). "The influence of electro-dialytic remediation on dioxin (PCDD/PCDF) levels in fly ash and air pollution control residues." *Chemosphere* **148**: 380-387.

12 See their exact statement citation in chapter 5.7 starting with "According ..." *ibid.*

13 See Table 2 in cited literature source.

can treat the same wastes as incineration without the creation of POPs contaminated residues or POPs emissions.

While there are incinerators operating and generating large volumes of residues efforts must be taken to prevent the leaching of POPs from them. (Astrup 2008) has written: *“Residues should always be stabilized or treated to minimize future release by leaching. Stabilization and treatment should naturally reflect the choice of final disposal”*, and it must be stated that even waste with PCDD/Fs concentration below the current Low POPs Content Level for PCDD/Fs (and for any other adopted LPCL) requires treatment and careful handling.

The scale of the problem is noted by scientific consultants BiPRO on page 296 of their report: *“In total only 24% of the overall discharge of PCDD/PCDF-TEQ to waste is covered by the lowest discussed LPC limit of 1 ppb. The situation would not change significantly at a limit of 0.1 ppb. This is due to high volume low contaminated wastes streams like MSW, bottom ashes and slags, sewage sludge and compost which transport the remaining 76%”* (BiPRO 2005).

This raises the question of “what does the current **Low POPs Content Level** mean for practical engineers?” The answer is quite clear: it is no obstacle for any technically achievable (practical) use of residues. It was quite openly said in the article by Dias Ferreira et al.: *“According to the Basel Convention, PCDD/PCDF levels in these materials is low ($<15 \mu\text{g WHO-TEQ kg}^{-1}$) and the fly ash and APC residue could eventually be valorized, for instance as construction material, provided end-of-waste criteria are set and that a risk assessment of individual options is carried out, including the end-of-life stage when the materials become waste again.”* (Dias-Ferreira, Kirkelund et al. 2016) This is a **very concerning interpretation of Low POPs Content Level** as risk assessment, in most cases, does not look at potential for spreading of PCDD/Fs and other POPs from WI residues as demonstrated in various cases including a well-known example from Newcastle (Pless-Mullooli, Edwards et al. 2000, Pless-Mullooli, Edwards et al. 2001, Watson 2001, Pless-Mullooli 2003).

The major problem of the **reuse applications of fly ash** is that this way of management of the wastes containing POPs **should be avoided and works against the major objective of the Stockholm Convention** *“to protect human health and the environment from persistent organic pollutants.”* Reuse of fly ash with significant levels of dioxins represents a serious threat to human health and the environment as demonstrated in case studies in chapter 9 of this study. In many cases, **it leads to uncontrolled handling of the waste** because of the adoption of the **wrong threshold at**

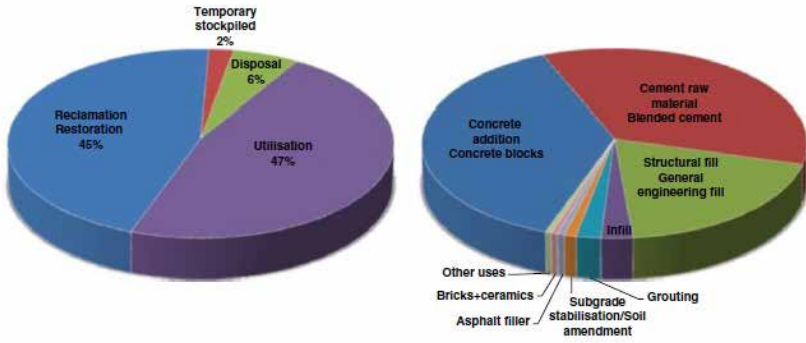


Figure 3: Use and disposal rates for coal fly ash in EU (15 member states). Source: (ECOA 2008) in (Lichtfouse, Schwarzbauer et al. 2013).

global level which gives the wrong signal to legislators, managers and all other stakeholders.

Reuse of most WI APC residues is in contradiction with one of the requirements of article 6 of the Convention that such hazardous wastes are:

“(iii) Not permitted to be subjected to disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants;”

Many of listed methods above lead to reuse or recycling of wastes containing significant levels of dioxins and other POPs. **The key reason for acceptance by national governments and waste managers of this situation is the far too high (weak) Low POPs Level Content for PCDD/Fs and a non-existent Low POPs Level Content for DL PCBs.**

Graphs at Figure 3 show the use and disposal rates for coal fly ash in EU (15 member states) as presented in Lichtfouse, Schwarzbauer et al. (2013). Coal fly ash is reused to about 25% of its volume globally (Wang 2008). These rates can help us to have a better picture about the trend of using WI fly ash, although Lichtfouse, Schwarzbauer et al. (2013) stated that MSWI fly ashes

“arising from flue gas treatment are partially recovered in some cases only (i.e. some industrial processes are used to recover certain fractions of residues), but, in general, the residues are still sent for disposal, often by landfill and commonly following specific treatments. Its possible employ is limited to some applications, as for example as geopolymers (Luna Galiano, Fernández Pereira et al. 2011) or inert materials (Zacco, Gianoncelli et al.

2012), after the stabilization of leachable metals. However, certain problems with stabilization technologies cannot be ignored, such as long-term stability and the cost of stabilization chemicals.”
(Lichtfouse, Schwarzbauer et al. 2013)

6. DISPOSAL OF ASHES CONTAINING DIOXINS

There are different definitions of wastes containing or not-containing dioxins. For many parties to the Stockholm Convention the provisional Low POPs Content Level is simply used for this definition. The issue of how the level was set is discussed further in this study (see chapter 11). The main focus of regulators has been on the content of heavy metals in WI fly ash and/or APC residues as they are believed to be more risky compounds than dioxins in many countries. Therefore, stabilization of fly ash/APC residue is suggested in order to prevent leaching of heavy metals. Following this concept the standards and leaching tests for stabilized waste are designed to assess heavy metals. Dioxin content is not assessed because there is no legislative requirement established, and dioxins are believed to be bound like heavy metals to the ash, although clearly, the behavior of dioxins can be different to metals as demonstrated by many studies (see chapter 7).

BiPRO (2005) suggested stabilization and solidification of any waste with PCDD/Fs concentrations above 1 ppb (= 1,000 ng TEQ kg⁻¹) before its application to soil, which is defined as any use at terrain surface e.g. including cover of landfills. Stabilization/solidification as a pretreatment method is defined in General Technical Guidelines for POPs wastes (Basel Convention 2015): *“Stabilization and solidification are to be used in conjunction for them to be environmentally sound. The stabilization of waste refers to the chemical changes of the hazardous constituents in the waste to convert the constituents into a less soluble, mobile or toxic form. The solidification of the waste refers to changes in the physical properties of a waste to increase the compressive strength, decrease the permeability and encapsulate the hazardous constituents.”*

There are different stabilization and/or solidification processes used to treat fly ash. Landfill is generally the final disposal method after stabilization or solidification of the fly ash, however more and more common is the use of fly ash in mixed and solidified/stabilized wastes which are then used for backfilling of old mines or remediated sites (see also some of case studies in chapter 9). It is a questionable practice as this application of fly ash is not safe. By utilizing fly ash in this way we create new group of wastes with high levels of dioxins, which will likely become a new environ-

mental burden, or Superfund site (US EPA 2015). Potential concerns are well demonstrated in some case studies in this report.

Tanaka, Tojo et al. (2005) suggested that *“in landfill of incineration residues, dioxins, chloride, and calcium ions are concentrated, and additional processes to remove them are needed in some cases.”*

Other ways of disposal of fly ash are some thermal processes like vitrification (Amutha Rani, Boccaccini et al. 2008, Wang, Yan et al. 2010), melting or hazardous waste incineration. They are discussed in numerous studies. For example, Japan has listed the following disposal options for WI residues containing high levels of dioxin (see Table 2) in its Stockholm Convention National Implementation Plan: fusion, incineration at high temperature, vapor-phase hydrogen (hydrogen dechlorination), supercritical water oxidation, sodium reduction, and photochemical splitting (UV radiation). Some of these methods are more described in chapters 14 and 15. After these treatments, waste can be landfilled as municipal or industrial wastes or recycled if their dioxins concentration meets the standard (Government of Japan 2006).

6.1 STABILIZATION OF FLY ASH

As noted earlier in this report both bottom ash and APC residues such as fly ash pose an environmental threat and human health risk due to their releases of PCCD/Fs and heavy metals. In countries where they have numerous incinerators operating, the residues are a significant problem requiring pretreatment before disposal by regulation. Treatment that is accepted by regulators e.g. in Japan include thermal stabilization (e.g. melting), stabilization and solidification (S/S) with cementitious material as well as chemical stabilization and acid extraction.

One study compared the merits and disadvantages of each process (Ecke, Sakanakura et al. 2000) concluding that melting was superior in terms of dioxin content reduction (or bioavailability) but was relatively expensive due to the high energy inputs required making it a magnitude of order more expensive than other options. Cementitious and chemical stabilization were relatively easy to conduct but increased the bulk weight of the disposed material by 40% and 10% respectively. Acid extraction was noted as relatively inexpensive, “proven and reliable” but only had a small market share.

Stabilization and solidification is a common practice in many countries and was widely studied mainly with regards to leaching of heavy metals (Lampris, Stegemann et al. 2009, Bie, Chen et al. 2016, Tang, Liu et al. 2016). Slow release of heavy metals from the treated (stabilized) fly ash



Figure 4: This picture shows the light grey surface of the APC residues in the Bishops Cleeve landfill, one of the fly ash disposal sites in UK. The inset picture shows a 40 mph speed limit sign at the side of the site access road. Source: Watson (2015).

was found in a wet environment, thus making it still hazardous to the environment (Sun, Li et al. 2016). The solidification of fly ash with 25% cement increased the leachate contents of higher chlorinated benzenes and biphenyls in another, older study (Fischer, Lorenz et al. 1992). These examples show the importance of careful assessment of all circumstances in each individual case and also it shows again that no one followed the fate of dioxins in fly ash. Chapter 9 of this report includes two case studies focused on solidification and/or stabilization processes and processing sites, one of which is described in more detail in Annex 16.3.

6.1.1 Phosphation

This process involves the addition of phosphoric acid to the incinerator ash, and once the mixture is sufficiently dried it is roasted in a calciner at 600-900 °C for one hour resulting in a fine sand like material (Piantone, Bodenau et al. 2003). This process was promoted by Solvay “*The metals Pb and Zn, initially distributed in the silicate and carbonate phases, are*

broadly redistributed in the phosphate neoformations after carbonate dissolution, thus guaranteeing a more permanent stabilization” (Piantone, Bodenan et al. 2003). While the authors of this study also claim that the process destroys the dioxins in the waste no data was provided in relation to the emissions and releases of dioxin during the treatment process. The levels of dioxin present in the waste before and after treatment were not clearly presented in the study.

Phosphation is just one example of a chemical method of fly ash stabilization. The most commonly used stabilizing agents are: gypsum, phosphate, bleach, sulfides (sodium thiosulfate, sodium sulfide) and polymer organic stabilizers (Sun, Li et al. 2016).

6.2 MELTING

One method for treating ash prior to disposal is melting or vitrification. The energy used to conduct melting is high and according to some studies achieves significant toxicity reduction though this may be related more closely to bioavailability than actual reductions in the PCDD/Fs concentrations. Melting of ash forms a glassy slag that is less prone to leaching than untreated ash. By “locking” the PCDD/Fs into the glassy matrix it becomes less available in terms of human exposure. In some studies, it is suggested that this process then allows the resulting treated ash to be used for structural purposes or as fill for construction. However, if the slag was allowed to cool slowly, higher dioxin releases occurred, Using water as a rapid quench cooling agent resulted in less dioxin release and more useful physical characteristics for the slag in terms of construction (Kim, Seo et al. 2005). However, it is important to note that this study did not provide data about dust emissions and concentrations of PCDD/Fs in the dust from the melting process of bottom ash.

7. PCDD/Fs (POPs) IN LEACHATE MUST BE ADDRESSED

In most studies fly ash is considered to be potentially toxic because of salts or heavy metal leaching and being released into the environment. Therefore the majority of studies have focused more on tests of salts (Alba, Gassó et al. 1997, Li, Bertos et al. 2007, Quina, Bordado et al. 2011) or heavy metals leaching or releases (Rosen, Bierman et al. 1994, Kikuchi 2001, Ferreira, Ribeiro et al. 2003, Aubert, Husson et al. 2004, Haiying, Youcai et al. 2007, Wang, Liu et al. 2008, Quina, Bordado et al. 2011, Anastasiadou, Christopoulos et al. 2012, Bie, Chen et al. 2016, Tang, Liu et al. 2016) than on potential or real dioxin releases. This lack of attention in most countries to dioxin is mainly due to weak legislative and regulatory measures to prevent POPs releases (including Low POPs Content Level)



Figure 5: Storage of waste incineration ashes on fire in a hazardous waste incinerator Vyškov, Czech Republic in May 2005. Photo by South Moravian Fire Brigade.

which did not lead to an adequate focus on PCDD/Fs releases. However, in some Asian countries like, for example, Japan and Korea strict legislation with limit values of either 3 or 1 ng TEQ g⁻¹ were applied for dioxins.

The attention to PCDD/Fs releases is certainly justified as noted by Ferreira and Ribeiro et al (2003) who confirm that, *“It has been found that most of the environmental constraints regarding MSW fly ash applications are related to the leaching behavior of the final products”* (Ferreira, Ribeiro et al. 2003).

The leachability tests currently performed in many countries may not be applicable to substances like dioxin, because their behavior changes depending on the changes of the characteristics of the local environment. The leachability tests of wastes performed commercially are, in most cases, generally carried out in ideal laboratory conditions and do not correspond to the behavior of wastes in the environment where they are deposited. In U.S. leachate tests a mild acid solution is used to simulate landfill conditions. In Australia, only water is used in leachate tests which poorly reflects the average reducing environment of a landfill and underestimates leaching of chemicals. Salinity and pH fluctuations and humic content are just three of a variety of factors that can determine leaching rates from incinerator residues and other contaminated wastes. Therefore, the chemists themselves call for a change to these procedures. For example, M. Podhola from Chemical University, Prague in his study of stabilized wastes stated: *“A specifically prepared leachability test may be considered more suitable. Such test should stimulate conditions of subsequent deposition of the waste, if these conditions are known. Obviously, it is not possible to carry out these tests exclusively in the commercial manner. Apparently, they will have to be carried out in cooperation with research establishment”* (Podhola 2005).

