

## Summary of Session “Non-Thermal Sources and Source Inventories”

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This session covers two broad areas: non-thermal sources of POPs and release inventories. Within the non-thermal sources, three areas can be identified namely, issues related to polychlorinated biphenyls (PCB), to polybrominated flame retardants (BFR) and electronic waste, and to non-combustion sources of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF). With respect to the inventories, there are some papers that present “full inventories” and others address to one or a few sectors to increase the database for future inventory making. Within both areas, the thermal sources are the focus of concern.

### Non-thermal sources:

Three papers address **PCB**. Zenegg *et al.* summarize the results of PCB measurements in 1,348 sealants present in Swiss buildings, which were built between 1950 and 1980. A screening test for the presence of chlorine was applied and positive samples were analyzed for PCB by conventional GC/MS or GC/ECD methods. PCB could be quantified in 647 samples whereby 48 % of these had concentrations greater than 20 mg/kg; and 567 were greater than 50 mg/kg. The majority of the joint sealants exhibited a profile of medium chlorinated PCB mixtures similar to Clophen A50, Aroclor 1248 or 1254. Especially buildings erected between 1970 and 1975 showed the highest concentrations (more than 0.1 g PCB/kg). The authors estimate that there are still between 50 and 150 tons of PCB present in Swiss buildings. PCB in joint sealants are an important source of PCB indoor pollution, which was confirmed in this study. The mean concentration from 160 samples was 0.79 µg PCB/m<sup>3</sup> (median = 0.41 µg PCB/m<sup>3</sup>). The tentative Swiss guideline concentration for PCB in indoor air of 6 µg/m<sup>3</sup> was exceeded only in one case. Switzerland as a Party to the Stockholm Convention on POPs has to take legal measures to address PCB in sealants and therefore has issued guidelines to address renovation or torn down of PCB-containing constructions as well as documentation for disposal and technical guidelines on improving emission control. Yamashita *et al.* performed congener-specific analyses of the technical PCB mixtures, such as Chlorofen from Poland, and analyzed for PCDD, PCDF, and polychlorinated naphthalenes (PCN). At a limit of quantification of 0.01 µg/g, no PCDD and no tetra- through hexachlorinated PCDF could be quantified in Chlorofen. The concentrations of C<sub>7</sub>DF and C<sub>8</sub>DF were equivalent to 44.7 ng TEQ/g of Chlorofen. 97 % of the 353 µg/g of PCN came from the octachlorinated congener. Taniyasu *et al.* analyzed technical Clophen A60. The PCB profile was dominated by hexa- and heptachlorinated homologs. Tetra- through octachlorinated PCDF were quantified to 12 µg PCDF/g of Clophen A60 equivalent to a TEQ of 595 ng/kg. Dioxin-like PCB contributed to 89 % of the total TEQ of 5,908 ng TEQ/kg of Clophen A60.

Two papers address BFR. Schlummer *et al.* analyzed five polymer mixtures and four mixed WEEE (waste electric and electronic equipment) polymer fractions for polybrominated dibenzo-*p*-dioxins (PBDD) and polybrominated dibenzofurans (PBDF) and compared with the German threshold limits of 1 µg/kg for the sum of the four Br<sub>4</sub>/Br<sub>5</sub> DD/DF and of 5 µg/kg for the sum of six low-brominated PBDD/PBDF. The concentrations in all nine samples exceeded at least one of the limit values what means that the products are not allowed to be placed on the market. The concentrations of four BFR, namely tetrabromobisphenol A

(TBBPA), decabromodiphenyl ether (DecaBDE), octabromodiphenyl ether (octaDBE) and 1,2-bis-tribromophenoxyethane (TBPE) were identified at percentages between 0.25 and 2.5 % in housing-based samples and between 0.1 and 0.7 % in mixed WEEE polymers. OctaBDE was found in three of the five housing samples at concentrations exceeding the 0.1 % threshold set in EU Directive 2003/11/EC. No correlation was found between concentration of BFR and PBDD/PBDF. These findings on the presence of BFR and PBDD/PBDF may have consequences for the waste disposal/material recovery policies in the European Union. Borgnes *et al.* report results from incineration tests in Norway, Sweden, and Germany on the emissions of polychlorinated and polybrominated dibenzodioxins and dibenzofurans. The work was done in the context of Norwegian plans for the reduction of emissions of BFR. The emission results for PCDD/PCDF and PBDD/PBDF from the large-scale waste incinerators showed that the incineration efficiency and operating conditions of the flue gas treatment equipment are of greater importance than the bromine input.

