

POPs in hazardous waste incineration

Prof. Dr. C. Vandecasteele, Dr. J. Van Caneghem
University of Leuven, Department of Chemical Engineering, Willem de Croylaan 46, B-3001 Leuven, Belgium

Introduction

Persistent Organic Pollutants (POPs) are toxic organic chemicals. Due to a combination of their physical and chemical properties, after release into the environment, they

- remain intact for exceptionally long periods of time (many years);
- become widely distributed throughout the environment (soil, water and, most notably, air);
- accumulate in the fatty tissue of living organisms including humans, so that they are found at higher concentrations in organisms higher in the food chain.

Toxic effects of POPs can include cancer, allergies and damage to the central and peripheral nervous systems. Some POPs are endocrine disruptors, meaning that they affect systems in the human body that are controlled by hormones. In this way, they can cause sexual development problems, brain development problems, feminizing of males etc. Because cell growth and differentiation during the development of a foetus is regulated by hormones, a foetus is very sensitive to chemicals that affect the hormonal balances. Therefore, doses of endocrine disruptors that have no effect on the mother can cause severe birth defects.

The Stockholm Convention, which was adopted in 2001 and entered into force in 2004, is relative to the release of POPs into the environment. Initially the convention considered twelve pesticides and industrial chemicals; in 2009 nine new chemicals were added. To date five other chemicals, including chlorinated naphthalenes and pentachlorophenol, are under review for addition to the list. Parties that ratified the convention must take measures to

- eliminate the production and use (Annex A) of the *pesticides* aldrin, chlordane, chlordecone, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), hexachlorocyclohexane (α -, β - and lindane), mirex, pentachlorobenzene, toxaphene and the *industrial chemicals* polychlorinated biphenyls (PCBs), hexabromobiphenyl, and tetra-, penta-, hexa-, and heptabromodiphenylether;
- restrict the production and use (Annex B) of the *pesticide* DDT and the *industrial chemicals* perfluoro-octane sulfonic acid and its salts and perfluoro-octane sulfonyl fluoride;
- reduce the unintentional release of the following chemicals (Annex C): polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), hexachlorobenzene (HCB), pentachlorobenzene and polychlorinated biphenyls (PCBs).

Besides the chemicals listed by the Stockholm convention, many other substances released to the environment have persistent characteristics. Examples are unintentionally formed polybrominated dibenzo-p-dioxins, polybrominated dibenzofurans (PBDD/Fs) and phthalates (used as plasticiser).

Figure 1 gives structural formulae of some important POPs.

