

FORMATION AND SOURCES I

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About 30 oral and poster presentations have been aggregated for the session "Sources and Formation I". These papers will be briefly summarized according to the following two topical areas:

Formation and releases from non-incineration sources;

Formation and releases from waste incineration.

Formation and releases from non-incineration sources

Some papers address PCDD/PCDF releases inventories with the one for Japan being the most complete and having the broadest coverage (Konda). In its Basic Guidelines Japan has declared to achieve a 90 % reduction of dioxin emissions by the end of March 2003. The inventories assist to follow the progress in achieving this goal. The paper presents the estimated annual emissions into the air and to water of PCDD, PCDF and dioxin-like PCB for three consecutive: 7,300-7,550 g WHO-TEQ for 1997, 3,310-3,570 g WHO-TEQ for 1998, and 2,620-2,820 g WHO-TEQ for 1999. Of these, releases into water were found to be negligibly small when compared with those to air. So far, more than 60 % release reduction has been achieved. Up to now, it was impossible to quantify releases from sources such as open burning, forest fires, and from stored waste PCB and other products including various organic chlorine compounds. – Another emission inventory is from Taiwan (Chen), where by using the emission factors established by US-EPA, total releases to air were estimated to be 68.95 g TEQ/a. According to this inventory, the largest sources are secondary copper smelters (39 %), followed by small size medical waste incinerators (14.4 %), electric arc furnaces and cement kilns (10 % each). Aliyeva *et al.* address an inventory of potential sources of chloroorganic pollutants, which may serve as dioxin precursors in the city of Sumgait, Azerbaijan. This region has been heavily used by different industries such as chemical, metallurgical, and machinery with major chlorine use since the 1950s. Liquid and solid discharges from the production processes and primitive furnaces for solid waste disposal together with improper dumping have resulted in a number of polluted spots of unknown contamination and effects to be determined, monitored and reduced. To add information on emissions of dioxin-like PCB, Dyke reported concentrations of individual PCB congeners and the contribution of coplanar and mono-ortho substituted PCB to the total WHO-TEQ (including 7 PCDD, 10 PCDF, 12 PCB) from various emitters. Most PCB congeners were below the limit of quantification in the stack emissions from modern installations such as coal fired power stations (oil-fueled), municipal solid waste incinerators, sewage sludge incinerator, and medical waste incinerator. The maximum concentration measured for these PCB was 0.02 ng WHO-TEQ_{PCB}/Nm³. Certainly more data is needed for dioxin-like PCB in releases from known dioxin sources.

The problem of uncontrolled dumpsites also arises in Brazil (Carvalhoes *et al.*) where in the State of São Paulo residues from rubber, metal, plastic, pharmaceutical industries have been

disposed of. Before the dumpsite has been closed it has been ignited and the materials contained burned in a totally uncontrolled manner. PCDD/PCDF concentrations were measured in leachate waters and gave between 1.1 and 12 pg TEQ/L.

Other papers address single sources such as the impact of forest fires on soil concentrations (Kim *et al.*) where elevated concentrations of PCDD/PCDF have been detected in the ashes after these fires. However, with time, the soil concentrations decreased again which led to the hypothesis that a major portion of the PCDD/PCDF originating from forest fires may be re-introduced into the atmosphere or hydrosphere, if present. Special single events such as fireworks or bonfires attract researchers to measure PCDD/PCDF emissions. Such a sampling campaign was performed in Taiwan during the Fonpau Festival in 2001 (Chou *et al.*). The difficulty to correctly assign elevated ambient air concentrations to this special event is reflected in the data where at four sampling locations during the firework lower concentrations were measured than before and afterwards. Parameters which may have an impact on the concentrations are sulfur-containing materials in the firecrackers, other nearby sources, meteorological conditions. The influence of the load on dioxin emissions from a Diesel engine was studied by a Korean research group (Kim *et al.*) with the result of slightly decreasing emission with increasing loads (25 % to 75 % load).

A wide range of PCDD/PCDF concentrations was found in a study from Japan (Ikeguchi and Tanaka) in the emissions from industrial waste wood incinerators. Interestingly, the lowest (0.08 ng TEQ/m³) and the highest (57 ng TEQ/m³) concentration were from an incinerator burning construction and demolition wastes. At combustion temperatures in the range of 1,000-1,100 °C, contamination of the feed material does not seem to have an influence on the dioxin concentration in the stack emission, whereas at lower temperatures, chlorine in the input increases the dioxin levels. – Abrasion from tires as a source of PCDD/PCDF was discussed by Henkelmann *et al.* First, the matrix developed to be a difficult one for analysis. Ten tire samples were analyzed for PCDD/PCDF and dioxin-like PCB and it was found that also PCB contribute to the total WHO-TEQ. With a mean concentration of 10 pg WHO-TEQ/g for PCDD/PCDF and 2 pg WHO-TEQ/g for PCB, the annual release to the German environment through abrasion of tires would result in a flux of 726-787 mg WHO-TEQ (of these 120-130 mg TEQ from PCB).