Older studies on the behavior of dioxins in soils supported the original idea that dioxins are fixed by a strong bond to fly ash and bottom ash with minimal release. An Italian study from 1986 reported that the Seveso soil profiles did not show a significant translocation of the PCDD/Fs in the soil environment (Ratti, Belli et al. 1986). A German study from 1992 showed that only a little movement was found within 8 years in the surroundings of two industrial plants in southwest Germany and there was no appreciable loss of PCDD/Fs (Hagenmaier, She et al. 1992). Another German study asserted that only highly chlorinated congeners were detected in the solution obtained from leaching experiments following the method of the German DIN 38414 test and so on (Fischer, Lorenz et al. 1992).

However, studies conducted in the 1990s disprove the idea of a strong bonding of dioxins to fly ash and ash or slag. Takeshita and Akimoto

(1991) proposed the leachability of PCDD/Fs from fly ash by rain using a fly ash column. They showed that PCDD/Fs associated with water-soluble salts such as NaCl and CaCl₂ in the ash were eluted in the beginning of the elution, whereas those associated with slightly water-soluble particles such as calcium hydroxide were eluted in the latter half. Another report from 1995 focused on leaching of dioxins from fly ash and soils under fire-extinguishing water activity suggested that fire-extinguishing water use resulted in significant amounts of PCDD/Fs in the leachate (Schramm, Merk et al. 1995). Such a theoretical situation can become real when **WI ash storage sites are engulfed in flames** as happened in a hazardous waste incinerator in Vyškov, Czech Republic in May 2005 (see photo at Figure 5).

Korean scientists Yong-Jin Kim, Dong-Hoon Lee and Masahiro Osako studied PCDD/Fs leachability under circumstances comparable to those in landfills theoretically and in laboratory conditions. In the theoretical review, it was shown that dissolved humic matters (DHM) could influence the actual solubility and leachability of PCDD/Fs. The higher concentration of DHM showed the higher leachability of PCDD/Fs. In the leaching test, three different DHM concentrations and solution pH levels were applied to fly ash samples to simulate the various characteristics of municipal solid waste leachate. It was proved experimentally that the leachability of PCDD/Fs increased with increasing DHM concentration in all pH conditions. The highest leachability was shown at the highest pH. Iso-mer distribution patterns of PCDD/Fs in all leachates were similar (Kim, Lee et al. 2002). The increased leaching concentrations of dioxins with advanced humification and relatively good correlation to dissolved organic carbon (DOC) was also demonstrated in another study from Korea (Kim and Osako 2004).

A previous study by these scientists states that a mixture of bottom ash and fly ash shows a higher leachability of dioxins (Osako, Kim et al. 2002). This leads to the opinion that DHM are formed due to the presence of non-combusted carbon in bottom ash. The results also show several shortcomings in procedures of waste testing, because dioxins behave differently than heavy metals. Because of that, the authors of the study propose to rethink certain methods of testing (Osako, Kim et al. 2002).

The PAHs leaching behavior is also similar to PCDD/Fs. Comans, Zuiver et al. (2003) state that the PAHs strong solubility is enhanced by the high concentration of humic acid in the leachate.

Sakai, Urano and Takatsuki published another study focused on leaching of dioxins and PCBs from fly ash. Leaching tests with and without surfactants were conducted in order to understand the influence of surfactant-

like substances on POPs leaching. In those tests, LAS (linear alkylbenzene sulfonate) and humic acid was used as surfactant-like substances. Shredder residues from car/electrical goods recycling and fly ash from a MSW incinerator were used in the analyses and leaching tests. Furthermore, an experiment was carried out to understand the influence of fine particles to the leaching concentration of POPs. The results of the leaching tests indicate that surfactant-like substances increase the leaching concentration of POPs, and fine particles related closely to the transport behavior of POPs (Sakai, Urano et al. 1997).

As a result, it is not appropriate for incinerated ash to be dumped with municipal solid wastes, as they have a high potential to come into contact with high levels of organic matter, and therefore increase PCDD/DF levels in leachate (Choi and Lee 2006). This has particular relevance for the application of ash as a landfill cover.

The most recent study focused on leaching of PCDD/Fs from incineration residues with pure water, 2% non-ionic surfactant solution, 5% ethanol solution, and 5% acetic acid solution as leaching solvents (Yasuhara and Katami 2007). This study led to the following conclusions:

1. *Dioxins in bottom ash were leached much more effectively by ethanol solution and by acetic acid solution than by pure water. There was no difference in the leachability of dioxins by pure water and by non-ionic surfactant solutions.*
2. *Dioxins in fly ash were leached much more effectively by non-ionic surfactant solution, and by ethanol and acetic acid solutions than by pure water. High content of carbon in ash might assist to transport dioxins as a colloidal form by mobilization with surfactant or water soluble organic solvents.*
3. *Elution ratios using pure water (36 L) ranged from 0.1 to 1 ppm for bottom ash and from 0.001 to 0.01 ppm for fly ash.*
4. *Elution ratios using non-ionic surfactant solution (9 L) ranged from 0.1 to 1 ppm for bottom ash and from 0.2 to 10 ppm for fly ash.*
5. *Elution ratios using ethanol solution and acetic acid solution (each 9 L) ranged from 10 to 100 ppm for bottom ash and from 0.2 to 10 ppm for fly ash (Yasuhara and Katami 2007).*

Leaching levels of dioxins in this recent Japanese study are higher than leaching scenarios summarized in report by EU consultants from BiPRO, (see Table 10-2 on page 396 of their report), where the highest value is 2.5% (BiPRO 2005). Lichtfouse, Schwarzbauer et al. (2013) highlight the incompleteness of leaching tests:

“Indeed, external factors may be poorly reflected in leaching tests in the form as they are commonly used. ... The presence of humic acids is important for leaching of persistent organic pollutants (Sakai, Urano et al. 2000, van der Sloot, Kosson et al. 2001, Kim, Lee et al. 2002, Osako, Kim et al. 2002, Comans, Zuiver et al. 2003). However, humic acids tend to be absent in leaching tests. In view of environmental impact, this may be a significant problem when the leachability is much higher than predicted by leaching tests.” (Reijnders 2005)

8. POPs IN WASTE INCINERATION RESIDUES

By addressing PCDD/Fs and proper treatment of WI fly ash and other APC residues other POPs contained in these wastes can also be addressed. In a previous study from 2005 focused on WI residues (Petrlik and Ryder 2005) the other POPs and their levels observed in these wastes were listed. From those POPs already listed under the Stockholm Convention we can identify the following POPs in WI ashes: hexachlorobenzene (HCB), pentachlorobenzene (PeCB), hexachlorobutadiene (HCBd), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs) as well as residues of all POPs not destroyed during incineration processes such as, for example, polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) as well as other BFRs or organochlorinated pesticides, including DDT.

Apart from POPs listed under Stockholm Convention the following chemicals exhibiting POPs-like characteristics or high toxicity have been identified in WI residues; polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) and/or polybromochlorinated dibenzo-p-dioxins and dibenzofurans (PBCDD/Fs), polychlorinated dibenzothiophenes (PCDTs), and polycyclic aromatic hydrocarbons (PAHs) including chlorinated PAHs¹⁴ (Miyake, Tang et al. 2012). This list is definitely not exhaustive.

14 One study detected much more aromatic chemicals to be present in WI fly ash: “The total of 128 aromatic monocarboxylic acids (ACAs) including 36 mono- to tetrachlorinated compounds were qualitatively detected in fly ash. They are structurally classified into five groups; polycyclic aromatic hydrocarbons (PAHs), biphenyls, oxa-PAHs, oxo-PAHs, and hydroxy-PAHs. ... The detection of polychlorinated benzoic acids and biphenyl carboxylic acids, possibly candidates for the precursors of polychlorinated dibenzo-p-dioxins and dibenzofurans, might imply the existence of novel pathways. Akimoto, Y., S. Nito and Y. Inouye (1997). “Aromatic carboxylic acids generated from MSW incinerator fly ash.” *Chemosphere* 34(2): 251-261.

9. CASE STUDIES - SUMMARY

The following case studies demonstrate that POPs wastes (fly ash and other APC residues) even with dioxins below the current provisional Low POPs Content Level of 15 ppb can cause severe problems:

- (1) When used freely in areas accessible to free range chicken or cattle for example, **leads to contamination of the food chain**, and potentially harmful human exposure to POPs, and dioxins in particular.

Newcastle, UK (Byker Waste Incinerator) – Wastes showing dioxin concentrations 750 - 3.5-times lower than provisional “Low POPs Content Level” for dioxins set out by the Basel Convention at a level of 15 ppb (Basel Convention 2015) were used in Newcastle for reconstruction of foot-paths. This use has resulted in contamination of poultry eggs which, on average, exceeded by 6.4 to 8.8 times the limit for the content of dioxins in eggs set out later in the European Union (2.5 pg WHO-TEQ g⁻¹). This case and its analysis by Pless-Mulloli, Schilling et al. (2001a) was also used by

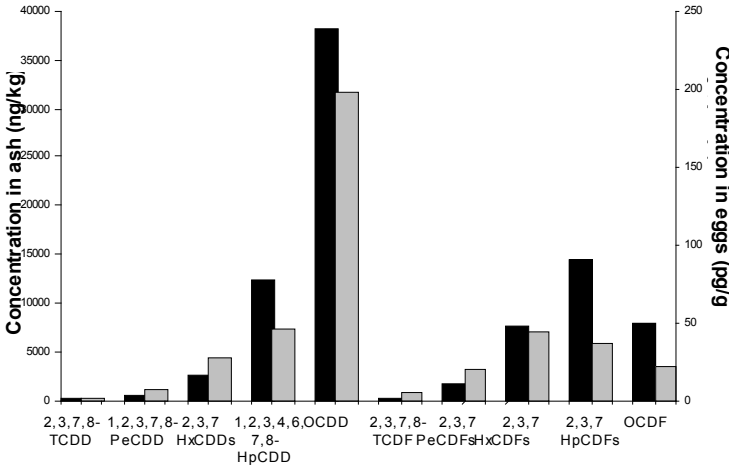


Figure 6: Dioxin pattern in sample from Westmacott Street, Newcastle: ash 2123 ng I-TEQ kg⁻¹, incinerator pattern, eggs 18 pg I-TEQ g⁻¹ lipid basis, incinerator pattern, chickens had access to ash. Source: Pless-Mulloli, Schilling et al. (2001a).

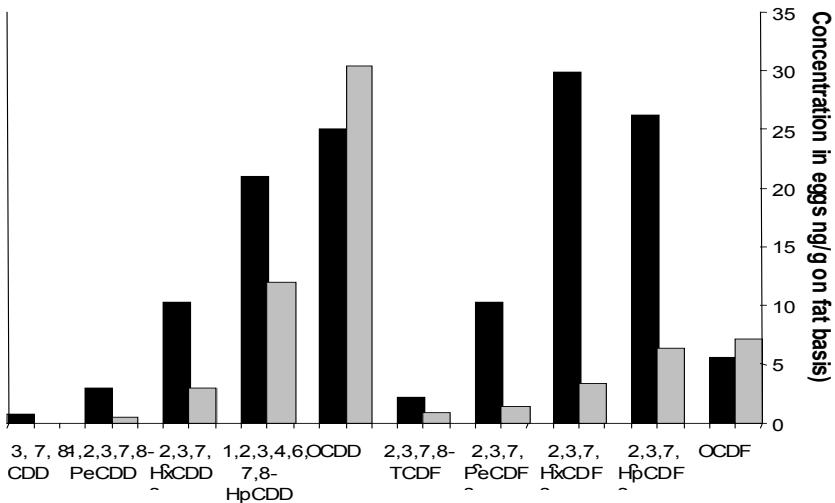


Figure 7: Dioxin pattern in sample from Coxlodge, Newcastle: ash 4,224 ng I-TEQ kg⁻¹ incinerator pattern, eggs 1.5 pg I-TEQ g⁻¹ lipid basis non-incinerator pattern, chickens did not have access to ash.
 Source: Pless-Mulloli, Schilling et al. (2001a).

BiPRO as basis for definition of the worst case human exposure scenario; **“Criterion Y: Worst case scenario for human health risks” – Low POPs Content Level at 1 ppb** (BiPRO 2005). Ash levels (0.02 – 4.22 ppb) – soil on allotments (accessible for chickens) (0.007 – 0.292 ppb) – chicken eggs (0.4 – 56 pg TEQ g⁻¹ – limit EU 2.5 pg TEQ g⁻¹).

The following graphs show the difference between contamination and dioxin patterns in egg samples from Newcastle, when chickens had and did not have access to WI ash. Both graphs are sourced from the study by Pless-Mulloli, Schilling et al. (2001a).

Taiwan – “Toxic Egg Event” has shown that adding fly ash into the duck feed by the farmers had a strong tendency to be a major source for the ducks’ daily intake of POPs. Therefore, the PCDD/Fs content in the feed and soil which was contaminated by illegal fly ash landfills should be paid more attention (Lee, Shih et al. 2009). In December 2005, duck egg contamination at a level of 32.6 pg TEQ g⁻¹ fat was observed in Changhua County (The Epoch Times 2005). It is almost 13-times higher than current EU food standard, and almost 22-fold the mean level of PCDD/Fs (1.5 pg WHO-TEQ g⁻¹ fat) in free range poultry (chicken) eggs in Taiwan (Hsu, Chen et al. 2010).

- (2) **In spite of its solidification/stabilization ash can be carried by wind into surroundings as fine dust** and contaminate the environment around facilities for solidification and/or landfills with solidified monoliths.