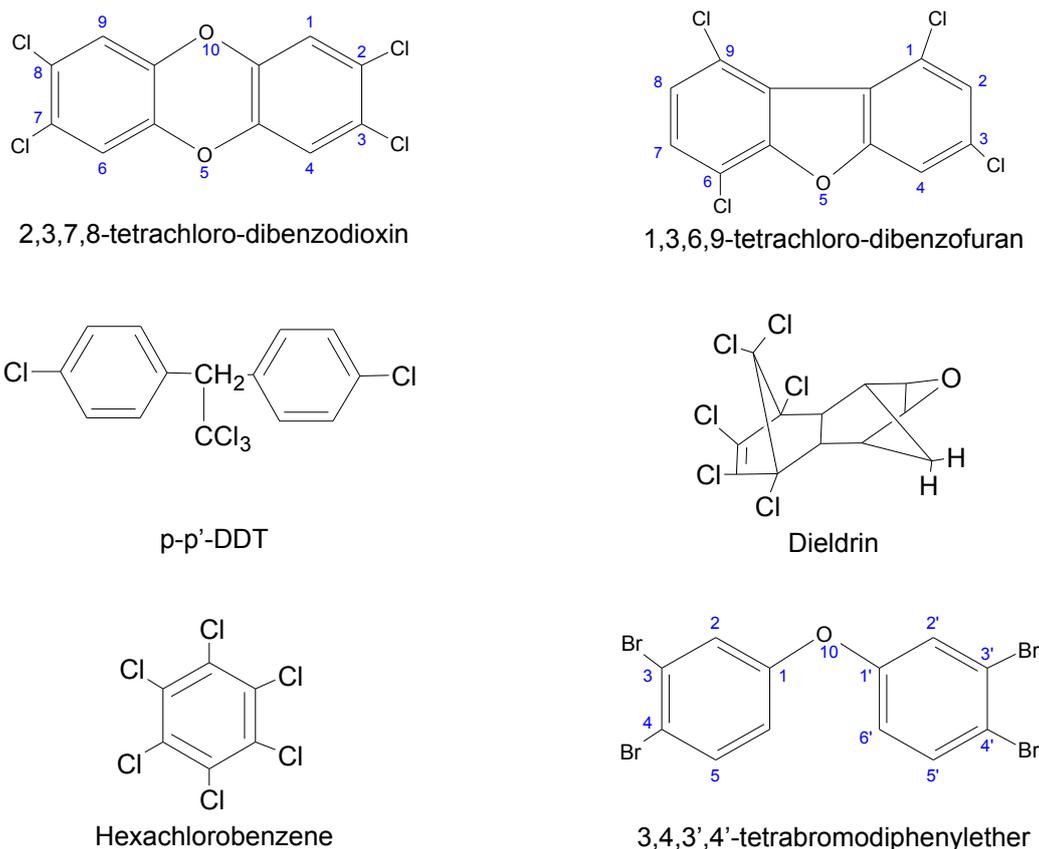


Figure 1. Structural formulae of some POPs

Sources of POPs

Chlorinated pesticides were used worldwide as insecticides until the mid-1970s, when their production and use was banned in most countries. Because of their persistence, humans are still exposed to them, mainly by eating fish, meat and dairy, which contain relatively high amounts of fat (Crinnion, 2009). In a study conducted in Texas, USA, p,p-DEE (a persistent metabolite of p,p-DDT, which is the most ubiquitous chlorinated pesticide (metabolite)) was found in the blood serum of 99.5% of the examined individuals (Crinnion, 2009). This could be related to the fact that DDT is an annex B POP and can still be used for disease vector control. Although the production and use of POP pesticides was stopped more than 30 years ago, important stocks remain, especially in the former USSR (241 000 ton), Africa (27 400 ton), Latin America (11 300 ton), Asia (6 500 ton) and in the Near East (4 500 ton) (FAO website). FAO, the Food and Agriculture Organization of the United Nations, indicates that “currently the only available technology for the destruction of most obsolete pesticides is dedicated high temperature incineration” (FAO website).

PCBs were produced between 1929 and the mid-1980s, mainly in North America and Europe. The total global production of PCBs is estimated at 1.35 million ton (Breivek et al., 2007). They were used as dielectric fluids in transformers and capacitors (closed applications) and in open applications such as ink and lubricants. Although the production of PCBs was stopped more than 20 years ago, closed applications are still the main source of PCBs to the environment. Industrial thermal processes involving carbon and chlorine and incineration of waste (containing PCBs or not), are considered less important sources (Van Gerven et al., 2004). Breivek et al. (2007) estimated the global cumulative PCB emission from 1930 to 2005 at 1.3 to 12% of the total PCB production. Food, more specifically fish, meat and dairy, is the major (> 90%) contributor to humane intake of PCBs (ATSDR, 2000).

PCDD/Fs were never produced intentionally as marketable products, but originate as *unwanted*

byproducts of industrial and thermal processes. PCDD/Fs are for example formed as an unwanted byproduct in the production of chlorinated phenols. The well-known Seveso incident in 1976 is an example of unintentional release of large amounts of PCDD/Fs. Due to an accident in a trichlorophenol production plant, a chemical cloud containing several kg of the most toxic dioxin 2,3,7,8-tetraCDD was released, directly intoxicating more than 5000 people and contaminating soil and buildings in an area of 90 ha around the plant (Hites, 2011). Besides the production of chlorinated chemicals, also thermal industrial processes, including coal fired power generation, ferrous and non-ferrous metal production, and waste incineration are known sources of PCDD/Fs. The formation of PCDD/Fs takes place at temperatures between 200 and 600°C. Two main formation routes have been proposed in literature: precursor condensation and “de novo” synthesis, as shown in Figure 2 (Altarawneh et al., 2009). A solid matrix such as a fine dust particle and a metal catalyst (typically Cu or one of its salts) are crucial for (heterogeneous) PCDD/F formation. In the precursor mechanism two precursor molecules such as chlorinated phenols and/or chlorinated benzenes combine to form PCDD/Fs. In de novo synthesis, PCDD/Fs are formed through the breakdown of a carbon matrix in a series of oxidation and chlorination steps (Everaert and Baeyens, 2002; Altarawneh et al., 2009).

