DIOXIN CONGENER PROFILES OF HOUSEHOLD DUST SHAPED BY INDOOR ACTIVITIES

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Introduction

In 1984, Lamparski et al.[1] reported the presence of dioxins in dried municipal sewage sludge samples from 1933, 1981 and 1982. Besides the obvious dominating presence of OCDD and HpCDD congeners, they identified the pair of 1,2,3,7/1,2,3,8-TCDD amongst the largest components within the series of tetrachlorinated dibenzo-*p*-dioxin isomers. At the time, it was speculated that their existence was the result of condensation reactions between chlorophenols possibly formed during chlorination processes (e.g., wastewater treatment, household bleaches). Other authors also reported the detection of the isomers' pair in sewage sludges from POTW in Mississippi[2], or observed the pair as part of a group of coeluting isomers in wastewater treatment sludges from Brazil[3]. Others misidentified the pair for 2,3,7,8-TCDD[4] in a Mississippi sewage sludge. Laboratories analyzing sewage sludges and POTW wastewater effluents routinely detect the pair 1,2,3,7/1,2,3,8-TCDD as the major TCDD component, which has undeniably become part of the sewage sludge signature. However, no technical product has been connected with the pair. Our interest in the laundry activities originated with the detection and dominating presence of this same pair of TCDD isomers in house dusts from various locations throughout the USA. With the exception of the sewage sludge, the pair is not detected or, when it is detected, it is not dominating the TCDD profiles in samples from outside the house (e.g., soil, combustion emission). Because wastewaters generated by laundering and bathing are considered to be the major input sources for POTWs[5], and the TCDD pair was routinely detected in both sewage sludges and house dusts, a connection to garments was suspected. As early as 1987, Kanetoshi et al.[6,7] showed that the widely used antimicrobial agent triclosan is easily chlorinated with sodium hypochlorite to polychlorinated hydroxydiphenylethers. The latter are also known as pre-dioxins, which can form dioxins (including 1,2,3,8-TCDD)[7] when exposed to heat, and to some extent to UV irradiation. Berry et al.[8] found PCDD/Fs in common everyday materials including dryer lint, vacuum cleaner dust, room air filters. Horstmann and McLachlan[9,10] found low-ppt to high-ppb concentrations of PCDD/Fs in various new clothing from different manufacturers. Pentachlorophenol (PCP) was found in some of the garments and was considered the main source of the contamination. One of the clothing samples displayed a congener profile reminiscent of chloranil-based dyes. The authors showed that PCDD/Fs are transferred from the textile to the human skin during wearing. In addition, evidence was found indicating that contaminated textiles are a major source of PCDD/Fs in house dusts. Based on the authors' evaluation, domestic dust is apparently a sink for PCDD/F from skin scale and shredded textile fibers. Studies of wastewaters from apartment buildings showed the presence of PCDD/Fs[11]. Krizanec et al.[12] reviewed the sources of dioxins and dioxin-like compounds in textiles and chemicals used in the textile sector. Cigarette smoke also contributes to the dioxin make up of the household dust[13]. These reports along with other significant contributions from various scientists around the world and our study, which includes congener profiles analyses, provided the foundations for the development of a model describing sources of PCDD/Fs in house dusts. The model further stresses the importance of indoor activities[14] on the dioxin composition of household dust.

Materials and Methods

The sample extractions, fractionations, analyses, and quality assurance/quality control procedures were carried out according to an enhanced version of USEPA Method 8290[20]. The labeled standards solutions containing the extraction standards (seventeen 2,3,7,8-chloro-subsituted $^{13}C_{12}$ labeled PCDD/F congeners), cleanup standards (seven labeled PCDD/Fs), injection standards (three labeled PCDD/Fs) were prepared from individual standard solutions obtained from Cambridge Isotope Laboratories (CIL, Andover, MS, USA). The unlabeled PCDD/F congeners were obtained from already made mixtures at a specified concentration from Wellington Labs (Guelph, ON, Canada). The seven-point initial calibration solutions (0.25 pg/μL to 500 pg/μL) for PCDD/Fs were prepared using the above standard solutions except for the unlabeled congeners, which were obtained from Cambridge Isotope Laboratories. One microliter of the final extract was injected in a splitless mode onto a capillary column (60-m DB-5MS) coupled to a magnetic sector instrument and analyzed under high-resolution

GC (Agilent 6890 Series; Palo Alto, CA, USA) and MS conditions (Waters AutoSpec Ultima; <100 ppm mass resolution at 5 percent peak width). A typical analytical sequence comprised the analysis of the batch control spike, followed by a spiked solvent blank, the laboratory method blank, a number of samples of the same extraction batch before closing with an injection of the batch control spike. The analytical sequence does not exceed 12 H. The mass resolutions, response factors, GC column performance, and system steadiness are verified at the beginning and at the end of each analytical sequence.