Wuhan - fly ash stored at open space area in waste incinerator -

Wuhan MSWI's surroundings located in Hanyang city was one of the areas where free range chicken eggs were collected for an IPEN study carried out in 2013 – 2015. In the MSWI neighborhood, eggs were collected which have shown the highest level of both chlorinated and brominated dioxins (PCDD/Fs and PBDD/Fs) measured among all collected samples in China for that project. Both pooled egg samples from the vicinity of Wuhan waste incinerators exceeded EU standards for dioxin content in chicken eggs (European Commission 2011) by almost three and five times, respectively. The level of HCB in sample Wuhan 1 was 74.5 ng g^{-1} fresh weight, which is almost four times higher than the standard set for HCB content in chicken eggs in the EU. The value of HCB in pooled eggs sample Wuhan 1 was almost double in comparison with the highest HCB level among the collection of samples from IPEN's The Egg Report from 2005, which was 250 ng g^{-1} fat (DiGangi and Petrlik 2005).



Figure 8: Fly ash in big bags stored exposed to the elements in MSW incinerator in Hanyang city, Wuhan, China. Source: (Zhang, Huang et al. 2015).

The eggs in sample Wuhan 1 (which is the site closer to the waste incinerators in Hanyang city) showed extremely high levels of PBDD/Fs (27.3 pg WHO-TEQ g⁻¹ fat) (Petrlik 2015). There were stored open big bags with fly ash exposed to the elements for long periods in the waste incinerator premises, as we discovered in pictures from one of the articles published about this MSWI (see Figure 8); (Zhang, Huang et al. 2015). We believe this might be one of the reasons why there were such high levels of dioxins in eggs collected from the neighborhood of the waste incinerator. The houses where we collected egg samples were later destroyed and are going to be replaced by a “green belt” around waste incinerator.

Taiwan - landfill for fly ash monoliths on the south of the island – Dioxin levels in fig leaves doubled in the surroundings of the fly ash monolith landfill in comparison with an urban site. Without proper control and management, landfill sites for solidified monoliths of fly ash can pose a serious hazard not only to the surrounding environment but also people who live far away because PCDD/Fs may undergo atmospheric transport and deposit in distant areas and are therefore important to consider, concluded Wang et al. (2006) in their study.



Figure 9: One of the sites, where waste incineration fly ash is land-filled in Taiwan. Photo by Jindrich Petrlik, Arnika, January 2017.

Hurka, Czech Republic – Dioxin levels in sediments in a rural area are one order of magnitude higher than those in industrial areas of the country because of dust and potentially other releases from the reprocessing plant where fly ash from WI and a metallurgical plant has been processed for more than decade. This case study is presented in more detailed Annex (see Annex 16.3).

- (3) When residues are **landfilled/backfilled it may be cheap or good business for someone in the short term** but the eventual **clean-up (remediation) can become very expensive** later on (It simply creates new environmental burdens not to destroy POPs at the earliest opportunity).



Figure 10: This is the neighborhood area of the site in Hurka, in the Czech Republic, where different types of wastes are treated including APC residues from waste incineration and metallurgy. Airborne dust is carried out of the area and contaminates surrounding natural ecosystems. Photo by Jindrich Petrlík, Arnika, June 2010.



Figure 11: “You could smell it, you could see it, but you didn’t know what it was,” said pastor R. L. Gundy of Mount Sinai Missionary Baptist Church, who has been diagnosed with prostate cancer. Source: Morrison (2009)

Jacksonville, USA - The Jacksonville Ash Superfund site is considered “Current Human Exposure Not Under Control” because ash contaminated soil above residential remedial goals is present at or near the surface in residential areas. There are over 1,500 residential properties where the exposure pathway is direct contact with contaminated soil. ATSDR has determined that there is not an immediate health threat, but the exposure is a long-term health threat. (US EPA 2015) According to the 1990 U.S. Census, more than 30 thousand inhabitants lived in the area of four sites contaminated with ash (US EPA ROD 2006). More than 4,000 ash site residents said the city violated their civil rights, and sued for dumping ash in the predominantly poor, black neighborhoods and exposing them to health risks. The city settled for \$75 million in 2006 (Morrison 2009). A \$94 million clean-up (remediation) project has started in 2009 at the site (Morrison 2009).

Mydlovary, Czech Republic – Fly ash is used in a mixture of wastes for backfilling the lagoons remaining after uranium ore reprocessing at a plant in Mydlovary, Southern Bohemia (Czech Republic). Preparation of these mixed wastes is happening in Hurka (mentioned in another case study). In ten years there might be as much as half of the total volume (of the total amount) of dioxins concentrated in the biggest dioxin contaminated site in Europe. This is in the area of a chlorine chemical plant (Spolana Neratovice) which produced pesticides used for Agent Orange (the herbicide connected with dioxin contamination in Vietnam) and where the amount of PCDD/Fs in decontaminated material was estimated at 372 g TEQ in total (Čtk 2007). Decontamination of Spolana cost more than 2 billion Czech crowns (\$80 million).

(4) POPs in residues can **harm persons exposed to these materials**, especially workers handling WI residues and maintaining incinerators, therefore **all exposure pathways should be evaluated**.



Figure 12: Aerial photo of the lagoons remaining after uranium ore reprocessing at a plant in Mydlovary, Southern Bohemia (Czech Republic). The lagoons are already partly filled with waste mixtures including fly ash. Source: mail.oakrupkovo.cz

Osaka prefecture, Japan –The concentrations of dioxin among the blood of the workers in Toyono Gun incinerator who had engaged in maintenance of the furnace, the electric dust collector, and the wet scrubber of the incinerator were higher compared with those of residents in surrounding areas. Blood dioxins level of workers ranged from 13.4 to 805.8 pg I-TEQ g⁻¹ fat and their mean was 84.8 pg I-TEQ g⁻¹ fat. The blood dioxin level of 253 persons from several parts of Japan measured by the Environment Agency in 1998 ranged from 0.9 to 33 pg I-TEQ g⁻¹ fat (mean 19 pg I-TEQ g⁻¹ fat). Blood dioxins levels of workers were higher than those of regular residents.

- (5) Residues should not be moved across borders and left in the care of “not in my backyard” regimes with silent consent of MEAs due to **weak definition of POPs waste through Low POPs Content Level.**



Figure 13: Fly ash sample collection in waste incinerator in China showing working conditions in the waste incinerator. Source: Tang, Liu et al. (2016).



Figure 14: Small storage area of the mixture Polho made of WI fly ash. Site near village Belaruchi, Belarus in 2007. Photo by Center of Environmental Solutions (CES), Belarus.

Belaruchi, Belarus – In Belaruchi, ash waste was found which was declared as a “mining binder” called Polho, in reality it was a mixture made from WI ash and was discovered in an abandoned area near the village of Belaruchi, Belarus in 2007. That was just a small part of 5,000 tons of the mixed WI ash export granted to German company UTR to CEE countries including Poland, Belarus and Ukraine (Gluszynski 2007).

The Ufa Dioxin laboratory “Tayfun” based in Ufa has measured levels of PCDD/Fs in this mixture at 1.626 ng TEQ g⁻¹ d.m. (GU Tayfun 2007). This case shows that export of fly ash with dioxin levels over one thousand ng TEQ kg⁻¹ from developed countries to countries with economies in transition or developing countries, under the label of recycled material, is happening. This is due to very high (weak) Low POPs Content Levels so it does not breach the Basel Convention requirements. The amount of waste found in Belaruchi as construction material was low but the total amount of 5,000 tons WI ash exported from Germany in 1993 – 94 was similar to historic cases of exports from Philadelphia, USA. The **Khian Sea, a Philadelphia ship**, attempted to unload 13,000 tons of incinerator ash in



Figure 15: Pictures documenting the story of the Khian Sea odyssey where no country wanted the waste incineration ash which was finally dumped in Haiti (first photo). Photo: Essential Action, Source: Krunk (2016).

Haiti and ended up dumping some of the material in an unknown location (Godwin 1993). There were also more cases of other residues from industrial processes which were dumped in Western Ukraine and had an origin in some EU countries (Wuttke, Skrylnikov et al. 2011).

Guinea - In the late 1980s, about 15,000 tons of WI residues from municipal incinerators in Philadelphia (USA) was disposed of in Guinea. The waste which was labeled as raw material for building bricks, but was in reality, a dangerous mixture of heavy metals as well as dioxins, which was dumped on the island of Kassa near the capital of Guinea on the mainland. Officials were prompted to take action as the waste caused a noxious smell and killed vegetation. In the end, the waste was returned to the US where it was buried in a landfill (Krunk 2016). The case of the Probo Coala ship (AI and Greenpeace 2012) which brought toxic waste to the Ivory Coast (Cote d'Ivoire) shows that such cases are still happening.

- (6) It is not necessarily safe to store residues in salt water or near the sea shore in spite of certain safety measures as it can contribute to overall contamination of the seas by POPs.

Phuket, Thailand; Chengsi village, Taiwan; Cocos (Keeling) Islands, Australia cases show that waste incineration residues are often stored next to waste incineration plants located near the sea shore, often without any barrier to prevent dioxins leaking into the sea or brackish waters. This includes fly ash with PCDD/Fs content of several thousand ng TEQ kg⁻¹ (over 1 ppb). No leaching tests were conducted at such sites for leaching



Figure 16: MSW incinerator in Phuket, Thailand with small pile of ash in front. Photo by Jindrich Petrlik, Arnika, December 2010.



Figure 17: From the comparison between the photomap from 2007 (left side) and 2010 (right side), it is clear that land use has changed around the waste incinerator in Phuket. The large grey area at the south-east edge of the incinerator was an area with fly ash dumping in 2007. Source: Petrlik (2011).

into salt water. Since fishing populations generally are at higher risk than non-fishing populations (Svensson, Nilsson et al. 1995, Kiviranta, Vartiainen et al. 2002, Weintraub and Birnbaum 2008, Merlo, Desvignes et al. 2011), these risk scenarios are relevant for Asian countries, where the consumption of fish and sea food is usually high. Contaminated aquatic food chains may also affect human exposure via consumption of wild-bird eggs (Ryan, Dewailly et al. 1997). Elevated POPs levels have been found in some of the fish and shellfish samples taken in 2010 from Phuket from a mangrove area next an ash dump site. Close to the waste incinerator, levels of PCDD/Fs and DL PCBs in wild bird eggs of 6 pg BEQ g⁻¹ fat were also reported (Petrlik 2011).

- (7) WI ash from small medical waste incinerators can directly affect not only personnel of hospitals but also patients.



Figure 18: Small medical waste incinerator at Samoa. Photo by Lee Bell.

Small and medium size medical waste incinerators - e.g. Pakistan, Ghana, Cameroon, Mozambique or Peru - Ash from small medical waste incinerators which are spread over many developing countries is mostly dumped next to these incinerators in the areas around hospitals, and in some cases also at sites accessible for animals, like in Peshawar, where the ash was used to cover an old municipal waste landfill.

In Ghana, heavy metals were analyzed in incinerator ash (the incinerator is on Figure 35). The study revealed high concentrations for zinc, lead,



Figure 19: Ash pit in the garden of one of small medical waste incinerators in Lahore as it was in 2005 (see also Annex 16.4). Photo by Jindrich Petrlik, Arnika, March 2005.

chromium, and cadmium in bottom ash and these were above allowable limits for disposal in landfill. (Adama, Esena et al. 2016). As the incinerators are similar in different African countries, Mochungong used data from the Mozambique MedWI to assess environmental impact of three small waste incinerators in Cameroon. He found total levels of PCDD/Fs of 346 ng WHO-TEQ kg⁻¹ in incinerator ash from Mozambique facility (Mochungong 2011).

The incinerator in the north of the international Jorge Chavez Airport in Lima burned different kinds of waste generated in the airport and quarantine waste collected until 2001. The incinerator does not operate these days. Samples from this area were taken for analysis; the results showed the presence of 0.36 ng -TEQ g⁻¹. The ash from the incinerator was stored at a landfill in Zapallal studied in 2011 about which authors of Swedish EPA report concluded that PCDD/Fs *“levels in eggs¹⁵ and plants were clearly elevated as compared to levels in samples from reference sites. Based on homologue distribution patterns in ash and soil samples, it can be concluded that the waste site is a source for PCDD/Fs and PCBs affecting the surroundings”* (Swedish EPA 2011).

Levels observed in samples from a Pakistani MedWI in 2005 ranged between 50 and 2,514 ng WHO-TEQ kg⁻¹ (Arnika - Toxics and Waste Programme and SDPI 2006). These are not levels to which patients in hospitals should be exposed, and WI residues are often stored right next door to small MedWI installations within hospital areas. One example is visible on Figure 19.

15 Levels of PCDD/Fs in free range poultry eggs varied between 3.4 and 4.4 pg TEQ g⁻¹ fat, they exceeded current EU standard for dioxins in eggs set at 2.5 pg TEQ g⁻¹ fat.

10. EXPOSURE SCENARIOS

For establishing workable limit values for POPs in wastes, exposure scenarios should be evaluated for both the levels of evaluated POP as well as for potential disposal methods used. Fly ash with PCDD/Fs content below the **provisional Low POPs Content Level** (as defined in Basel Convention's Technical Guidelines for POPs wastes) are currently used in recycling and reuse operations (agricultural use, construction of roads, cement etc.). It is also subject to solidification and stabilization before it is landfilled or used as backfilling material as we have demonstrated in this study. Several case studies (see chapter 9) gathered from the literature or researched by IPEN and its participating organizations show **real exposure scenarios** happening at different sites in the world in both developed as well as developing countries or countries with economies in transition.

These case studies demonstrate that people living near applications of fly ash, APC residues or other kinds of wastes contaminated with dioxins below LPCL thresholds, are exposed by eating food raised on contaminated soil (exposure route **contaminated waste – soil/dust/sediment – food – ingestion by human**), by inhalation of dust originating from stored/landfilled/and handled fly ash (exposure route **contaminated waste – dust – inhalation by human**). To a lesser degree, but still a plausible route of exposure is direct digestion of soil or dust, which is more often associated with the behavior of children (pica behavior) but can be relevant also to workers at sites contaminated with dioxin-containing dust or soil where eating and smoking can lead to ingestion (exposure route **contaminated waste – dust – ingestion by human**).