Disposal options for POPs and POP-containing waste

The two main disposal options for POPs i.e. landfilling and incineration are discussed in this paragraph. Furthermore attention is given to the fate of POPs during recycling of POP containing goods such as waste of electrical and electronic equipment (WEEE).

POPs in landfills

In a recent review, Weber et al. (2011) illustrate that historically POPs were dumped in often badly engineered and unsustainably located landfill sites and dumps. Only a small percentage of the PCBs has been destroyed; between 13 and 17% is still in use in transformers and capacitors, and most of the remainder has been sent to landfills. In these landfills they may eventually leach or volatilize, thus contaminating the environment and entering the food chain. A landfill that was regularly flooded accidentally and contained approximately 20 ton of PCBs distributed in e.g. capacitors was found to be the main contamination source for fish in the Saane River, Switzerland. Also POP pesticides have been and are sometimes disposed in inadequate landfills. In Poland e.g., ten thousand ton of POP pesticides were buried in underground “cemeteries” and there is increasing evidence of groundwater contamination and of elevated concentrations of pesticides in the air around these landfills. Because of the long-term persistence of POPs, with half-lives of 100 years and beyond, also engineered landfills do not guarantee they will contain these persistent pollutants: liners and gas and leachate collection systems may degrade long before the POPs in the landfill are destroyed. The costs of the landfill aftercare required to protect the environment and humans from the toxic effects of POPs are enormous. Weber et al. (2011) conclude that POPs and other persistent toxic substances should not be deposited, but destroyed and that existing critical landfills are most likely to require remediation.

POPs and recycling

According to the EU waste hierarchy, recycling of materials is in general to be preferred over incineration with energy recovery. However, in wastes containing POPs or contaminated with POPs, the fate of these should be considered, mainly for health and safety reasons. During recycling POPs are often not destroyed and can accumulate or dissipate in the environment and eventually do harm to people. This is illustrated here for a few recycling techniques applied in Europe or in the rest of the world. Rideout and Teschke (2004) reviewed the fate of PCDD/Fs in municipal wastewater treatment sludge recycled as fertilizer on arable land. They concluded that repeated application of sludge on lands to graze cattle likely results in increased human exposure to PCDD/Fs through consumption of dairy-products and meat. Another example is recycling of plastics and printed circuit boards from electrical and electronic equipment. These components can contain high concentrations of brominated flame retardants (BFRs) including polybrominated diphenyl ethers (PBDE) (Figure 1), which are contaminated with or can act as precursor for polybrominated di-benzodioxins and furans (PBDD/Fs). In Europe, directive 2002/96/EC sets targets for the recovery, reuse and recycling of

different WEEE categories and imposes the selective removal before recycling of PCB-containing components, of printed circuit boards (> 10 dm²) and of BFR-containing plastics. However, in often rudimentary facilities for WEEE recycling in developing countries, including South-east Asia, India and China, valuable metals such as copper and tin are recovered by burning printed circuit boards with supplementary fuel in open fires. In these fires, the conditions (T, O₂, C, metal catalysts, Cl and Br) for formation and release of POPs are met. This is confirmed by numerous recent studies reporting high concentrations of PCDD/Fs, PBDD/Fs, PCBs and PBDEs in air, soil and house dust in rudimentary WEEE recycling facilities (Tue et al., 2010; Ma et al., 2009; Gullet et al., 2007) and high concentrations of PCDD/Fs, PCBs and PBDEs in hair and cord blood samples of workers in facilities for WEEE recycling in China (Zhang et al., 2010; Ma et al., 2011).