Formation and releases from waste incineration

Results from full-scale incinerators were used to elucidate the relationship between chloroaromatics and dioxin concentrations by analyzing at different locations with different temperatures (Blumenstock *et al.*). In these experiments, traditional dioxin analysis (HRGS/HRMS9 as well as REMPI-TOFMS have been applied. The stability of chlorobenzenes in incineration processes may be used as easy-to-monitor surrogates to predict PCDD/PCDF concentrations (as TEQ) in combustion processes. Disturbed combustion conditions for seconds or minutes - expressed as CO peaks - can cause long-term increases of chloroaromatics and PCDD/PCDF. Memory effects were also studied by Weber *et al.* at a modern fluidized-bed incinerator. The incinerator was equipped with active carbon-spray, a common method in Japan to remove dioxins, other lipophilic organic substances and heavy metals, and a semi-dry system for removal of acid gases, and a bagfilter. In general increasing PCDD/PCDF concentrations in the fly ashes were found with increasing CO values at 15 min sampling intervals (consistent with the pulse of the bagfilter). However, there were some exemptions, which were explained by the

fact that memory effects in the cooling section may result in a "delay" of the occurrence of PCDD/PCDF in the bagfilter. When enlarging the sampling time to 2-4 hours, the correlation between PCDD/PCDF in fly ashes and CO concentration became considerably stronger. Although other parameters such as O₂ or HCl concentration play a role in the formation of PCDD/PCDF, the combustion conditions play an important role. In fluidized-bed incinerators, the majority of PCDD/PCDF are formed *via de novo* synthesis during fly ash catalyzed degradation of unburned carbon (e.g., soot). However, with the degradation rate of unburned carbon at 20-600 °C to be unknown such formation pathway can only be postulated but being supported by the findings of Zimmermann *et al.* (see also paper by Blumenstock *et al.*). – The effect of air on the formation of PCDD/PCDF during municipal solid waste incineration was studied by Ishibashi and coworkers. From laboratory scale experiments with defined artificial waste and varying chlorine contents. The results led to the conclusion that PCDD/PCDF formation can be significantly reduced by avoiding the generation of localized fuel-rich regions in the combustion chamber or by increasing the turbulence. Gullett and coworkers studied formation/degradation mechanisms at an entrained flow reactor. In a first set of experiments degradation of PCDD/PCDF in fly ash at temperatures ranging from 1,000 °C to 240 °C in the flow reactor and in a fixed bed reactor at temperatures between 200 °C and 300 °C was monitored. The results showed that more than 90 % of the PCDD was degraded in a N₂ atmosphere whereas in air, the decrease was only at about 70 %. Overall, the net degradation process is greater than the formation process. For PCDF, an overall net destruction was observed in an N₂ environment, whereas in air a slight OCDF formation was observed. The results confirm that competing processes of formation and destruction occur simultaneously. However, in an oxidative environment both processes may be in the same order of magnitude whereas in a reducing environment the overall destruction is favored. In a second set of experiments, formation rates of PCDD/PCDF from fly ash (as the sole carbon source and in the absence of a flame) and methane have been studied. Highest formation rates were found for as-received fly ashes (= AR) in the absence (N₂) or the presence of O₂. Nevertheless, dioxin formation also occurred with treated fly ashes (pretreated in N₂ = EX or oxidized in air at 500 °C = OX; resulting in °C contents of 0.5 and 0.2 wt%, *resp.*). The formation rates in N₂ atmosphere suggest that the O species necessary for PCDD/PCDF formation can be derived from the fly ash itself. The addition of 500 ppm of Cl₂ at 1,000 °C in either AIR or N₂ resulted in substantial increases in reactivity for all three fly ashes (e.g., >2,500 ng/g·s for AR ≈ EX). When methane was added prior to the fly ash injection, the rates were significantly reduced indicating that the flame species may affect the gas-phase chlorination agent and the surface reactivity.

The influence of copper, temperature, carbon, HCl and moisture on the dioxin concentrations in the sintering process were simulated in a fixed-bed reactor by Kawamoto *et al.* It was found that CuCl₂ increases PCDD/PCDF concentrations more efficiently than CuO. Whereas PCDD/PCDF concentrations in the sinter mixture decrease between 30 and 500 °C, concentrations in the gases increase in this range indicating that PCDD/PCDF volatilize from the material. Activated coke in the sinter mixture retain PCDD/PCDF from desorption. Higher moisture content tends to give higher PCDD/PCDF concentrations in the flue gas.

There are some more papers in this section worth to be considered on an individual basis. The papers can be retrieved in Volume 50 of Organohalogen Compounds.