10.1 EXPOSURE VIA THE FOOD CHAIN: EXAMPLE OF POULTRY EGGS

Dioxins belong to the group of chemicals to which the human body is mostly exposed via food, and eggs have been found to be sensitive indicators of PCDD/Fs and PCBs contamination in soils and are an important exposure pathway from soil pollution to humans. Eggs from contaminated areas can readily lead to exposures which exceed thresholds for the protection of human health (DiGangi and Petrlik 2005, Weber, Watson et al. 2015) as several case studies in this study demonstrate. Graphs at Figures 6 and 7 in previous chapter 9 show the example documented in Newcastle (Pless-Mulloli, Schilling et al. 2001a) where exposure to dioxin from WI ash can be proven by analyzing specific dioxin patterns.



Figure 20: The waste incinerator in Košice was the putative source of dioxin contamination of free range chicken eggs collected in 2004 the surrounding area of the facility. Source: IPEN Dioxin PCBs and Waste Working Group, Spoločnosť priateľov Zeme et al. (2005).

10.1.1 Example of PCDD/Fs exposure caused by wood preserved with pentachlorophenol

The soil may become polluted not only through airborne contaminants, but, as in this case, as a result of dioxin emissions from the wooden elements of the henhouse. Construction materials, such as preserved wood or asbestos roofing, may become a source of contaminants (Winkler 2015). High levels of dioxins were found in chicken eggs at one site in Poland and wood preserved with pentachlorophenol contaminated by dioxins (as an undesirable by-product in this chemical preservative), was found to be the major source of contamination. Chicken eggs were found to contain, in samples collected in different years, 12.5 pg WHO-TEQ g⁻¹ and (Piskorska-Pliszczynska, Mikołajczyk et al. 2014) 29.8 pg WHO-TEQ g⁻¹ fat respectively (Piskorska-Pliszczynska, Strucinski et al. 2016). The wooden building material used for henhouse contained PCDD/Fs at a concentration of 3922.60 ± 560.93 pg WHO-TEQ g⁻¹. PCDD/Fs derived from this source have polluted the ground on which laying hens were foraging. The confirmation of this supposition was the detection of pentachlorophenol in the threshing floor material (11.0 ± 2.8 µg g⁻¹). PCDD/Fs levels

in wall scrapings ranged between 0.98 and 4.39 pg WHO-TEQ g⁻¹ while the threshing floor was 47.03 pg WHO-TEQ g⁻¹ (Piskorska-Pliszczynska, Strucinski et al. 2016).

Considering that dioxin contamination of the henhouse took years, one cannot exclude the possibility that consumers of eggs that originated from that farm were constantly exposed to elevated doses of dioxins. Therefore, the estimated intakes should be regarded as the worst case but realistic scenario. This example also shows what happens **when you store “waste” containing 4 ppb of PCDD/Fs**. The result is **contamination of the food source (hen’s egg) to level more than 10-times higher than the EU standard**.

A review of a similar exposure scenario to the above demonstrated case from Poland was conducted within a Swedish EPA study (Swedish EPA 2011) and showed that a serious risk scenario is prevailing if waste wood fractions are reused as bedding or construction material in animal food production facilities. Considering that PCDD/Fs waste wood concentrations of 40-50 ng WHO-TEQ kg⁻¹ resulted in severe egg contamination (33-88 pg WHO-TEQ g⁻¹ fat (Diletti, Ceci et al. 2005), the LPCL of 15 000 ng TEQ kg⁻¹ (15 ppb) is not low enough to prevent contamination from this waste fraction. Contaminated waste wood fractions can also enter biofuel incineration facilities, resulting in higher pollutant concentrations in the residues.

10.1.2 City of Menen, Belgium

One study (Nouwen, Provoost et al. 2004) analyzed DL PCBs and dioxins in eggs, soil and vegetables around the city of Menen in Belgium. This area had a number of potential sources of POPs pollution including informal cable burning operations, a dye factory, metal recycling and pressed board manufacture. Prior to 1984 there was also the use of incinerator ash for road surfacing. Open waste fires also occurred in this area. The results of the study noted that concentrations were ranging from 12.14 to 42.18 ng WHO-TEQ kg⁻¹ d.m. Three pooled samples of six free-range eggs each contained 28.4, 31.3 and 39.7 pg WHO-TEQ g⁻¹ fat respectively. Twenty samples of vegetables including endive, beans, lettuce, pumpkins, cucumber, carrots and leek were analyzed. Concentrations varied from 0.02 to 0.15 pg WHO-TEQ g⁻¹ fw. (Nouwen, Provoost et al. 2004). The results demonstrated that egg contamination was significant but also that certain vegetables can uptake contaminants to different degrees.



Figure 21: Artisanal recycling site in Samut Sakhon, Thailand. Photo by Jindrich Petrlik, Arnika, February 2015.

10.1.3 Example of exposure to dioxins at e-waste “recycling” site in Thailand

Complex contamination by POPs can occur in residues from incineration or burning of e-waste either in controlled or uncontrolled processes. We have examined one such place in Samut, Sakhon, Thailand, where informal “recycling” workshops are concentrated in an industrial estate park. The local community burns wastes including e-waste and pick unburnt metal parts of the wastes. We have collected chicken egg samples at this site together with samples of ash and unburned residues. The level of PCDD/Fs in ash was found to be $12.8 \text{ ng WHO-TEQ kg}^{-1} \text{ d.m.}$ while in free range chicken eggs it was $84.4 \text{ pg WHO-TEQ g}^{-1} \text{ fat.}$ The eggs also contained high levels of PBDD/Fs ($19.35 \pm 3.55 \text{ pg WHO-TEQ g}^{-1} \text{ fat.}$). This example shows that levels of dioxins above 10 ppt can lead to a seriously high exceedance of the EU standard set for food although the unburned residues (ash) were most likely not the only source of egg contamination as the dioxin patterns are not fully identical as the graph at Figure 22 shows.

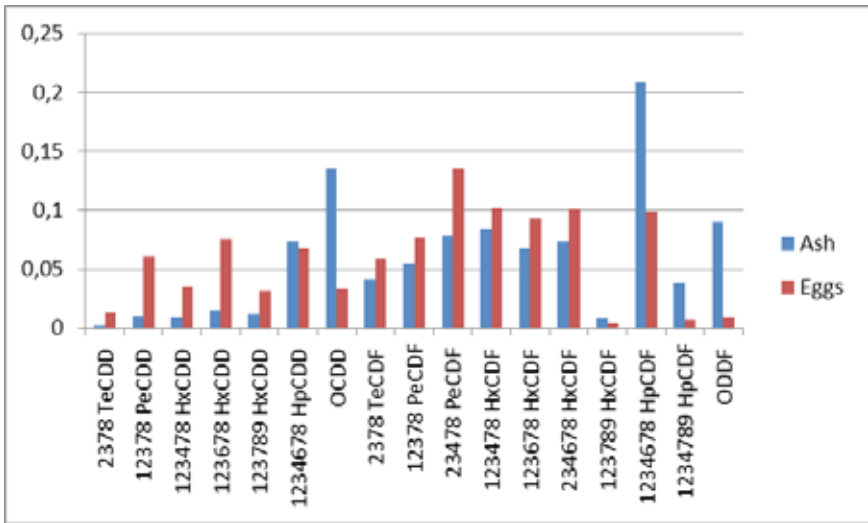


Figure 22. Dioxin congener pattern for ash and free range chicken eggs samples from e-waste and other waste metal reclamation site in Samut Sakhon, Thailand.

10.1.4 Ducks fed with waste incineration fly ash example

For incineration residues, several options for recycling and reuse seem to exist. A serious risk scenario prevails if the material is used in areas close to animal food production facilities or if the application allows direct contact with the waste by local residents or workers (Swedish EPA 2011). This was demonstrated in the example of Byker ash deposited on allotments in Newcastle documented by several reports and studies (Pless-Mulloli, Edwards et al. 2000, Pless-Mulloli, Edwards et al. 2001, Watson 2001, Pless-Mulloli 2003) and summarized also as one of the reviewed case studies in this study (see chapter 9).

Since moderately elevated environmental levels (e.g. 10-50 ng TEQ kg⁻¹ in the ground) are high enough to cause significant exposure levels for local residents living under rural conditions and relying on locally produced food, the impact from highly contaminated waste in certain areas can be detrimental if the waste is reused with limited awareness of possible consequences. Experiments with ducks that were fed with contaminated fly ash (containing 201 ng TEQ kg⁻¹ or 0.2 ppb), showed that the eggs became contaminated despite a restricted bioavailability of PCDD/Fs in solid matrices and low ash concentrations (Shih, Wang et al. 2009).

10.1.5 Conclusion for free range eggs contamination scenario

Weber et al. (2015) suggested that contamination levels in soil used for the production of free-range eggs should ideally be less than 2 ng TEQ kg⁻¹ d.m. for the sum of PCDD/Fs and DL PCBs (and certainly less than 5 ng TEQ kg⁻¹ d.m.) based on conclusions of the recent report on POPs in free range chicken eggs in Netherlands (Hoogenboom, ten Dam et al. 2014). Levels higher than this will present the risk of exceeding tolerable daily intakes for PCDD/Fs and DL PCB in humans from chicken eggs.

10.2 SOIL INGESTION EXPOSURE ROUTE

Children from communities living near unsecured landfills or storage of fly ash or APC residue also can be exposed due to their pica behavior (Moya and Phillips 2014, Watson and Petrlik 2015). Calabrese et al. for example, reported that: *“Several soil ingestion studies have indicated that some children ingest substantial amounts of soil on given days. Although the EPA has assumed that 95% of children ingest 200 mg soil/day or less for exposure assessment purposes, some children have been observed to ingest up to 25-60 g soil during a single day”* (Calabrese, Stanek et al. 1997). So by eating this amount of soil, a child of 25 kg weight can reach its TDI by ingestion of soil contaminated by PCDD/Fs and DL PCBs at level of 2 ng WHO-TEQ kg⁻¹.

This exposure route was also discussed in more in depth in the Swedish EPA report: *“For direct exposure via ingestion of soil, the levels in waste/solid matrices should probably not exceed 200-1 000 ng TEQ kg-1 for adults. This range is estimated from exposure dose calculations using assumptions for adults that must be verified, e.g. for occupational exposure scenarios. ... Results from a number of studies of soil show that if 100% internal accessibility is assumed, the exposure dose via ingestion of soil is overestimated, since the accessibility usually ranges 20-60%.”* (Swedish EPA 2011). In light of this statement our estimated level for childrens' exposure should probably also be increased to 4 – 10 ng WHO-TEQ kg⁻¹ level of PCDD/Fs and DL PCBs in soil.

11. DISCUSSION ABOUT EXPOSURE SCENARIOS AND SUGGESTIONS FOR A DEFINITION OF LOW POPs CONTENT LEVEL FOR PCDD/Fs

Exposure scenarios were taken as a key element for suggestions on Low POPs Content Level definitions for dioxins (and dioxin-like PCBs) in previous studies:

1. BiPRO (2005). Study to facilitate the implementation of certain waste related provisions of the Regulation on Persistent Organic Pollutants (POPs); (BiPRO 2005)
2. Swedish EPA (2011). Low POP Content Limit OF PCDD/Fs in Waste. Evaluation of human health risks; (Swedish EPA 2011)
3. Bell, L., et al. (2016). Assessment of POPs contaminated sites and the need for stringent soil standards for food and feed safety; (Bell, Weber et al. 2016)

The BiPRO report suggested for PCDD/Fs a Low POPs Content Level at 3 potential levels: 1 ppb, 10 ppb and 15 ppb (= 1,000 or 10,000 or 15,000 ng TEQ kg⁻¹), and 15 ppb was the level adopted by the EU, although its consultants' report stated that "*health risk might not be excluded by >1 ppb low POP content limit*" (BiPRO 2005). The major reason for selecting the 15 ppb as the LPCL in EU was the concern not to have to treat (dispose of) too much waste "*in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants*", and an explanation is given in the graph at Figure 24 showing an estimation of the volume of the waste in thousand tons that would need to be "*destroyed or irreversibly transformed*" every year after setting certain LPCL values. However **the graph (Figure 24) reflects the situation in the EU in 2005, current estimate would look different as levels of PCDD/Fs in fly ash of MSWI decreased and most likely less waste would be above 1 ppb (requiring special treatment).**

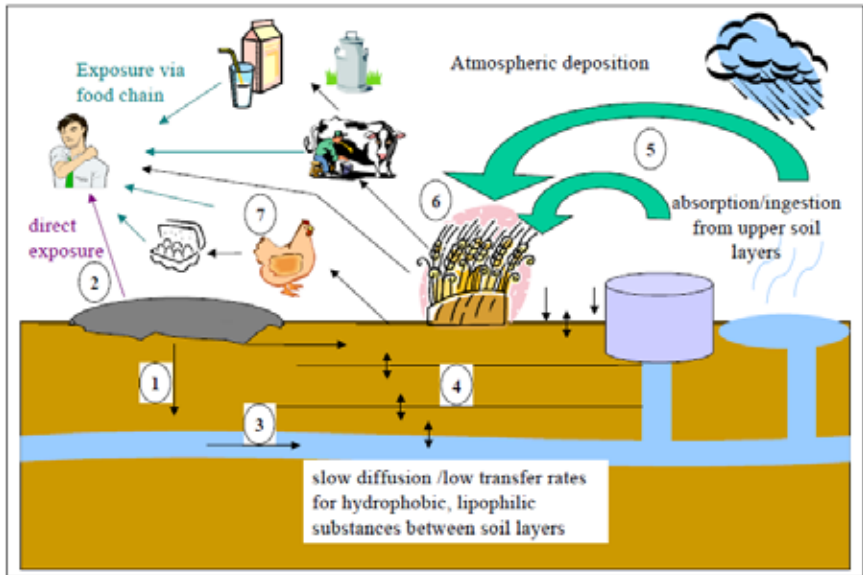


Figure 23. Exposure pathways as defined in BiPRO report.
 Source: BiPRO (2005).