Four papers address **non-thermal sources**. Dudzinska *et al.* measured PCDD/PCDF in leachates from a modern landfill in Poland. Samples were taken in 2003 and 2004 from two basins of the landfill. The concentrations in the leachates from the older Basin 1 were 36 and 26 ng WHO-TEQ/L, respectively, and 7.8 and 22 g WHO-TEQ/L for the newer Basin 2, respectively. The authors conclude that PCDD/PCDF concentrations in landfill leachates may play an important role in dioxin mass balances. Mariani *et al.* investigated bioexsiccation as a new technology for the treatment of municipal solid waste. PCDD/PCDF were analyzed at such a plant in Italy before and after the biofilter and in nearby ambient air. Two sampling campaigns were performed, the first in November 2002 and the second in March 2003. Interestingly, higher concentrations were found in ambient air (0.092-0.181 pg ITEQ/m<sup>3</sup>) than before (0.042-0.129 pg ITEQ/m<sup>3</sup>) and after the biofilter (0.033-0.036 pg ITEQ/m<sup>3</sup>). Boštjan *et al.* analyzed six disperse dyes for PCDD/PCDF. The two black dyes, chemically they were mixtures of anthraquinone and azo substances, had concentrations of 50 and 170 ng WHO-TEQ/kg; the profile was dominated by C<sub>18</sub>DD. A third dyestuff had 10 ng TEQ/kg whereas the PCDD/PCDF concentrations of the remaining three samples were below the limit of quantification (5 ng/kg per congener). Further, two dyeing experiments were conducted at a laboratory scale utilizing Dye 1. After the dyeing and finishing process, the C<sub>18</sub>DD and TEQ concentration were increased compared to the input (in absolute values): input = 15 pg TEQ; output = 73 pg TEQ. The authors conclude that in the textile process, PCDD/PCDF and especially C<sub>18</sub>DD are formed, most probably from precursors. Finally, Dyke and Amendola estimated the PCDD/PCDF release from chemical production facilities that use large quantities of chlorine. Six companies with 22 production sites participated in the evaluation. It was found that PCDD/PCDF releases could not be attributed to single production processes since effluents or wastes are typically routed to central units for treatment. In general, the database was more complete for releases to air and water than with wastes. Changes were identified especially at plants that have upgraded the hazardous waste incinerators to meet the requirements of the Clean Air Act. The results will feed into the dioxin release inventory developed by US-EPA.

### Source Inventories:

Two presentations address **regional or global release inventories**: Quass *et al.* estimated PCDD/PCDF releases in 13 EU candidate countries. They use top-down approaches by applying activity rates split into the European NFR categories and emission factors from UNEP's Toolkit. With this approach the first regional air emission inventory gave 3,300 g TEQ/a released from four main source categories, namely energy production, metallurgical and mineral productions (summarized as "industrial production"), waste treatment, and

fires/wood preservation. In order to reduce uncertainty, an emission measurement program has started and first results are available. These measured data from Polish in the metal sector and cement works in Estonia were in good agreement with emission factors from the Toolkit. Fiedler presents five national PCDD/PCDF release inventories where the emissions to air, water, land, products, and residues were estimated by applying the UNEP Toolkit. Uncontrolled combustion processes such as open burning of domestic waste and agricultural/forest fires typically dominate releases to air. With the present emission factor, the use of biomass for cooking and energy generation seems to be an important source of PCDD/PCDF as well as hospital waste incineration. So far, the experience has shown that it is not possible to determine one common emission factor per person and year for developing countries. The emissions to air vary between 0.2 µg TEQ per year and inhabitant (for Vietnam) and 22 µg TEQ per year and inhabitant (for Argentina).

**National inventories or sectorial/regional** considerations are presented in several papers: Jin *et al.* report the PCDD/PCDF emission inventory from China, which has been established as a contribution of its reporting under the Stockholm Convention on POPs. The total releases were estimated between 7,144 and 13,575 g TEQ per year to all release vectors. The central estimate of the emissions to air was 2,773 g TEQ/a. With more than one billion populations, waste generation and waste management is a major problem in China and thus, this activity is a major polluter to air. Other important sources to air include sinter plants, iron and steel industry, cement kilns, and crematoria. Sludges from chloralkali plants, the pulp and paper industry and production of pentachlorophenol/pentachlorophenate have to be mentioned when considering aqueous and solid releases.