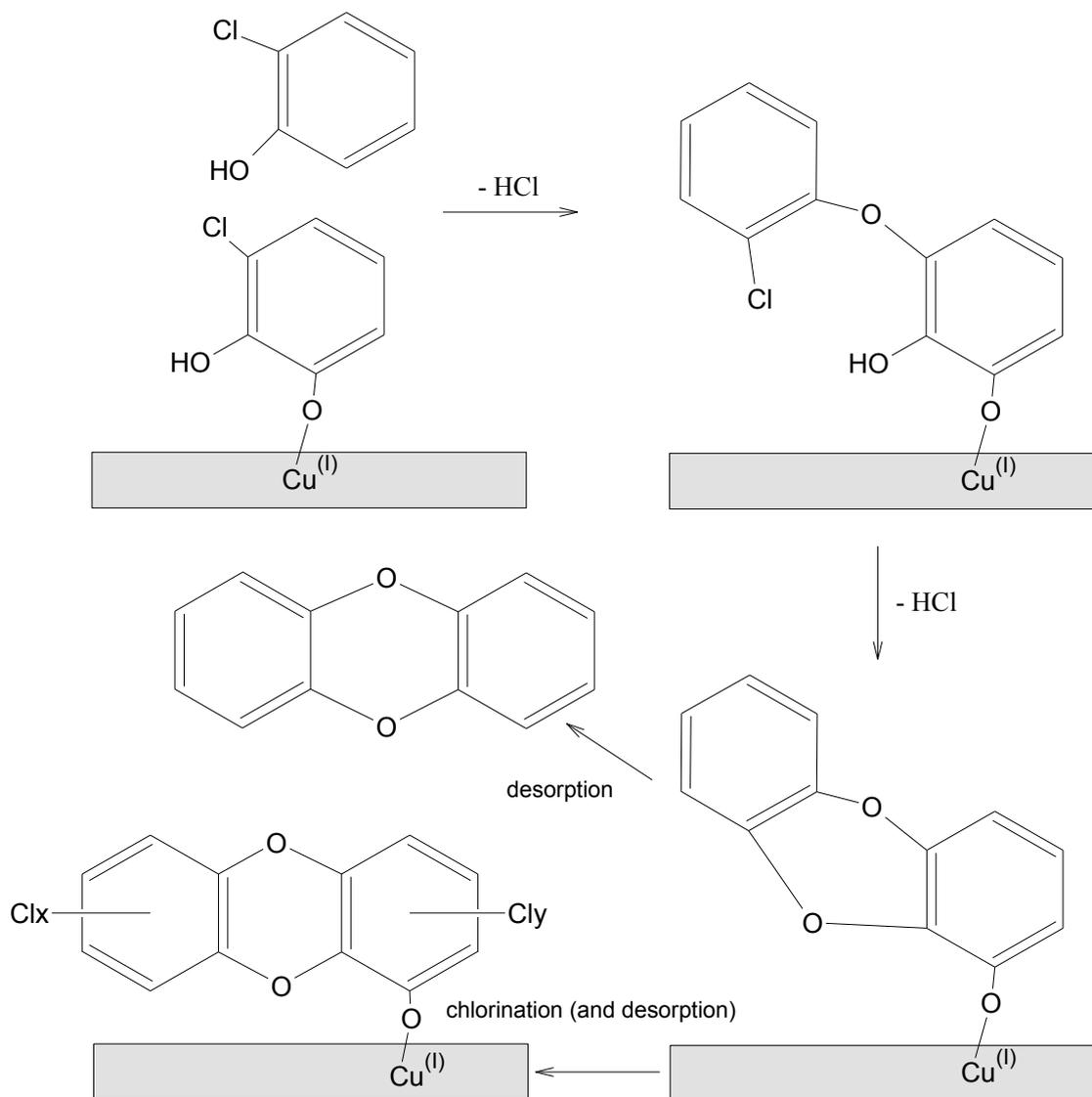


Figure 2: Proposed Eley-Rideal mechanism for PCDD formation through precursor condensation

Destruction of POPs in hazardous waste incineration

A hazardous waste mix for incineration in a dedicated waste incinerator may partly consist of annex A POPs, e.g. PCB oils from dismantled transformers and chlorinated pesticides, and/or may contain wastes contaminated with POPs, e.g. activated carbon filters used for flue gas cleaning in combustion installations, and industrial sludge. In such an incinerator, process conditions are optimized to destroy

these POPs. However, during the cooling of the combustion gases, new POPs, mainly PCDD/Fs and PCBs (Sakai et al., 1999, 2001; Abad et al., 2000, 2002) are formed (Everaert and Baeyens, 2002; Altarawneh et al., 2009). These POPs are not only emitted with the flue gases at the stack, but are also found in the incineration residues, predominantly in the fly and boiler ashes and in the flue gas cleaning residues. The challenge of hazardous waste incineration is to destroy annex A POPs as completely as possible, while minimizing the formation and release of annex C POPs.