Results and Discussion

In a typical U.S. residence, samples were collected from incoming tap water, outgoing clothes washer wastewater, clothes dryer vent, lint, clothes, detergent, fabric softener, bleaching agent, air filter, and living room wipes. The room where the dryer was located was vacuumed before the start of the experiments. This included the rear of the unit. The drum and lint trap were all cleaned before the start of the experiment. The dryer vent sample was obtained from the vent using a sandwiched PUF/XAD-2 resin cartridge. No PCDD/F congeners were detected in the tap water and the fabric softener above the USEPA method's reporting limits, while the bleaching agent showed primarily low-molecular weight PCDF congeners. From a congener profile point of view, of the 2,3,7,8-substituted congeners, 1,2,3,4,6,7,8-HpCDD (averaging 10 percent of the sum of 17 congeners) and OCDD (averaging 80 percent of the sum of 17 congeners) were dominant in the wipes, lint isolated from various types of clothes (new/worn, white/color), air conditioning unit intake filters, the clothes dryer vent, and—albeit low levels—garments and wastewaters from worn white and color clothing washing cycles. In our study, the lint produced from drying worn clothes show higher levels of PCDD/Fs (approximately 80 percent of the sum of the 17 congeners is OCDD) than the new clothes regardless of the clothes' color being washed. A similar observation was made for the wastewaters from washing worn clothes versus new clothes. The results associated with the clothes dryer vent show that over 4,000 pg total PCDD/Fs (Cl_4-Cl_8) per load are emitted from the dryer vent to the outside world; 68 percent of which is OCDD (or 81 percent of the sum of 17 congeners) most likely associated with the fine lint particles because of its low vapor pressure. The lint deposited inside the duct leading to the sorbent was incorporated in the sample before the extraction. In this experiment, a cleaned 10-cm duct and four drying cycles lasting 3.5 H were used.

Congener profiling typically relies on the various 2,3,7,8-substituted congeners' relationship to another parameter (e.g., sum of the 17 congeners, sum of 136 congeners, or their contribution to the TEQ). When the sum of congeners is the parameter, the data point to dominance by OCDD with little information available about other congeners. A more detailed analysis of the congener profiles might include the non 2,3,7,8-substituted congeners such as the isomeric pair 1,2,3,7/1,2,3,8-TCDD. The latter can be particularly valuable when, strictly from a profiling point of view, it constitutes the majority of the TCDD response (Figure 1). It is important to note that, from a congener profiling perspective, dominant does not necessarily imply high absolute concentrations. The isomeric pair—although at very low levels—was found in both air conditioning intake filters, the combined lint from two loads of laundry using bleach in the washing cycles (1^{st} load: whites; 2^{nd} load: towels; lint weight: 4.56 g; 1,2,3,7/1,2,3,8-TCDD: 0.31 pg/g), and the clothes dryer vent (1,2,3,7/1,2,3,8-TCDD: 14.3 pg/four loads). The amount of lint recovered from individual washing-drying loads ranged from 0.3 g to 1.8 g, which prevents the detection of minute quantities of the TCDD isomeric pair. Elevated detection limits in the wastewaters (low recoveries) and wipe (0.06 g dust collected on top of the TV/stereo system from the room where laundry is folded) samples also affected the detection of the isomeric pair. The latter was never found in any of our controls (laboratory method blanks and standards used) or in the new clothes (above the detection limit of 0.020 pg/g).

This particular TCDD isomeric pair is an example where non 2,3,7,8-substituted congeners can be used as a marker for a particular source of dioxins in samples susceptible to receive contributions from multiple sources. Based on our observations and published information on the formation of 1,2,3,8-TCDD, it is believed that the isomer(s) responsible for the characteristic sewage peak is (are) formed while heat-drying clothes. We were able to verify that the sewage peak is absent in the dust from a household with no dryer. Finally, the TCDD isomeric pair points out how indoor activities can influence the congener pattern in household dusts.

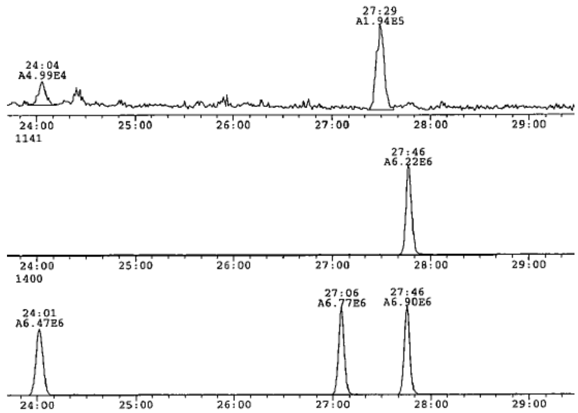

Figure 1: Selected ion current profiles for TCDD (top trace; m/z 322), $^{37}Cl_4$-2,3,7,8-TCDD (middle trace; m/z 328), and $^{13}C_{12}$-TCDD (bottom trace; m/z 332) in the dust from one of the air conditioning intake filters. The peak at retention time 24:04 min. is 1,3,6,8-TCDD (5.3 pg/g). The peak at retention time 27:29 min. is where the isomers 1,2,3,7/1,2,3,8-TCDD (19.5 pg/g) are expected to co-elute. Other peaks include $^{13}C_{12}$-1,2,3,4-TCDD (retention time 27:06 min.), $^{13}C_{12}$-1,3,6,8-TCDD (retention time 24:01 min.) and $^{13}C_{12}$-2,3,7,8-TCDD (retention time 27:46 min.).