Müller *et al.* present data from sugarcane fires in laboratory and field experiments, Queensland, Australia. Special sampling equipment has been developed and applied to catch the smokes from the rapidly spreading sugarcane fires. Emission factors – including PCDD, PCDF, and dioxin-like PCB - from about 1 pg TEQ/g C to about 20 pg TEQ/g C were found whereby the field experiments generated the lower ones (up to 2.9 pg TEQ/g C). Interestingly, in the laboratory experiments, the PCDF-based TEQ share was 52 % but in the field measurements, the PCDF contributed only with 8 % to the total TEQ. In addition, the “fire behavior” was different in field and laboratory experiments. The results imply that emission inventories using emission factors obtained from laboratory study may overestimate the emissions from this activity. Fabrellas *et al.* analyzed 89 samples from 41 furnaces of the Spanish cement industry, which represent 70 % of the national production capacity. All emissions were below 0.1 ng TEQ/m<sup>3</sup> and the use of refuse-derived fuels did not increase the emissions. The emission factors to air were calculated to be between 37 and 29 ng TEQ/t of clinker or cement, respectively. From the 30 or 40 million tons of clinker or cement, respectively, produced annually in Spain, the air releases from this sector was calculated to 1.07 g TEQ for the year 2002. Aries *et al.* report PCDD/PCDF and PCB emissions from iron ore sintering in three integrated steel plants. The mean concentrations from the three plants were 1.15, 1.08, and 1.07 ng I-TEQ/m<sup>3</sup> and 0.098, 0.65, and 0.054 ng TEQ/m<sup>3</sup> for the dioxin-like PCB. Thus, the PCB only contribute between 5 % and 11 % to the total TEQ. From these results, an annual emission of 29 g TEQ/year from UK sinter plants can be estimated, whereby only 2 g TEQ per year are from dioxin-like PCB. First results are presented from hospital waste incinerators in Medellin, Colombia, by Aristizabal Zuluaga *et al.* The three plants had capacities between 40 and 150 kg/h, combustion temperatures between 700 °C and 850 °C in the primary chamber and between 950 °C and 1,050 °C in the secondary chamber. The lowest emission, 0.84 ng I-TEQ/Nm<sup>3</sup>, was measured at the incinerator that had sophisticated flue gas cleaning equipment (including bagfilter and activated carbon). Higher emissions were detected at the one that only had an electrostatic precipitator (16.2 ng I-TEQ/Nm<sup>3</sup>) and

the one that did not have any flue gas cleaning equipment (30.3 ng I-TEQ/Nm<sup>3</sup>). The first incinerator would comply with the present legislation in Colombia that sets a limit value of 1.0 ng I-TEQ/Nm<sup>3</sup> but since the limit may be changed to 0.1 g I-TEQ/Nm<sup>3</sup>, all incinerators have to be upgraded to comply with future legislation.

François *et al.* summarize stack monitoring and environmental monitoring data from the Flemish region of Belgium. It was recognized that stack emissions from industry in Flanders decreased from 194 g TEQ/a (in 1995) to 6.2 g TEQ/a (in 2002). Elevated deposition data found in the neighborhood of a large non-ferrous metal plant (>50 pg TEQ/m<sup>2</sup> day) were attributed to a combination of stack emissions and revolatilization of stored fine granular input materials. A special situation exists at the city of Menen, which in the past has suffered from the emissions of two nearby waste incinerators and from open fires. After the findings of high concentrations of PCB 126 (41 pg TEQ/m<sup>2</sup> day) in Menen in 2002 - other cities only had around 5 pg TEQ/m<sup>2</sup> day - a monitoring program was started and it was shown that deposition of PCB 126 generally is higher than the one for PCDD/PCDF and that no correlation exists between the two datasets. In its program, the Flemish region includes monitoring of dioxin-like PCB and first data are available from shredder plants. Koch *et al.* performed a mass balance approach and compared deposition data at a Bugsinsee in Germany with emissions reported under EMEP under the Long-Range Transboundary Air Pollution Convention. Six POPs (PCDD/PCDF, PCB, PAH, DDX, CBz, HCH) and lead were evaluated. It was found that the deposition rates at this lake in northeast Germany were at the lower end of deposition rates measured elsewhere. For most pollutants, the cumulative deposition in sediment cores for the years 1985-2000 and 1970-2000, respectively, were substantially higher than the emission inventory data.

Gass *et al.* present further insight into start-up conditions at municipal waste incinerators and besides PCDD/PCDF emissions also analyzed chlorobenzenes and chlorophenols. It was found that all three classes of compounds behave similar and that their concentrations are related to poor combustion conditions, which go along with elevated CO concentrations. *E.g.*, at CO concentrations greater than 500 mg/m<sup>3</sup>, chlorophenols were elevated with 60 µg/Nm<sup>3</sup> whereas at optimal combustion conditions around 3-15 µg/Nm<sup>3</sup> would be considered normal. The authors conclude that during the three hours after starting waste-feeding and for cold-start-up procedures, the CO-concentration should be below 100 mg/Nm<sup>3</sup> to meet the 0.1 ng TEQ/Nm<sup>3</sup> limit. Idcak *et al.* present results of PCDD/PCDF, PCB and PAH measurements from flares burning biogas generated at five landfills. Low concentrations have been found in all samples, especially for PCDD/PCDF where the concentrations were far below 0.1 ng TEQ/m<sup>3</sup>; PCB TEQ for the three coplanar PCB exhibited quite large ranges from 0.00002 to 1.7 ng TEQ/m<sup>3</sup>. PAH were from 0.2 to 1.7 µg/m<sup>3</sup> for the six Borneff congeners. Kim *et al.* report results for PCDD/PCDF, PCB, and HCB from two municipal waste incinerators burning 250 and 50 t/h, respectively, two sinter plants, four furnaces from ferrous and non-ferrous foundries. Highest stack concentrations were found at the sinter plants (0.0-1.4 ng TEQ/m<sup>3</sup> for PCDD/PCDF, 0.067-0.11 ng TEQ/m<sup>3</sup> for PCB, and 74-127 ng/m<sup>3</sup> for HCB).