Waste incineration was traditionally considered an important source of POP emission to air. In present state-of-the-art waste incinerators, however, both preventive measures such as limiting the flue gas residence time at PCDD/F formation temperatures, and flue gas treatment e.g. adsorption to activated carbon, minimise the presence of POPs in the flue gas emitted at the stack. Because of these measures, state-of-the-art waste incinerators easily comply with the stringent European PCDD/F emission limit for waste incinerators (0.1 ng TEQ/m³) and are only small contributors to total PCDD/F emissions. This will be illustrated by means of an installation comprising two rotary kilns for hazardous waste incineration located in Flanders (Belgium), of which the flue gas cleaning consists of an electrostatic precipitator, a four step gas washing and an active carbon dioxin filter (Figure 3). In these kilns, about 100 000 ton of hazardous waste is incinerated per year; about 1.4% of the input consists of PCBs and about 0.1% of chlorinated pesticides.

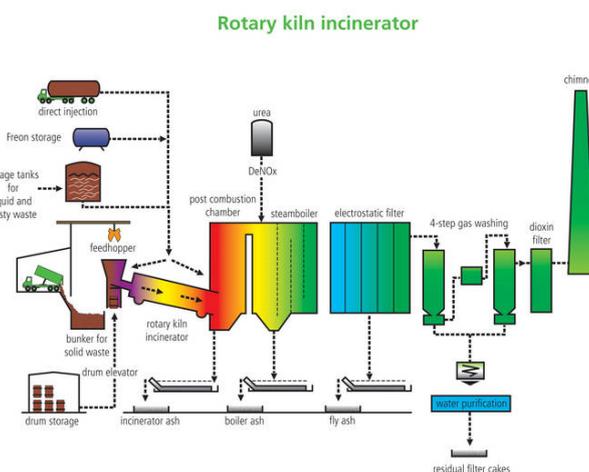


Figure 3. Schematic overview of a rotary kiln for hazardous waste incineration

Table 1 compares the amount of PCDD/Fs and PCBs emitted at the stack of the kilns with the total emission to air in Flanders. The share of these rotary kilns in the total PCDD/F emission is only 0.017%, compared to 55% for uncontrolled backyard burning of various (bio)wastes (Wevers et al., 2007). For PCBs, the main emission sources are open applications such as chlorinated rubber paint and latex paint, which account for 75% of the total emission, whereas closed applications including capacitors and transformers account for 25% (Covaci et al., 2007). The share of the considered rotary kilns in the PCB emissions is only 0.0014%.

Table 1. Comparison of PCDD/F and PCB emission in Flanders

| | PCDD/Fs (g TEQ/year) | PCBs (kg/year) |
|-----------------------------------|----------------------|--------------------|
| Emission to air of rotary kilns | 0.007 | 0.03 |
| Total emission to air in Flanders | 42.3 ^a | 2 130 ^b |
| Share of rotary kilns (%) | 0.017 | 0.0014 |

^a VMM core set of environmental data, 2010

Table 1 showed that hazardous waste incinerators are only minor sources of PCDD/F emissions to air. However, since in the past, before adequate measures were taken to reduce PCDD/F emissions, waste incinerators were known as significant PCDD/F emission sources, in some cases concern is still expressed that people living in the vicinity might be exposed to high PCDD/F doses. Several studies showed however that to date this is no longer the case, in line with the very low concentration of PCDD/Fs in the flue gases of hazardous waste incinerators. Schuhmacher et al. (2004a and 2004b) for example, determined the PCDD/F concentration in adipose tissue and breast milk of people living in the vicinity of a hazardous waste incinerator in Tarragona, Spain. Figure 4 shows that the concentration of 17 PCDD/Fs in breast milk of women living near the considered hazardous waste incinerator decreased between 1996, before the incinerator started operating, and 2002. Based on results of the study, as well as other environmental and biological data Schuhmacher et al. (2004a and 2004b) concluded that “living in the vicinity of the hazardous waste incinerator should not involve additional health risks due to PCDD/Fs”.