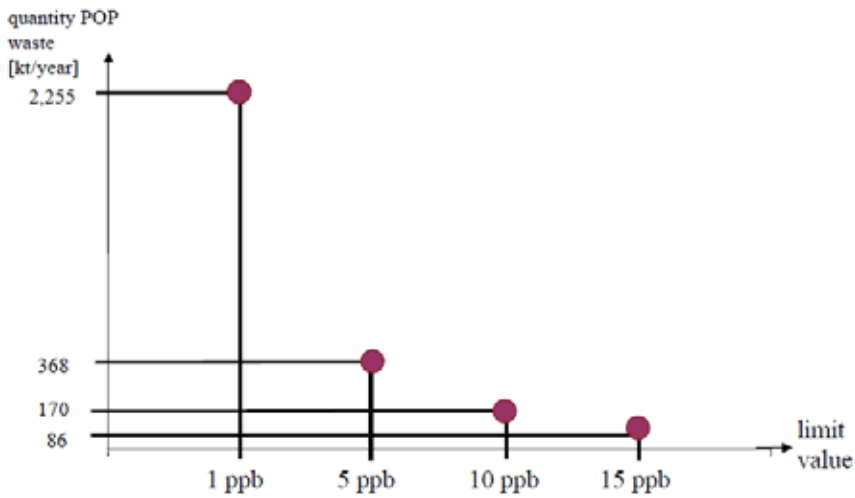


Figure 24: Estimated annual quantities of waste classified “POP waste” due to its PCDD/Fs concentration (ng TEQ g⁻¹) in relation to different low POP content limits. Reflects only the situation within EU in 2005. Source: BiPRO (2005).

The BiPRO study suggested additional measures to **ban unsolidified application of waste material to soil if the PCDD/PCDF concentration of 1 ppb is exceeded**, if 15 ppb was chosen as the Low POPs Content Level. This suggestion was based on the assumption of studies by Pless-Mulloli et al. (2001a) and by Nouwen et al. (2004) that “correlate a 7-10 pg/g fat concentration in eggs to a soil/material concentration of 0.4 - 0.9 ppb the critical value of 30 pg/g fat could be expected to be exceeded at soil/material levels of >1 ppb. The project team is aware that the calculation is loaded with considerable uncertainty. However the assessment shows that risks might exist that require specific provisions on management for all wastes exceeding levels of 1 ppb” (BiPRO 2005).

The additional measure of a ban for unsolidified application of waste material to soil if PCDD/Fs concentration of 1 ppb is exceeded **was never enforced in the EU** and neither did the EU push for this additional measure to be approved under Basel or Stockholm Convention documents.

The graph at Figure 25 shows the more rapid (efficient) uptake of DL PCBs in eggs when compared to the PCDD/Fs. It indicated that DL PCBs are a serious concern for human consumption in their own right and that in combination with PCDD/Fs represent a significant human health hazard which has not been addressed in risk assessment calculations

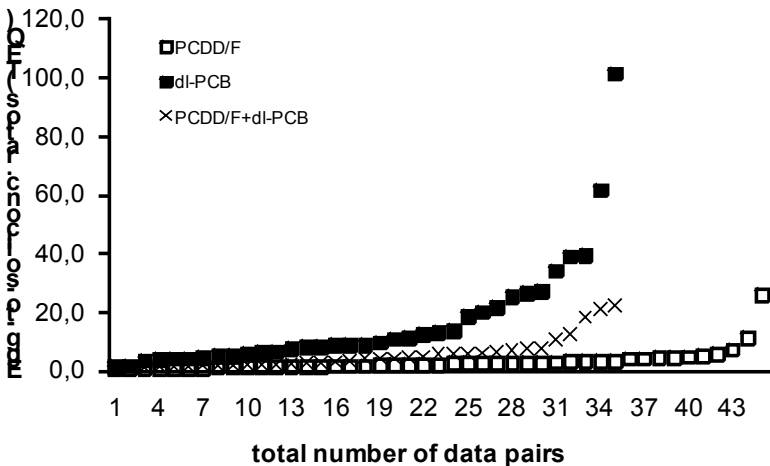


Figure 25: The transfer of DL PCBs from soil to egg is more efficient than the transfer of PCDD/Fs. DL PCBs can therefore constitute a significant risk for food chain transfer, even at low environmental concentrations. Source: Swedish EPA (2011)

when determining current Low POPs levels for waste or permissible soil concentrations.

A Swedish EPA study (Swedish EPA 2011) assumed that egg/soil concentration ratios for PCDD/Fs ranges between 0.4 and 7 (minimum level and mean + one standard deviation) demonstrating that a PCDD/Fs level of 30 pg TEQ g⁻¹ fat in egg will be exceeded at soil concentrations of approximately 4 to 75 ng TEQ kg⁻¹ d.m. and that consequently, the European maximum level of 3 pg TEQ g⁻¹ fat in eggs can be exceeded at levels that are ten times lower (i.e. 4 to 75 ng TEQ kg⁻¹ d.w.). This was found to be highly concerning as it meant that the assumed “safe” waste concentration of 1,000 ng TEQ kg⁻¹ significantly underestimates risk related to home produced hens eggs. Risk assessments that derived the “safe” level failed to incorporate DL PCBs into the assessment which are transferred to eggs at a much higher efficiency than PCDD/Fs. Most human exposure to these compounds is by diet at background levels and the margin between tolerable daily intake and levels that may be harmful is very marginal. This means that any additional source of these contaminants may result in the exceedance of safe thresholds in terms of tolerable daily intake (TDI) which is currently 2 pg TEQ kg⁻¹ b.w. Unless the full contribution of DL PCBs to dietary intake via food sources, such as eggs, is taken into account there is a significant risk that any risk assessment for TDI purposes is underestimating human exposure (Swedish EPA 2011).

Findings by Bell, Weber et al. (2016) are in agreement with Swedish EPA study “*It has recently been established that relatively low levels of PCB contamination of soil can contaminate livestock,...*” and they further continued, “*ashes from residential sources. Ashes with contamination levels as low as 50 ng TEQ/kg can be risk sources. Even if such ash is “diluted” on soils the PCDD/Fs can re-accumulate over time with repeated applications. It is therefore alarming that the current provisional “low POPs” limit established by the Basel Convention on behalf of the Stockholm Convention for dioxin contaminated waste is 15,000 ng TEQ/kg. This is far too high and needs urgently to be re-evaluated and dramatically reduced*” (Bell, Weber et al. 2016).

Other studies have demonstrated how easily contaminated wastes and recycled materials containing POPs have been able to contaminate the food chain for humans via their introduction into poultry and livestock environments as feed and bedding (Malisch 2000, Bernard, Broeckaert et al. 2002, Llerena, Abad et al. 2003, Hoogenboom, Bovee et al. 2004, Hoogenboom, Heres et al. 2009). Studies by Diletti, Ceci et al. (2005) and Brambilla, Fochi et al. (2009) demonstrated that contaminated waste wood shavings used as animal bedding resulted in egg and meat concentrations as high as 88.1 and 45.2 pg WHO-TEQ g⁻¹ fat for PCDD/Fs. This



Figure 26: Promotion of use of mixed fly ash and bottom ash as a foundation for sidewalks in the Czech Republic. Levels of PCDD/Fs in this mixture are about 0.05 – 0.1 ppb in WHO-TEQ. Source: Letter sent by company Termizo, operating MWI in Liberec to mayors in the region.

is despite the wood waste reporting only 40 - 50 ng WHO-TEQ kg⁻¹. This has particular relevance to the Low POPs Concentration Level as the authors state “*Considerable risks related to recycling of PCDD/Fs contaminated waste will therefore exist at residue levels corresponding to the suggested LPCL of 15,000 ng TEQ kg⁻¹ (15 ppb)*” (Swedish EPA 2011).

12. EXAMPLES OF LEGISLATIVE LEVELS FOR PCDD/Fs IN DIFFERENT COUNTRIES

We have demonstrated in the previous text and by numerous examples that the Low POPs Content Level for dioxins is often understood as a definition threshold between hazardous and non-hazardous waste, although it should not be perceived in that way. Scientists and engineers in several studies encourage valorization or reuse of fly ash with a content of dioxins below the LPCL (Wang, Chen et al. 2010, Dias-Ferreira, Kirkelund et al. 2016).¹⁶ However, in some developed countries there are stricter limits applied for PCDD/Fs content in wastes with a similar practical meaning as LPCL. Some legislative limit values were collected for comparison of PCDD/Fs levels measured in Guiyu (Xu, Tao et al. 2013). We have enlarged this selection and summarized them in Table 2.¹⁷ The BiPRO report listed legislative limits within EU member states prior to 2005 (BiPRO 2005). Legislation related to LPCL and POPs waste handling can also be found in Basel Convention's General Technical Guidelines for POPs waste (Basel Convention 2015).

16 E.g. "According to the Basel Convention, PCDD/PCDF levels in these materials is low (<15 mg WHO-TEQ kg⁻¹) and the fly ash and APC residue could eventually be valorized, for instance as construction material..." Dias-Ferreira, C., G. M. Kirkelund and P. E. Jensen (2016). "The influence of electro-dialytic remediation on dioxin (PCDD/PCDF) levels in fly ash and air pollution control residues." *Chemosphere* **148**: 380-387.

17 Limit values in Table 2 relate to the date of their source.

TABLE 2: EXAMPLES OF DIFFERENT LEGISLATIVE GUIDELINES FOR PCDD/Fs LEVELS IN SOIL, CONTAMINATED SITES OR WASTE. LEVELS ARE IN ng TEQ kg⁻¹

Country	Guidelines	Recommended action	Refs.
The Netherlands	1	For agricultural farming	(UNEP Chemicals 1999)
The Netherlands	10	For dairy farming	
Canada	4	Protection of environment and human health	(CCME 2002)
Germany	5	For agricultural purpose	(UNEP Chemicals 1999)
Sweden	10	For sensitive uses	
New Zealand	10	For human, plant and livestock health	(MfE and MoH 1997)
Japan	1000	The quality standard for general soil	(Government of Japan 2012)
Japan	250	The level need to survey	
Japan	150	The quality standard for bottom sediment	
Japan	3000	WI residues suitable for reclamation or recycling	(Government of Japan 2006)
Republic of Korea	3000	Waste standard (similar to Japan)	(Government of Republic of Korea 2009)
United States	1000	The remediation value of soil	(US EPA 1998)
Czech Republic	500	The remediation value of soil - living zone	
Czech Republic	1000	The remediation value of soil - recreational area	
Czech Republic	10000	The remediation value of soil - industrial zone	(BIPRO 2005)
Czech Republic	100	The level need to survey	
Sweden	250	Sensitive	
European Union	100	Sewage sludge	
Austria	100	Sewage sludge	
Austria	100	Required ESM for waste	(Stockholm Convention on POPs 2008)

Those definitions closest to the Low POP Content Level are levels set for intervention at contaminated sites and/or remediation values as these are



Figure 27: Interim storage of mixed fly ash and bottom ash from MWI Liberec, Czech Republic before its use as construction material in one of the municipalities. Levels of PCDD/Fs in this material are 0.05 – 0.1 ppb in WHO-TEQ. There used to be a prohibition not to dispose of fly ash any other way than at a hazardous waste landfill. It has changed since 2005.

levels evaluated as being so dangerous that action for cleanup of the soil (i.e. the destruction of toxic chemicals) is warranted.

Breivik, Gioia et al. (2011) warned that keeping the levels for POPs content and other legislative rules on POPs waste strict within developed countries but with less strict levels (rules) for their transboundary movement will lead to the situation which they observed in Africa. Specifically, it can lead to export of materials declared as construction materials because no regulations like Low POPs Content Level will stop them at the borders as these levels will be so high that any waste could move abroad unhindered. Gioia exposed the problem with potential exports of another problematic waste to Africa namely ships containing PCBs (Gioia, Eckhardt et al. 2011) and we have reported several cases when WI residues were the subject of transboundary movement. The aim is not to stop any movement of waste but stop movement of problematic waste to countries where there is no capacity to destroy very difficult POPs wastes as it will result in inappropriate management and environmental contamination.

There is also a need to make the Low POPs Content Level for PCDD/Fs stricter for legislative reasons, and some countries have already undertaken this initiative and set stricter limits for PCDD/Fs in wastes/contami-

nated soil than then the current LPCL. Several countries also established additional limits for dioxin content in soils or wastes for specific uses like application on soils. This level is missing in both the Stockholm and Basel Convention documents. Although the EU was advised by BiPRO (2005) to establish such an additional level (1 ppb) for PCDD/Fs in wastes for application to soil it never followed that suggestion. This level is still too high for waste that should be applied to soil.¹⁸

18 Recent studies have shown that dioxin and PCB levels in eggs from free range chickens frequently exceed EU food standards of 2.5 pg TEQ g⁻¹ fat for PCDD/Fs or 5 pg TEQ g⁻¹ fat for the sum of PCDD/Fs and dl-PCB when soil concentrations are at levels around 2 to 4 ng PCDD/F-TEQ kg⁻¹. Weber, R., A. Watson, J. Petrlik, A. Winski, O. Schwedler, C. Baitinger and P. Behnisch (2015). "High levels of PCDD/Fs, PBDD/F and PCB in eggs around pollution sources demonstrates the need to review standards." *Organohalogen Compd* 77(2015): 615-618, Bell, L., R. Weber, B. De Borst, M. C. Paun, I. Holoubek, S. Kakareka, J. Petrlik, A. Watson and J. Vijgen (2016). Assessment of POPs contaminated sites and the need for stringent soil standards for food and feed safety. Expert meeting on Best Available Techniques and Best Environmental Practices and Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional Persistent Organic Pollutants under the Stockholm Convention. Bratislava, Slovakia, 25-27 October 2016.

13. PCDD/Fs LEVELS MEASURED IN WASTE INCINERATION FLY ASH AND APC RESIDUES

PCDD/Fs levels in different types of wastes can be found in the graph at Figure 28 (Watson 2015). Concentrations of PCDD/Fs in bottom ashes, slags, boiler ash, fly ash and other APC residues are different. The highest levels of the contaminants are in the fraction of APC residues more commonly known as fly ash, although they are different in nature to other residues.

Polychlorinated dioxins in bottom ash from modern waste incinerators are at a comparable level with compost, sewage sludge and municipal solid waste, and they vary in contamination but the range of contamination is usually below 0.05 ppb and comparable with, or only one order of magnitude higher than, levels that are currently detected in the soil compartment, according to BiPRO (2005). The situation is different in smaller and older waste incinerators mostly located in developing countries and countries with economies in transition, mainly because they are partly mixed with soot and the level of dioxin content can exceed one thousand ng TEQ kg⁻¹ (see Annex 16.4), which is comparable with those observed in fly ashes from modern waste incinerators.

