

## GAS- AND SOLID-PHASE PARTITIONING OF PCDDs/Fs ON MSWI FLY ASH AND THE EFFECTS OF SAMPLING

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### Introduction

Semi-volatile organic compounds (SOCs), including polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/Fs), are partitioned as gas-phase and particle-bound products of many industrial combustion processes. This gas/particle partitioning of SOC has severe implications on both monitoring and control technologies. While particle-bound PCDDs/Fs are largely controlled by particulate collection devices such as fabric filters or electrostatic precipitators (ESPs), the gas-phase fraction may escape. Additionally, current real-time or near-real-time monitor development has focused on detection of the gas-phase fraction of SOC, including PCDDs/Fs<sup>1,2</sup>. Post filter gas-phase PCDDs/Fs have been reported to be greater than 50% of the total PCDD/F emissions when sampling the raw gas downstream of the boiler of a large scale municipal solid waste incinerator (MSWI) producing a low (<1%) carbon content fly ash<sup>3</sup>. Others have reported that 50-90% of the PCDDs/Fs formed from thermal processes can be present in the fly ash fraction<sup>4</sup>.

One of the major difficulties with the evaluation of the actual partitioning of SOC as emitted by the combustion process is the potential change, or bias, introduced during sampling. The ratio of gas-phase to surface-bound SOC is strongly affected by the temperature, vapor pressures, particle number density and size distribution, and particle properties. Current sampling techniques, involving the separation of the particles from the flue gas via filters, have the potential to severely bias the partitioning by increasing the particle density and contact between the gas and particles.

The purpose of the present contribution was to assess the potential bias to the actual emission gas/particle-phase partitioning using conventional sampling techniques. A novel sampling technique was developed and used to determine the actual partitioning during formation on MSWI fly ash in an entrained flow reactor (EFR). This partitioning was examined from both a reactor emissions and total formation view point in order to relate to sampling and monitoring applications in addition to mechanistic implications.

### Methods and Materials

The experimental work for the present contribution was performed according to three tasks. In Task 1, the potential bias to the partitioning of PCDDs/Fs when using a filter to separate the particles from the stack gas during sampling was investigated. In order to assess the potential adsorption of gas-phase PCDDs/Fs as a function of fly ash loading, glass fiber filters (Whatman

GF/A, 11 cm) were loaded ( $0 - 5.42 \text{ mg/cm}^2$ ) with a toluene-extracted (Soxhlet, 48 hours) fly ash collected from the ESP of a grate-fired MSWI (EPA EX FA). Details of this fly ash can be found elsewhere<sup>5</sup>. A standard solution (40  $\mu\text{L}$ ) containing 23 of the 2,3,7,8-substituted mono-octa PCDD/F congeners (at 2.5 ng/ $\mu\text{L}$  each, 50:50 mix of ED-4135 and EF-4134, Cambridge Isotope Laboratory) was added upstream of the filter (150 °C) by injection at 200 °C into a flue gas from a hydrogen flame. After 10 minutes, the system was cooled and analyzed in three factions: (1) a toluene rinse of the front half of the set-up from the injection point to the filter, (2) a toluene extract (Soxhlet, 24 hours) of the filter, and (3) the combined toluene-filled impinger (to trap gas-phase PCDDs/Fs) and a toluene rinse of all post-filter glassware leading up to the impinger. The results from this study are reported in percent recovery of the spiked PCDDs/Fs in relation to the total PCDDs/Fs recovered. Total recoveries in comparison to the amount spiked were between 70-115%. As in all tasks, all samples were analyzed for mono-octa PCDDs/Fs according to a modification of U.S. EPA Method 0023a<sup>6</sup>. In supplemental experiments, the potential for desorption of PCDDs/Fs spiked onto the fly ash was investigated as a function of temperature (125-280 °C). In these tests, both the fly ash and the downstream trap were analyzed for all PCDDs/Fs congeners in order to complete the mass balance.