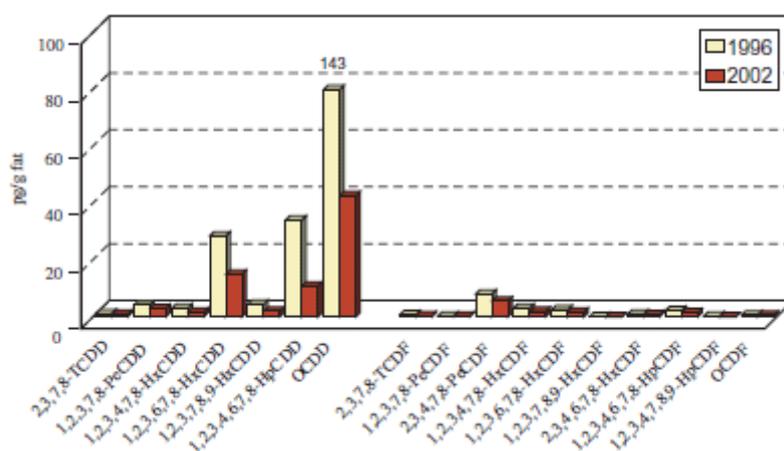


Figure 4. Comparison of PCDD/F concentrations in breast milk of woman living near a hazardous waste incinerator in Tarragona, Spain.

Many studies on destruction and formation of POPs in waste incinerators only consider POPs in the flue gas. However, also the solid outputs of hazardous waste incinerators i.e. bottom ash, boiler and fly ash and flue gas cleaning residue (FGCR), contain POPs. The POPs in the boiler and fly ash and in the FGCR are newly formed, as is the case for the POPs in the flue gas. The POPs in the bottom ash can also remain from the incinerated waste.

As mentioned, the waste input of hazardous waste incinerators may contain considerable amounts of POPs and also the flue gas and solid outputs of these incinerators contain POPs. Therefore, it is worthwhile investigating whether hazardous waste incinerators should be considered an overall POP sink or source. In an attempt to answer this question, Van Caneghem et al. (2010a) compared the amount of PCBs in the input (i.e. the waste to be incinerated) with the amount in the outputs of state-of-the-art rotary kilns for hazardous waste incineration. Next to POPs in the flue gas, also POPs in bottom ash, boiler and fly ash, and flue gas cleaning residue (FGCR) were considered. Van Caneghem et al. (2010a) concluded that the input waste contained about 235 million times more PCBs than the flue gas emitted at the stack and at least 13 000 times more than all incinerator outputs together. These figures correspond to a PCB destruction and removal efficiency of 99.999998% and a destruction efficiency of at least 99.992%. For other POPs, e.g. PCDD/Fs, it was not possible to draw up a mass balance since the amounts of PCDD/Fs in the input could not be accurately determined given the heterogeneity of the waste.

In addition to this comparison, Van Caneghem et al. (2010a) developed a methodology to compare the total amount of POPs -and not only the different POP groups separately- in the inputs and outputs of waste incinerators. In this methodology, the masses of the different POP-groups are multiplied with a weighing factor based on minimal risk doses (MRDs¹) for non-cancer effects or based on potency factors² for cancer effects and are then aggregated to give an overall weighed POP mass. The ratio of the total weighed POP mass in the input and the total weighed POP in the output indicates to which extent a waste incinerator is a POP sink or source. Table 2 gives the input over output ratios for the considered rotary kilns, when the following POP-groups were included for the determination of the total weighed POP masses: PCDD/Fs, dioxin-like PCBs, PCBs, hexachlorobenzene (HCB) and polyaromatic hydrocarbons (PAH). A distinction is made between POPs in the flue gas, which are emitted directly into the environment and POPs in the solid residues, which are solidified to prevent leaching of toxic substances and landfilled on a class I landfill, specially designed to prevent the solidified waste from entering into contact with the environment. The figures in Table 2 clearly demonstrate that the rotary kilns are a POP sink, in all cases considered.