PCDD/Fs levels in fly ash are higher than those in bottom ash. Contamination levels on average range from 0.5-5 ppb which is 1-2 orders of magnitude higher than current soil levels and can even peak at 30 ppb according to BiPRO (2005). These wastes should be precluded from direct contact with soils (e.g. use as fertiliser) in order to prevent negative impact on the environment and human health.

Some studies found the balance of polybrominated dioxins (PBDD/Fs) opposite – higher concentrations can be found in bottom ash rather than in fly ash, although they were found in much lower concentrations than PCDD/Fs (Preud'Homme and Potin-Gautier 2002, Wang, J et al. 2009).

TABLE 3: INFORMATION ABOUT PCDD/Fs LEVELS IN WI RESIDUES IN ng TEQ g⁻¹ COLLECTED BY EU CONSULTANTS IN 2005.

Waste incinerators	Ash type	Mean	Min	Max
MSWI (EU)	Fly ash, filter dust and other APC residues	1.46	0.00	35.7
	Bottom ash	0.02	0.00	0.4
HazWI (EU)	Fly ash and APC residues	0.31	0.0002	2.4
	Bottom ash	0.01	0.0001	5.8
MedWI (EU 10)	Bottom ash	0.16	0.015	0.3
	Fly ash	2.3	0.68	4.5

Source: BiPRO (2005).

Levels of PCDD/Fs at 96,000 ng TEQ g⁻¹ (= 96,000 ppb) measured in APC residues from Toyono-Gun Clean Center, a MSWI in Osaka Prefecture, Japan, is most likely the highest level observed during last two decades in WI residues. Levels observed by BiPRO (2005) in Europe are summarized in Table 3. They appear very low for HazWI in comparison with data available either for Czech Republic or Colombia, where levels of 140 (ALS 2012) or 181.5 ng TEQ g⁻¹ (Cobo, Gálvez et al. 2009) respectively were observed in filter cake and bag filter fly ash respectively from HazWI. A range of levels between 0.244 and 24.8 ng TEQ g⁻¹ was measured in fly

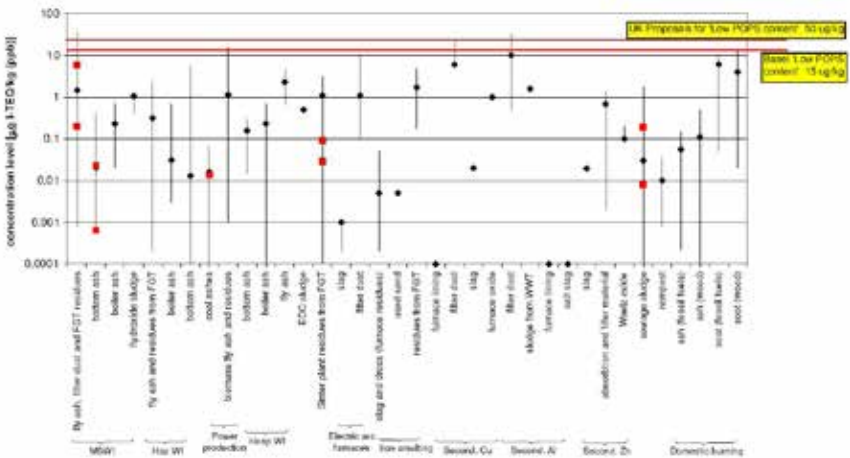


Figure 28: Graph showing range of PCDD/Fs levels in different industrial residues by Watson (2015).

ash from MSWI in Korea (Kim, Seo et al. 2005), while 0.034 – 2.500 ng TEQ g⁻¹ of PCDD/Fs and DL PCBs was observed in the fly ash of 15 MSWI in China recently (Pan, Yang et al. 2013). Higher dioxin levels in the range 9.5 – 20.4 ng TEQ g⁻¹ were found in fly ash from MedWI in China (Yan, Peng et al. 2007, Chen, Yan et al. 2008).

There is large amount of data available about levels of PCDD/Fs in WI residues, from developed countries in particular as they have better access to laboratories to measure dioxins (Ishida, Shiji et al. 1998, Shin and Chang 1999, Abad, Caixach et al. 2003, Matsui, Kashima et al. 2003, Osa-ko and Kim 2004, Mininni, Sbrilli et al. 2007, Wang, Chen et al. 2010). A broad body of data available up to 2005 was summarized in the report published by IPEN in 2005 (Petrlik and Ryder 2005). Vehlow, Bergfeldt et al. (2006) collected data about measurements from 2001 – 2004 for 47 MSWI and they observed a range of PCDD/Fs in fly ash from 0.1 – 9.4 ng TEQ g⁻¹.

14. ALTERNATIVE DISPOSAL OPTIONS FOR WI RESIDUES

Currently disposal options for WI residues are limited to landfill or deep void disposal, “valorization” (re-use as a construction or soil amendment “product”) either with or without pre-treatment to reduce leaching of metals and chemicals. IPEN does not support the generation of any ash through incineration but recognizes that there are large stockpiles of toxic ash around the world which are growing by millions of tons per annum. In order to prevent the leaching of POPs from existing and arising residues, measures must be taken by regulators to ensure that leaching is minimized while alternative, non-combustion based waste management systems that integrate with the circular economy, are implemented.

In the meantime, the problem of POPs releases from ash must be addressed. Several treatment techniques are outlined below that may potentially help meet the objective of reducing POPs emissions from WI residues. While some technologies are proven in their capacity for POPs destruction others have potential but are still at lab scale and have not been proven commercially or have not yet developed reliably high destruction efficiencies (DE).

14.1 PROVEN TECHNOLOGIES

Technologies that have been demonstrated to destroy POPs in contaminated soils have the best potential for destroying or removing POPs from ash and related residues. Generally, treatment of ash before disposal is limited to stabilization and the priority issue is to prevent metals leaching from the residue matrix. This treatment is not necessarily effective at preventing POPs leaching or being released in vapor form though it is more common that airborne particulate with adsorbed POPs is a primary form of fugitive releases to atmosphere.

14.1.1 Gas Phase Chemical Reduction

Japanese regulators from the Ministry of Environment tested the efficiency of GPCR on WI residue samples and other waste contaminated with dioxin. The result was a high DE without the generation of U-POPs.

GPCR can destroy high strength POPs in liquid, polymer and solid matrices including soil and ash.

TABLE 4: DESTRUCTION EFFICIENCY (DE) OF GPCR IN DESTROYING DIOXIN IN SOLID AND LIQUID WASTE

Matrix	Solid Material	Liquid and granular solid mix
Dioxin/furan TEQ in waste feed ng/g	6500	8.5
Dioxin/furan TEQ levels in outputs		
1. Treated material (ng/g)	0.087	0.00086
2. Scrubber water (ng/l)	0.013	0.0000021
3. Stack gas (ng/m ³)	0.0031	<0.016
Destruction efficiency % (DE)	99.99993	99.99999

Source: Hallett et al. 2013.5

The benefit of applying this technology to WI residues is that the ash component may be subject to re-use as a construction material or similar purpose however, the potential for destruction of metals in residues has not been fully tested with GPCR. So, the treatment may clear ash of POPs however they may still be subject to restricted use due to metal contamination.

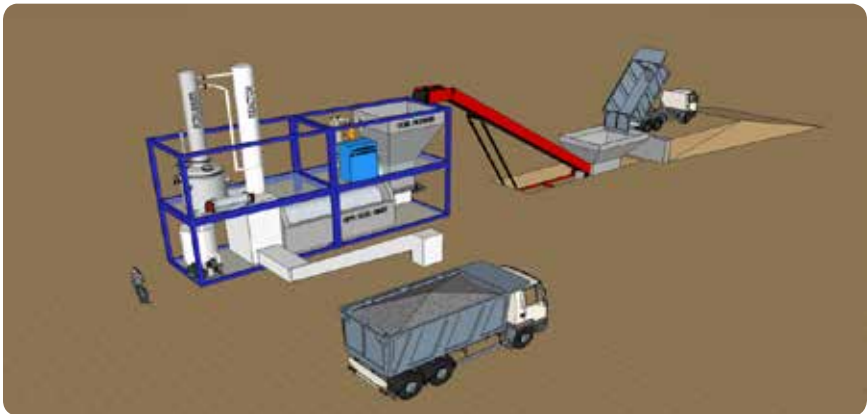


Figure 29: Semi-mobile GPCR plant designed for processing POPs contaminated soil. Source: Hallett et al. (2013)

14.1.2 Technology train – Indirect thermal desorption unit (ITDU) and Base catalyzed dechlorination (BCD)

This combination of technologies has the potential to effectively treat POPs contaminated WI residues based on its application to dioxin, PCB and other POPs contaminated soils. The two-step process requires that the bulky matrix (soil/ash) which is contaminated is fed into an indirect thermal desorption unit (ITDU). The material is heated indirectly within a vessel to the appropriate temperature causing the POPs to enter vapor phase. The POPs are then condensed to a small amount of high concentration chemical which must be destroyed in a second process. **Direct thermal desorption is not recommended** as the fuel source combustion gases will mix with the contaminated vapors requiring extensive APC equipment with high scrubbing efficiencies. Poorly operated APC on a direct thermal desorption unit will result in unacceptable emissions of POPs.

Once the small amount of condensed POPs waste has been collected it can be destroyed using a BCD process (although there are limitations with high strength POPs treatment). This technology train has been applied to the destruction of dioxin from a contaminated site in the Czech Republic. The ITDU at Spolana Neratovice, Czech Republic, heats contaminated materials to 500-600 °C stripping in absence of oxygen and POPs are collected in filter and condensation system.

According to Vijgen and McDowall (2009),

“The BCD process treats liquid and solid wastes in the presence of a reagent mixture consisting of a high boiling point hydrocarbon such as number 6 fuel oil, sodium hydroxide and a proprietary catalyst. When heated to about 300° C, the reagent produces highly reactive atomic hydrogen, which cleaves chemical bonds that confer toxicity to compounds. The residues produced from decomposition of heteroatomic compounds are carbon, and sodium salts of anions liberated during the complete decomposition reactions. After the thermal treatment reaction, the inorganic and carbonaceous solids are separated from the unreacted oil by centrifugation and drying. The oil is recovered for reuse in following treatment cycles.”

The reported destruction efficiencies for BCD in pilot runs at Spolana were very high as the data in Table 5 indicates (Kubal, Fairweather et al. 2004).



Figure 30 IDTU which was operating in Spolana Neratovice, Czech Republic. Photo by Jindrich Petrlik, Arnika, February, 2006.



Figure 31: BCD destroyed POPs as second processing step in Spolana Neratovice, Czech Republic. Source: Kubal, Fairweather et al. (2004).

TABLE 5: DIOXIN DESTRUCTION LEVELS BY BCD TECHNOLOGY IN SPOLANA NERATOVICE, CZECH REPUBLIC.

Material	Inlet ng I-TEQ kg⁻¹	Outlet Oil Matrix ng I-TEQ kg⁻¹
Chemical waste	209,000	0 (Reported value)
Chemical waste	200,000	4.3
Chemical waste	11,000	0.23
Chemical waste	47,000	0
Chemical waste	35,000	0
Dust	1,620,000	0.52
Chemical waste	78,000	0
Concentrate Aqueous	96,000	0
Concentrate Organic	876,000	0

Source: Kubal, Fairweather et al. (2004).

14.1.3 Supercritical water oxidation

Supercritical water treatment uses water in the critical temperature phase (647.3 K) and at critical pressure of 22.12 MPa to destroy POPs in differing matrices. Sako, Kawasaki et al. (2004) applied a version this process to dioxins in fly ash with dioxins extracted use supercritical fluid (CO₂) and adsorption onto activated carbon. The extracted dioxin was then destroyed by SCWO to a high level.

14.2 LABORATORY SCALE TREATMENT TECHNOLOGIES

These are technologies that have demonstrated some potential but have not reached commercial operation or exhibited sufficiently high DE at this stage of development but may be applicable to ash treatment after further development.

14.2.1 Non-thermal plasma

This is a low cost non-thermal plasma treatment which is operated under ambient temperatures. It does not suffer from sulphur or halogen poisoning. It has an interesting reaction with POPs waste (particularly with dioxin) in that the greatest destruction efficiency occurs as the concentration of the POPs increase. The highest destruction efficiency was encountered with tests on 2,3,7,8-TCDD. However the highest rate of destruction was well below regulatory standards of 99.9999% with the highest achieved level of 81% (Zhou, Yan et al. 2003).

14.2.2 UV irradiation (photolytic)

This process involves the use of semiconductor films such as TiO_2 , ZnO , CdS , and Fe_2O_3 to degrade dioxins by photocatalytic means with the application of UV or solar light. This is a low energy method operating at ambient temperature. According to Kulkarni, Crespo et al. (2008) the “*process use light to generate conduction band (CB) electrons and valence band (VB) holes (e^- and h^+) which are able to initiate redox chemical reactions on semiconductors. TiO_2 has been predominantly used as a semiconductor photocatalyst.*”

The output products from UV illuminated aqueous suspension containing 2-chlorodibenzo-p-dioxin and 2,7-dichlorodibenzo-p-dioxin was CO_2 and HCl with claimed complete degradation of the dioxin (Pelizzetti, Borgarello et al. 1988).

14.2.3 Chemical reaction

Chemical dehalogenation treatments using combination of chemical and metal reagents have had very good destruction and degradation rates for dioxins and PCBs. The use of low-valent alkali metal in alcohol, Mg and Zn /acidic or basic solution had significant dehalogenation properties (Krishnamurthy and Brown 1980). Mitoma, Uda et al. (2004) experienced excellent degradation efficiencies using metallic calcium in ethanol. Using this method PCDDs, PCDFs and PCB concentrations were significantly reduced in ethanol at ambient temperatures. The TEQ for the total residues of isomers was reduced from 22000 to 210 pg TEQ (Kulkarni, Crespo et al. 2008).