The Laundry Cycle (Fig. 2)
Clothes are worn, washed and dried. The drying process—involving heat-producing mechanical units—generates a certain amount of lint, which can also originates from clean clothes. The clean clothes we remove from the dryer are habitually shaken before folding. This action releases lint in the room where this is taking place. Assuming we follow the dryer manufacturer's instructions, the lint trapped on the filter is regularly discarded inside a garbage container. This action too locally produces a cloud of lint inside the house. If we consider that the filter itself is not a high-efficiency particle scrubber, extremely fine particles of lint will pass through the filter and will be emitted to the outside world. It is a well-known fact that high-molecular weight PCDD/F congeners tend to be found in the smallest particle sizes[15] while low-molecular weight congeners will be associated with larger particle sizes or found in the gaseous phase because of their higher vapor pressures. On their way out, the fine particles leak out the dryer's internal components particularly at the connection between the dryer and the hose. The rear of the dryer is where most of the lint accumulates. In this study, we did not see an indication that the dominant dioxin species (i.e., OCDD) found in the house dust are chemically formed during the drying process. One exception may be when the antimicrobial agent triclosan is exposed to a bleaching agent during the washing forming pre-dioxin compounds. The latter, which remained adsorbed onto the clothes, could possibly be converted into dioxins (e.g., 1,2,3,8-TCDD and 1,2,3,6,7,8-HxCDD)[6,7] during the drying cycle. The temperature inside the study dryer's drum ranged from 45^oC (minimum) to a maximum of $205^oC \pm 5^oC$. The heating element turned on/off every 30 s. The temperature measured at the sampling point was stable at 64^oC. Since we are not aware of other known and verifiable sources accounting for the pair 1,2,3,7/1,2,3,8-TCDD, when the pair dominates the TCDD homologue profile in house dusts, it suggests that lint from clothes dried with heat is a component of the household dust.

Any fabrics containing triclosan could replenish the source of pre-dioxins in the clothes during the next washing-drying cycle. Furthermore, clothes are known to contain dioxins. The congener profile is said to be reminiscent of pentachlorophenol[10], which, in some parts of the world, is used as a biocide to preserve cotton[10]. Textile dyes have also been found as a source of dioxins in clothes. However, it is difficult at this point in time to assess their relative importance due to the lack of data on the textile chemicals' congener profiles. Uptake of PCDD/Fs from the atmosphere into clothing is not considered as significant[9,10]. In any event, pre-dioxins and dioxins present in our clothes migrate from the clothes onto our skin, and from our skin onto the clothes[10]. Dead skin cells constitute a major component of house dust[9], and skin cells are replaced at the rate in the order of 40,000 cells per minute. It is estimated that 4 kg of dead skin cells are shed per person per year.

During our study, the clothes analyzed contain significantly lower amounts of dioxins compared to the house dust. At least, three—possibly additive—explanations can be offered. First, the house dust acts as a record of long-term practices and may just simply reflect fluctuations in dioxin concentrations in the clothes we purchased and wore over time. The second explanation is based on the concentrating effect resulting from drawing lint-particle-laden air into the dryer every time we dry our clothes. And finally, other sources of dioxins (e.g., fireplaces, smoking, cars exhaust…) beside the ones already mentioned for the laundry activities can contribute directly or indirectly through the clothes we wear. For example, certain authors reported adsorption and re-emission of nicotine from clothing fabrics and indoor building materials[16, 17]. PCDD/F congeners present in the tobacco steam-distill[18] during smoking[19] and are adsorbed onto clothing, which are washed and dried.

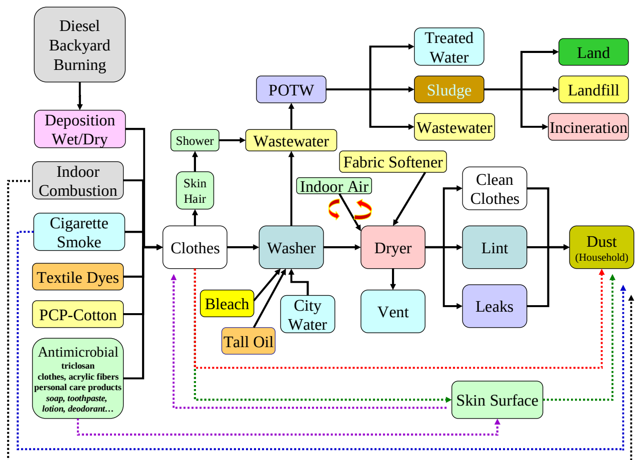

Figure 2: The Laundry Cycle

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