Table 2. Weighed POP input/output ratios for state-of-the-art rotary kilns

| Ratio | Weighed with MRD | Weighed with Potency factor |
|---------------------------|-----------------------|-----------------------------|
| Input/output via flue gas | 7 200 000 – 7 600 000 | 118 000 – 470 000 |
| Input/total output | 3 200 – 50 000 | 890 – 17 000 |

Table 3 gives the contribution of the different POP groups to the total weighed POP mass in the input and output of the considered rotary kilns. If the POP masses are weighed with MRDs, considering only non-cancer effects, PCDD/Fs, dioxin-like PCBs and PCBs contribute significantly to the total weighed POP mass. The contribution of PAHs (which although not strictly POPs were also considered) and HCB is in this case negligible. If the carcinogenicity of the POPs is however taken into account (POP masses weighed with cancer potency factors), also PAHs play an important role in the total weighed POP output;

Table 3. Contribution of different POP groups to total weighed POP output

| Contribution to total output (%) | PCDD/F | Dioxin-like PCBs | PCBs | PAH | HCB |
|--|---------|------------------|----------|--------|----------|
| POP masses weighed with MRDs | 20 - 90 | 10 - 55 | 1 - 25 | < 0.1 | < 0.1-3 |
| POP masses weighed with cancer potency factors | 20 - 85 | 10 - 60 | <0.1 - 7 | 5 - 15 | <0.1 - 2 |

General conclusions

- Incineration is the only treatment option for POPs or wastes containing or contaminated with POPs that destroys these persistent pollutants and prevents them from (re-)entering the environment and eventually the food chain.
- Hazardous waste incinerators that incinerate PCBs and pesticides along with other types of waste, are significant POP sinks.
- Due to adequate process measures and flue gas cleaning, the PCDD/F concentration in the flue gas of hazardous waste incinerators remains well below the European legal limit of 0.1 ng

¹ estimate of the amount of a substance, expressed in mg/ (kg_{body weight}·day), which can be ingested daily over a lifetime by humans without adverse non cancer health effects

² risk of developing cancer produced by a lifetime average daily dose of 1 mg/ (kg_{body weight}·day)

TEQ/m³.

- Emissions of PCDD/Fs and PCBs to air by hazardous waste incineration have only a very small share in the total PCDD/F and PCB emissions in industrialized countries.
- Living in the vicinity of a hazardous waste incinerator should not involve additional health risks due to PCDD/Fs or other POPs.

References

Abad E., Adrados A., Caixach J., Fabrellas B., Rivera J. Dioxin mass balance in a municipal waste incinerator. *Chemosphere* 40 (2000) p 1143-1147.

Abad E., Adrados A., Caixach J., Rivera J. Dioxin abatement strategies and mass balance at a municipal waste management plant. *Environmental Science and Technology* 36 (2002) p 92-99.

Altarawneh M., Dlugogorski Z., Kennedy E., Mackie J. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). *Progress in Energy and Combustion Science* 35 (2009) p 245-274.

ATSDR (Agency for Toxic Substances and Disease Registry). Toxicological profile on PCBs (2000). Available at <http://www.atsdr.cdc.gov/toxprofiles/index.asp>

Brevik K, Sweetman A, Pacyna JM, Jones KC. "Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 3. Update". *Science of the Total Environment* 377 (2007), 296–307.

Covaci A., Roosens L., Weijs L., Van Volsem S., Van Hooste H. MIRA (2011) Milieurapport Vlaanderen, Achtergronddocument 2011, Verspreiding van PCB's. Vlaamse Milieumaatschappij, www.milieurapport.be

Crinnion WJ. Chlorinated pesticides. Threats to health and importance of detection. *Alternative Medicine Review* 14 (2009) p 347-359.

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

Gullet BK., Linal WP., Touati A., Wasson S., Gatica S., King CJ. Characterization of air emissions and residual ash from open burning of electronic wastes during simulated rudimentary recycling operations. *Journal of Material Cycles and Waste Management* 9 (2007) p 69-79

Hites RA. Dioxins: An overview and history. *Environmental Science and Technology* (2011) 45 p 16-20.