14.2.4 Sub-critical water oxidation

When water is kept in liquid form above 100°C by exerting pressure it is deemed to be “subcritical”. Water used in this form as a solvent has potential to destroy POPs in WI ash and it has been used successfully for POPs treatment on sediments (Weber, Yoshida et al. 2002).

14.2.5 Steam distillation

Steam distillation was effected with microwave energy (2450 MHz) to treat contaminated sand, humus soil, and an industrial soil sample containing jet fuel. Microwave radiation penetrates the sample and heats water throughout the matrix. The developing steam caused volatile and semi-volatile organic pollutants to be removed from the soil without decomposition. The temperature necessary for microwave induced steam distillation was less than 100°C . Microwave treatment can be adjusted to

individual waste streams: depending on the soil, the contaminants and their concentrations, remediation treatment can be conducted in several steps (“Multiple Stage Steam Distillation”) until the desired cleanup level is reached. All contaminants could be removed to non-detectable or trace levels (Windgasse and Dauerman 1992).

14.2.6 Mechanochemical degradation (ball-milling)

This low-temperature mechanochemical hydrodechlorination process was applied to fly ash coming from a municipal waste incinerator in order to efficiently remove all traces of PCDDs, PCDFs and PCBs by Mitoma, Miyata et al. (2011). The most suitable degradation agent was found to be a mixture of metallic calcium and calcium oxide. A sample of fly ash with dioxin and DL PCBs content of 5,200 pg TEQ g⁻¹ was completely detoxified (no traces of PCDDs, PCDFs and PCBs detected) after ball-milling at 400 rpm over night (Mitoma, Miyata et al. 2011).

Before the above described study a less successful PCDD/Fs destruction experiment using mechanochemical treatment was held in China on medical waste incineration fly ash. It reached results of DE around 90 – 95% (Yan, Peng et al. 2007).

A critical review of application of mechanochemical destruction method (ball-milling) concluded that it

“has the potential to be a versatile technology usable with many different kind of solid waste in effective, safe, and cheap manner. However, at the moment, additional studies are necessary to understand thoroughly the pollutant behavior during high energy milling in solid phase reactions, when they are in pure form or in complex contaminated waste matrices. In particular, the effect of different type of milling actions (i.e., different devices) has not been investigated in detail.” (Cagnetta, Robertson et al. 2016)

15. ALTERNATIVE SOLUTIONS IN WASTE MANAGEMENT

There are many alternatives to the incineration of waste and they do not create toxic emissions or generate POPs through the production of ash and other residues. In most cases, other techniques are much less expensive to establish and maintain and don't require dedicated landfills to dispose of bulk ash and residue wastes. The most comprehensive alternative technique for waste management and resource recovery is a "Zero Waste" model.

As the world begins to recognize the limits to resource extraction and consumption which is a feature of the linear economy (extract, produce, consume, dispose, repeat) proposals have emerged for the conversion to a circular economy of which the EU has been a significant driver (European Commission 2017a). In a circular economy, priority is given to resource conservation through re-use and recycling, closed loop production techniques, avoidance of excessive consumption and minimizing the ecological footprint of production in line with sustainable development. Some EU countries are actively reconsidering the use of waste incineration with the French Environment, Energy and Marine affairs Minister, Ségolène Royal calling for an end to incineration in 2014 noting "*incinerators are a completely outdated technology, we should move to a Zero Waste economy*" (Royal 2014).

A recent statement of the European Commission (European Commission 2017b) on the future of waste-to-energy facilities (which are predominantly, but not exclusively waste incinerators) in a circular European economy recommended the removal of economic incentives to incineration and recognized that ongoing funding of incineration acted as a barrier to promoting more environmentally acceptable alternatives. The measures recommended by the EC include:

- introducing or increasing incineration taxes, especially for processes with low energy recovery while ensuring they are paired with higher landfill taxes;*
- phasing out support schemes for waste incineration and, where appropriate, redirecting support to higher-ranking processes in the waste hierarchy; and*

– *introducing a moratorium on new facilities and decommissioning older and less efficient ones.*” (European Commission 2017b); see page 8 in cited document.

A “Zero Waste” model of resource sustainability emphasizes maximization of the use of organic materials through composting and anaerobic digestion (a different, non-combustion, form of waste to energy), recycling, reusing and repurposing discards, industrial design of products to facilitate recycling and employment creation based on these foundations, while minimizing waste generating processes and reducing consumption (Connett 2013, Song, Li et al. 2015, Zaman 2015).

While the implementation of comprehensive Zero Waste management programs and infrastructure can dramatically reduce the volume of materials that are directed to landfill and incineration, a small fraction of the waste stream is not suited to recycling. This is usually because the material has become contaminated by toxic compounds (either inadvertently or as a deliberate additive) so that it would be unwise to recycle and redirect into the market or environment. Some examples include electronic waste, carpets and plastics contaminated with POPs such as brominated flame retardants. Recycling of such products reintroduces POPs into the market place with a high potential for increasing human exposure in unexpected exposure scenarios such as POPs from e-waste plastic being recycled into children’s toys (DiGangi and Strakova 2016). The most obvious solution to this problem is to substitute toxic additives to such products with non-toxic alternatives, however this still leaves a stockpile of decades of material production containing toxic chemicals that must be managed.

Other wastes may become mixed with non-hazardous materials that prevent efficient recycling such as wood mixed with paints, glues and plaster from construction and demolition practices. Other mixed wastes that are difficult to recycled are textiles contaminated with oils and paints. These wastes have become known as “residual” waste that are incompatible with recycling. Traditionally the solution has been to landfill or incinerate them with or without energy recovery. The key to minimizing such waste is to prevent mixing of materials while in use to enable source separation and recycling.

Other products in their waste phase may be difficult to recycle due to their design such as multi-layer laminated plastics used in packaging for food products such as potato chips. These packages use thin laminated coating of paper, aluminium and oil based polymers. Again, the long-term solution is industrial re-design to adapt the product to a circular economy model. Research to replace products such as packaging that are based on non-renewable and non-recyclable inputs are gathering pace. In this case,

plant-based materials (Schmid, Dallmann et al. 2012) are being developed to create the same performance characteristics as the older materials which are not sustainable or recyclable.

Eventually these design innovations will align products with the circular economy based on recycling and those articles that currently form the bulk of residual waste will gradually be removed from the market. The waste incinerator industry suggests that it has a role in the circular economy and that its role is to burn “residual waste” and generate energy. The incineration industry also claims that it has a role in the disposal of difficult wastes such as hazardous waste and medical waste that should not be recycled.

As the size of the residual waste fraction declines through product redesign and better source separation activity, incinerators, which have high sunk capital costs and maintenance costs, risk becoming stranded assets in a circular economy unless they maintain steady or growing hazardous waste or medical waste stream contracts.

For both of these waste streams (including POPs waste) there are currently a range of technologies and techniques for treatment that do not involve incineration or generate unintentional POPs. Some of these technologies have also been modified to treat not only hazardous waste but the residual fraction of municipal waste. This is an important transitional element for the circular economy as no amount of product redesign and substitution will address the large stockpiles of historically contaminated waste that currently exist and will be generated in the medium term while materials substitution gathers pace. Non-combustion technologies that do not generate POPs as emissions or residues should be adopted more broadly to manage this transition. A range of non-combustion technologies for the destruction of POPs wastes (and some other wastes) are described below.

15.1 MEDICAL WASTE

In the past, the dominant form of medical and infectious waste disposal was incineration. This was usually conducted by small scale incinerators with limited pollution control mechanisms though some countries have more advanced systems. Medical waste has a high chlorine content due to the extensive use of PVC plastics in the medical sector. These act as a precursor to dioxin formation making the incineration of medical waste a significant source of POPs from emissions and releases.

The alternative to MedWI is the use of industrial scale autoclaves. The main reason that medical waste is incinerated is due to its biohazard potential from infectious materials. High pressure steam autoclaves disinfect



Figure 32: Example of a steam autoclave for medical waste.
Source: United Medical Industries



Figure 33: Sanitech microwave disinfection unit. Source: Sanitech Industries, Inc.

the medical waste removing the biological hazard from the material. The remaining material is usually landfilled. Other methods include gas sterilization, irradiation and microwave treatments (Emmanuel 2012).

A modular microwave based medical waste treatment technology developed by U.S. based Sanitech Industries shreds the medical waste and subjects it to intense steam sterilization. The shredding and disinfection process results in an inert shredded material mainly consisting of plastics

and textile derived from the medical waste. This material does not necessarily have to be landfilled and has potential to be recycled with further development.

15.2 POPs AND OTHER HAZARDOUS WASTE

15.2.1 Gas Phase Chemical Reduction (GPCR)

(Destruction/treatment of POPs waste, organic hazardous wastes, contaminated soils, medical waste, sewage sludge, municipal residual waste, incinerator residues)

This innovative technology was developed for the purpose of destroying POPs waste using a hydrogen rich environment to decompose the waste to harmless by products. A commercial plant operating in Western Australia during the 1990's was able to destroy the entire PCB stockpile for that state and a large amount of imported PCBs from other Australian states and some offshore jurisdictions. It was demonstrated to be capable of destroying all POPs to a very high DE. GPCR has been successfully utilized in range of locations to destroy a variety of POPs waste as well as chemical weapons agents. More recently, vendors for the latest generation of the technology have adapted it to destroy municipal residual waste (and gen-



Figure 34: Eli Ecologic Gas Phase Chemical Reduction plant, Kwinana Western Australia. Source: Halett (2013).

erate energy) without generating toxic ash or residuals. It can also treat sewage waste which can have significant POPs concentrations without generating unintentional POPs. In its semi-modular form the technology can be adapted to contaminated soils and medical waste.

TABLE 6: EFFICIENCY OF HALOGENATED WASTE TREATMENT USING GPCR.

Project	Con-tami-nant	Destruction and Removal Efficiency (%)	Target Criteria (%)
US EPA - Bay City (oily water - 3 tests)	PCBs	99.9999	99.9999
US EPA - Bay City (oil - 3 tests)	PCBs	99.9999	99.9999
General Motors of Canada Limited (PCB Oil - 3 tests)	PCBs	99.9999996	99.9999
	PCBs	99.9999985	
	PCBs	99.9999808	
PCB Oil (Kwinana Regulatory Testing)	PCBs	99.999998	99.9999
DDT in Toluene (Kwinana Regulatory Testing)	DDT	99.999984	99.9999
PCB Oil (Japanese Regulatory Testing)	PCBs	99.99998098	99.9999
	PCBs	99.99999977	99.9999
HCB Treatment Trials (HCB crystals - 3 Tests)	HCB	99.999999	99.9999
	HCB	99.999999	99.9999
	HCB	99.99999	99.9999
Refrigerant Treatment (CFC R-12 - 1 Test)	Dichloro-difluoro-methane	> 99.999	99.99

Source: Halett et al. (2013)

Gas Phase Chemical Reduction is one of a suite of technologies that have successfully been applied to the destruction of POPs waste over the last few decades without generating unintentional POPs emissions or releases. Table 7 provides a summary of the characteristics of a range of those technologies, their experience and availability. While GPCR has the flexibility to be applied to a range of non-POPs wastes, others may be limited in the wastes they can treat due to feed requirements or design limitations (some technologies are more efficient with liquid waste stream destruction etc.). However, all of the technologies listed in Table 7 have the capacity to treat

some of the most intractable POPs wastes as an alternative to waste incineration.

TABLE 7: NON-COMBUSTION TECHNOLOGIES FOR DESTRUCTION OF POPS WASTE.

Technology	Capable of high Destruction Efficiency (DE)	Containment of all Residues / Wastes	Commercially available	Commercial Experience with POPS	Vendors
Base Catalyzed Decomposition	Yes	High	Yes	Extensive	several
Catalytic Hydrogenation	Yes	High	Yes	Limited	Two
Gas Phase Chemical Reduction	Yes	High	Yes	Moderate	One
Solvated Electron Technology	Yes	High	Yes	Limited	One
Sodium Reduction	yes	High	Yes	Extensive	Many
Super-Critical Water Oxidation	Yes	High	Yes	Moderate	Several
Copper Mediated Destruction	yes	High	Yes	Limited	One

15.3 MATERIALS SUBSTITUTION

Article 5 of the Stockholm Convention:

“(c) Promote the development and, where it deems appropriate, require the use of substitute or modified materials, products and processes to prevent the formation and release of the chemicals listed in Annex C, taking into consideration the general guidance on prevention and release reduction measures in Annex C and guidelines to be adopted by decision of the Conference of the Parties;” (Stockholm Convention 2010)

PVC leads to increased formation of dioxins in waste incineration processes (Shibamoto, Yasuhara et al. 2007), so substitution of PVC can lead to decreased risk of contamination of the environment from municipal waste incineration processes. The Stockholm Convention still hasn't taken seriously the approach of substitution of materials that lead to formation of U-POPs such as dioxins. While the language of article 5 of the convention promotes substitution of materials that prevent the generation of POPs there are clearly loopholes in the language that allow parties discretion as to whether they will take action.

There are more materials that should be substituted in order to prevent dioxin formation than just PVC of course but this plastic is a well-known example of a dioxin formation promotor during waste incineration and its decreased use and/or ban should lead to substantial decrease of dioxins in WI residues. Wood treatment by pentachlorophenol or copper based preservatives (Tame, Dlugogorski et al. 2007) are another good example of dioxin promoters requiring substitution.

16. ANNEXES

16.1 CASE “LANDFILLS WITH MONOLITHS OF SOLIDIFIED ASH AT TAIWAN”

There are 19 MSWIs in Taiwan, which currently produce approximately 168,000 tons of fly ash per year. After solidification, the solidified monoliths of fly ash are sent to the 15 landfill sites, which often treat not only solidified monoliths but also the municipal waste or bottom ash. The solidification treatments of fly ash in Taiwan are all based on the cement solidification.

One landfill site, which co-treated solidified monoliths of fly ash and bottom ash, was investigated comprehensively to characterize its PCDD/Fs distribution. The solidified monoliths, soil, banyan (a fig) leaves, groundwater in the monitoring wells and the treated landfill leachates in this landfill site for solidified monoliths of fly ash, were all sampled to clarify their PCDD/Fs characteristics (some results are summarized in Table 8). Although the PCDD/Fs leaching concentrations were considerably lower than the Taiwan regulation for solidified monoliths, the PCDD/Fs content in the surface soils of the landfill site were 460 times higher than that of urban soils and the highest value was 2.8 times higher than the Taiwan soil regulation (1,000 ng I-TEQ kg⁻¹). Because of the organic content of the soil, the releases or leaching of PCDD/Fs from solidified monoliths had finally accumulated in soils to reach a higher PCDD/Fs content, even higher than that of the solidified monoliths.

TABLE 8: COMPARISON OF PCDD/Fs CONTENT IN MONOLITHS, SOILS AND BANYAN LEAVES OF MONOLITHS LANDFILL AREA AND REFERENCE SITE.

Site	Mean concentration	Range
Surface soils of the landfill	1,260	92.4 - 2,810
Inner soils of the landfill	437	200 - 667
Solidified ash monoliths	367	134 - 561
Soil - urban area	2.74	-
Banyan leaves - monoliths area	4.20	1.92 - 11.4
Banyan leaves - urban area	2.48	1.29 - 3.82



Figure 35: One of the sites where the WI fly ash is landfilled in south part of Taiwan. Photo by Jindrich Petrlik, January 2017.

The elevated PCDD/Fs content in the soil reveals their potential for causing adverse health risk for humans, including the pathway of resuspension of soil particles and volatilization of PCDD/Fs from soil. The PCDD/Fs concentrations in the groundwater and the treated landfill leachates of the landfill site for solidified monoliths were both higher than that in the control samples, suggesting its potential to be a PCDD/Fs source for the nearby water environment. Without proper control and management, landfill sites for solidified monoliths of fly ash can present a serious hazard to the surrounding environment and are therefore important to consider. Although only one landfill site for solidified monoliths of fly ash was chosen for this investigation. The similar solidification treatments of fly ash and landfill processes should make the obtained results representative of other landfill sites.

16.2 CASE “HOSPITAL WASTE INCINERATOR IN GHANA”

Waste incineration is the main method for treating hospital waste in many developing countries although autoclaves are increasingly used. The incinerators are usually small and do not have sophisticated air pollution control or, in some cases, any pollution control. As noted earlier in this study POPs and heavy metals in the residues are a significant environmental and public health risk. A study in Ghana (Adama, Esena et al. 2016)



Figure 36: Medical waste incinerator in Ghana. Source: Adama, Esena et al. (2016)

revealed high concentrations in mg kg^{-1} for, Zn (164.17.69), Pb (143.80), Cr (99.30), and Cd (7.54) in bottom ash which exceeded regulatory limits for landfill disposal. The study also found soils within 60m radius of the incinerator to be polluted with the metals.

The metals which were analyzed in samples for the report all exceeded U.S. EPA criteria. The incinerator ash was contaminated to a significant degree and requires treatment before disposal however, in this case the authors report that the ash is dumped in an open pit close to the incinerator. These metals which contaminated the soil surrounding the site are at risk of leaching into groundwater and surface water around the site. Inhalation of the dust from the dump area also represents a significant health risk. There is the additional hazard that it may bio-accumulate in plants or animals that wander onto the dump site. Ongoing exposure to heavy metals in ash and soil could pose a direct health risk to waste workers at the incinerator site. In addition, passersby may be at risk. There could also be a risk to locals or those further afield who consume exposed plants and animals that may have accumulated heavy metals in their tissues. Other remote receptors may be impacted by water sources contaminated with heavy metals or by the inhalation of heavy metal laden dust from polluted soils or ash according to the authors (Adama, Esena et al. 2016).

16.3 CASE “WASTE STABILIZATION IN HURKA U TEMELINA, CZECH REPUBLIC”

The waste treatment facility Hurka is operated by the company Quail spol. s r. o., carrying out biodegradation and stabilization of waste. The resulting outputs are certified products serving as a filling layers under a biological layer, or for direct reclamation of sludge-drying beds, mines, and waste landfills. Former uranium processing plant lagoons in Mydlovary is a major facility where mixed waste products from Hurka are disposed of (see chapter 9).

In 2016 Arnika has organized new round of sampling with the aim of obtaining the most recent data on pollution surrounding the premises of the facility, and on the possible origin of the pollution. The monitoring focused on PCBs, PCDD/Fs, PAHs, and heavy metals, in samples of sediments taken in the surroundings of the facility. Further, assessment of wastes accepted by the facility was carried out from the point of view of the presence of POPs, on the basis of the waste records, and the overall balance of inputs and outputs concerning dioxin content was calculated.

From a comparison of the measured concentrations of contaminants with reference sites and/or with long-term average concentrations measured in a number of various sites, it followed that many-times higher concentrations of all the monitored contaminants were present. In the case of dioxins, the concentrations were one to two orders of magnitude higher, in comparison with reference values of a clean background site in Košetice (Holoubek, Klanova et al. 2007). The concentrations of PCBs and PAHs, found in the samples, were comparable with the values from highly burdened sites - such as the Elbe river sediments in Ústí nad Labem (PCBs) and the Černý Potok stream sediments in Ostrava (PAHs). By comparing the measured contaminant concentrations with legislative criteria, it was found that concentrations of substances ranked among PAHs and dioxins, and, further, of arsenic, lead, and antimony, exceeded indicators of soil pollution for other areas, in at least one of the places where samples were taken.

The waste treatment facility Hůrka treats waste containing the monitored contaminants. Releases of the stored materials may take place, and took place occasionally, from the facility. The occurrence of the contaminants in the individual places where samples were taken suggests that material was transported from the direction of the facility. In the surroundings of the site, no other potential source of the monitored contaminants is known. From these reasons, a conclusion may be drawn that the source of the contaminants found in the sediment samples was, with the highest likelihood, the waste treatment facility Hurka. This conclusion is in ac-



Figure 37: Fly ash solidification operation in Hurka.

Source: mail.oakrupkovo.cz



Figure 38: Moisturizing of fly ash in Hurka. Source: mail.oakrupkovo.cz

cordance with the results of previous study based on analyses of sediment samples taken by Arnika in longer period from 2009 until 2014 (Nekvapilová and Straková 2016).

According to the records, fly ash from flue gas treatment from MSWI and HazWI was accepted into the waste treatment facility in 2014 and 2015. The PCDD/Fs concentrations in the fly ash from HazWI were in the range of 15,000 – 100,000 ng I-TEQ kg⁻¹. From this, it follows that the waste treatment facility accepted wastes exceeding the Low POPs Content Level of PCDD/Fs (15 ppb). However, hazardous waste incinerators contributed to the total estimated PCDD/Fs amount entering the facility by less than 25 %, according to the calculations (see below).

For the period of 2014 and 2015, the estimated amounts of PCDD/Fs inputs into the facility were in total 32.67 – 33.5 g I-TEQ. The estimated amount of PCDD/Fs leaving the facility of interest in its certified product was 3.62 – 4.02 g I-TEQ, as a sum for the both years. Thus, the total estimated input of PCDD/Fs was eight-times higher than the estimated output in the certified product, in the same period. The fate of the remaining 28.65 – 29.88 g I-TEQ of PCDD/Fs is not clear, in 2014 and 2015. MSWI fly ash showed major share of the total dioxin content in wastes entering the facility due to their bigger volume (Mach 2017).

16.4 CASE: “PAKISTAN - SMALL MEDICAL WASTE INCINERATORS”

The following case study is based on data collected in 2005. Medical waste incineration is quite a common treatment for medical wastes in Pakistan. Medical waste is burned in small scale waste incinerators without any air pollution control devices (APC) and/or with a very simple one (Khan 2001). The residual ash is buried at general dump sites such as the one near Charsadda road (near Peshawar) and/or in deep holes with very poor or no lining to prevent the leaching of toxic substances from the ashes into underground water resources (for example in Shifa International Hospital, Islamabad or in SK Cancer Hospital, Lahore.)

A small-scale waste incinerator located in LRD Hospital, Peshawar contributes to the quantity of residual ash dumped at the Charsadda road dump site, where this ash was observed to be a potential source of dioxin contamination in free range chicken eggs collected from nearby village (IPEN Dioxin PCBs and Waste Working Group, SDPI et al. 2005).

Summarized levels of dioxins and dioxin-like PCBs in WHO-TEQ ranged from 50.56 up to 2,659.46 WHO-TEQ and dioxin-like PCBs contributed to these levels from 0.01 to 5.80 % (Arnika - Toxics and Waste Programme and SDPI 2006).

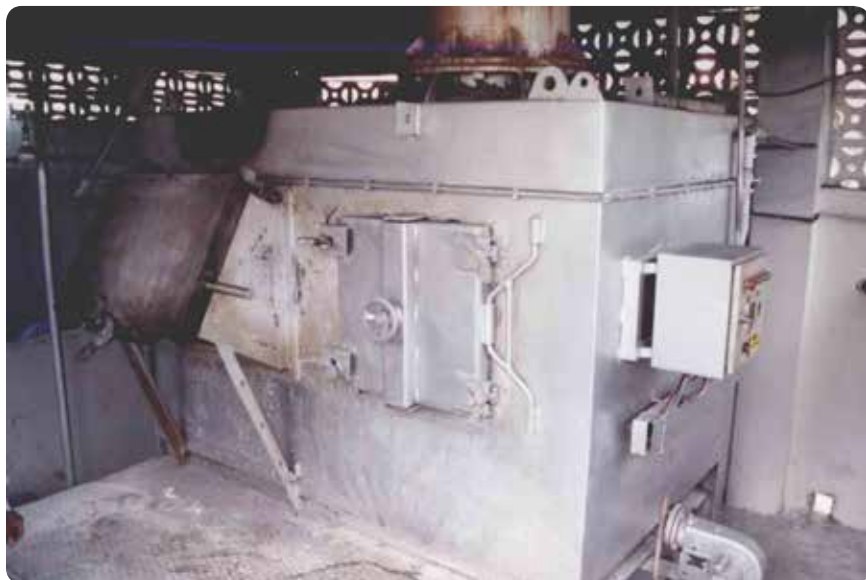


Figure 39: Double chamber furnace in one of small MedWI in Pakistan. Photo by Jindrich Petrlik, Arnika, March 2005.



Figure 40: MedW incinerator in Lady Reading (LRD) Hospital, Peshawar, Pakistan. Photo by Jindrich Petrlik, Arnika, March 2005.

TABLE 9. LEVELS OF DIOXINS (PCDD/Fs) AND DIOXIN-LIKE PCBS MEASURED IN WASTE INCINERATION AND BRICK KILN PRODUCTION RESIDUES FROM PAKISTAN IN pg TEQ g⁻¹.*

	LRD Hospital, Peshawar	PIMS Hospital, Islamabad	Queta Hospital	Al Shifa Hospital, Islamabad	Brick kiln, Ahmad Khel
PCDD/Fs (I-TEQ)	2,290.30	50.57	1,328.70	1,205.60	724.28
PCDD/Fs (WHO-TEQ)	2,513.73	50.49	1,514.65	1,272.05	823.86
PCBs (I-TEQ)	146.45	0.12	0.12	78.33	22.43
PCBs (WHO-TEQ)	145.73	0.07	0.11	77.88	22.20
WHO-TEQ	2,659.46	50.56	1,514.76	1,349.93	846.06
% of PCDD/Fs	94.49	99.77	99.99	94.20	97.35
% of PCBs	5.51	0.23	0.01	5.80	2.65

* Only detected and above LOD measured congeners included. For non-detected and below LOD measured congeners was given "0" value.

The LRD Hospital incinerator is one of 4 located within the North-Western Frontier Province. It was built using Minama technology (from a Chinese company) with two chambers without any air pollution control equipment (APC). It burns selected infectious waste from the hospital and runs for 4 - 8 hours per day with the exception of Sunday when it does not work at all. This is common in almost all other medical waste incinerators in Pakistan resulting in many start up and cool down operations occurring during the week which is the period when dioxin formation is greatest. The LRD Hospital waste incinerator was built in 2001 and is already obsolete. It burns about 250 kg of infectious waste per day. These are figures for small scale medical waste incinerators using one kiln.

There are non-combustion alternatives to waste incineration which can avoid U-POPs releases as required by the Stockholm Convention (Emmanuel and Stringer 2007, Emmanuel 2012). In the Tabba Heart Institute, Karachi there is already a suitable alternative to an incinerator installed, an autoclave.

The situation in Pakistan gives a representative picture of more developing countries (in India and/or Kenya), and it is similar to the situation described in case study from Ghana (see Annex 16.2) at the same time.

17.ABBREVIATIONS

APC	Air Pollution Control
BAT	best available technique
BCD	base-catalyzed decomposition
BEP	best environmental practice
BEQ	bioanalytical toxic equivalent
DE	destruction efficiency (used for performance evaluation by technologies treating POPs wastes)
DHM	dissolved humic matter
DL PCBs	dioxin-like polychlorinated biphenyls
d.m.	dry matter
GPCR	gas phase chemical reduction
HazWI	hazardous waste incineration (and/or incinerator)
I-TEQ	international toxic equivalent
IPEN	International POPs Elimination Network
ITDU	indirect thermal desorption unit
LAS	linear alkylbenzene sulfonate
LPCL	low POPs content level
MEA	multilateral environmental agreement
MedWI	medical waste incineration (and/or incinerator)
MSW	municipal solid waste
MSWI	municipal solid waste incineration (and/or incinerator)
NIP	National Implementation Plan
PAHs	polycyclic aromatic hydrocarbons
PBDD/Fs	polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs)
PCBs	polychlorinated biphenyls
PCDD/Fs	polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)
POPs	persistent organic pollutants
PVC	polyvinyl chloride (plastic)
SCWO	supercritical water oxidation

TDI	tolerable daily intake
TEQ	toxic equivalent (used to express dioxin levels re-calculated according their toxicity to humans and animals)
UNEP	United Nations Environmental Programme
WHO-TEQ	toxic equivalent calculated here by using Toxic Equivalence Factors (TEFs) defined by WHO expert group in 2005 (Van den Berg, Birnbaum et al. 2006)
WI	waste incineration
W-t-E	waste to energy (plants); waste incinerators using energy either for heating or electricity production

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