Ma J., Addinck R., Yun S., Cheng J., Wang W., Kannan K. Polybrominated dibenzo-p-dioxins/dibenzofurans and polybrominated diphenylethers in soil, vegetation, workshop-floor dust and electronic shredder residue from an electronic waste recycling facility and in soils from a chemical industrial complex in Eastern China. *Environmental Science & Technology* 43 (2009) p 7350-7356

Ma J., Cheng J., Wang W., Kunisue T., Wu M., Kannan K. Elevated concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans and polybrominated diphenyl ethers in hair from workers at an electronic waste recycling facility in Eastern China. *Journal of Hazardous Materials* 186 (2011) p 1966-1971

Rideout K., Teschke K. Potential for increased human foodborne exposure to PCDD/F when recycling sewage sludge on agricultural land. *Environmental Health Perspectives* 112 (2004) p 959-969

- Sakai S., Ukai T., Takatsuki H., Nakamura K., Kinoshita S., Takasuga T. Substance flow analysis of coplanar PCBs released from waste incineration processes. *Journal of Material Cycles and Waste Management* 1 (1999) p 62-74.
- Sakai S., Hayakawa K., Takatsuki H., Kawakami I. Dioxin-like PCBs released from waste incineration and their deposition flux. *Environmental Science and Technology* 35 (2001) p 3601-3607.
- Schuhmacher M., Domingo J.L., Hagberg J., Lindström G. PCDD/F and non-ortho PCB concentrations in adipose tissue of individuals living in the vicinity of a hazardous waste incinerator. *Chemosphere* 57 (2004) p 357-364.
- Schuhmacher M., Domingo J.L., Kiviranta H., Vartiainen T. Monitoring dioxins and furans in a population living near a hazardous waste incinerator: levels in breast milk. *Chemosphere* 57 (2004) p 43-49.
- Tue NM., Suzuki G., Takahashi S., Isobe T., Trang PTK., Viet PH., Tanabe S. Evaluation of dioxin-like activities in settled house dust from Vietnamese E-waste recycling sites. Relevance of polychlorinated dibenzo-p-dioxin/furans and dioxin-like PCBs. *Environmental Science & Technology* 44 (2010) p 9195-9200
- Van Caneghem J., Block C., Van Brecht A., Wauters G., Vandecasteele C. Mass balance for POPs in hazardous and municipal waste incinerators. *Chemosphere* 78 (2010a) p 701-708.
- Van Caneghem J., Block C., Van Brecht A., Van Royen P., Jaspers M., Wauters G., Vandecasteele C. Mass balance for POPs in a real scale fluidised bed combustor co-incinerating automotive shredder residue. *Journal of Hazardous Materials* 181 (2010b) p 827-835.
- Van Gerven T., Geysen D., Vandecasteele C. Estimation of the contribution of a municipal waste incinerator to the overall emission and human intake of PCBs in Wilrijk, Flanders. *Chemosphere* 54 (2004) p 1303-1308.
- Vlaamse Milieumaatschappij (VMM) Kernset milieudata (Core set Environmental Data), available at www.milieurapport.be/nl/feitencijfers, accessed september 2011
- Weber R., Watson A., Forter M., Oliaei F. Persisten organic pollutants and landfills – a review of past experiences and future challenges. *Waste Management & Research* 29 (2011) p 107-121
- Wevers M., De Fré R., Schoeters G., Matheeussen C., Van Hooste H. MIRA (2007) Milieu- en natuurrapport Vlaanderen, Achtergronddocument 2007, Verspreiding van POV's. Vlaamse Milieumaatschappij, <http://www.milieurapport.be/AG>
- Zhang J., Jiang Y., Zhou J., Wu B., Liang Y., Peng Z., Fange D., Liu B., Huang H., He C., Wang C., Lu F. Elevated body burdens of PBDEs, dioxins and PCBs on thyroid hormone homeostasis at an electronic waste recycling site in China. *Environmental Science & Technology* 44 (2010) p 3956-3962

Useful websites

<http://chm.pops.int/default.aspx>

<http://www.fao.org/agriculture/crops/obsolete-pesticides>

<http://www.febelauto.be>