In the second task, a method was developed to preserve the partitioning of PCDDs/Fs when sampling from an entrained flow reactor (EFR) designed to study formation from fly ash entrained in the stack gas of a combustion source. More details of this reactor set-up can be found elsewhere<sup>7</sup>. Tests showed that sampling the emissions (simulated flue gas and injected fly ash) from the EFR directly into an ice-water-cooled impinger containing 250 mL of dichloromethane could preserve the partitioning by trapping gas-phase PCDDs/Fs in the solvent and not extracting particle-bound PCDDs/Fs. Separating the solvent from the fly ash particles by filtration after the experiment and analyzing the filtrate and collected particles separately for mono-octa PCDDs/Fs allowed for a direct determination of the phase partitioning. A solvent recovery trap was used to recycle volatilized dichloromethane back to the impinger during the experiments.

In the third task, the method developed in Task 2 was used to determine the phase partitioning of PCDDs/Fs in the emissions from the EFR. Fly ash (FA) was injected over 30-60 min (ca. 1 g FA/h) into a flow of 5 L/min (STP) of  $\text{N}_2/\text{Cl}_2$  (ca. 300 ppm) at the top of the vertical reactor (VR) section of the EFR. The entire reactor flow was sampled by the solvent trap method described previously. The VR was flushed with nitrogen in order to collect residual fly ash remaining on the reactor wall after each experiment. These three fractions (solvent, filtered particles, residual VR deposits) were analyzed separately for mono-octa PCDDs/Fs. The VR was operated isothermally at either 300 or 400 °C for the experiments within this task.

### Results and Discussion

In Task 1, the potential for bias to the actual gas/particle partitioning of PCDDs/Fs from combustion sources associated with the use of filters during conventional sampling was investigated. A significant effect of filter loading on PCDDs/Fs recovery downstream of a glass fiber filter (at 150 °C) was observed for the mono-octa PCDD/F congeners added to the sampled gas stream. Downstream recoveries ranging from 57-79% were observed for tetra-octa PCDDs/Fs at loadings as low as  $0.5 \text{ mg/cm}^2$ , while minimal adsorption (<15% loss) of the mono-tri PCDDs/Fs was observed until loadings of  $1.7 \text{ mg/cm}^2$ . These results indicate that for a fly ash containing just moderate amounts of carbon (ca. 1.3%), adsorption of PCDDs/Fs can be

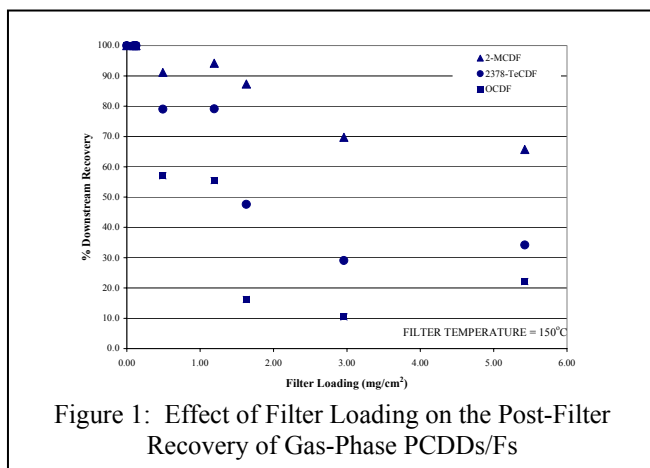


Figure 1: Effect of Filter Loading on the Post-Filter Recovery of Gas-Phase PCDDs/Fs

were detected from the EPA EX FA, as well as, dechlorination products. Additionally, the substitution of a carbon-reduced fly ash (EPA OX FA)<sup>8</sup> for the EPA EX FA clearly showed the importance of the carbon concentration in adsorption of gas-phase PCDDs/Fs. Hence, partitioning information derived from the separation of the front half (probe and filter) and back half (XAD-2 and water impinger) of a conventional Method 23 sampling train has significant potential for the introduction of bias to the actual partitioning.

In light of the above, a novel sampling technique was developed in Task 2 in order to investigate the gas/particle partitioning of PCDDs/Fs during formation on EPA EX FA in the EFR. Tests with PCDD/F standard-spiked impinger solutions, gas-phase PCDD/F standards, and particle-bound PCDD/F-laden fly ash in the impinger showed that dichloromethane was able to preserve the expected partitioning by keeping the gas-phase PCDDs/Fs in solution and not extracting the particle-phase. Extensive tests revealed that this method was a function of the fly ash type and amount, with the carbon content of the fly ash being the most important parameter. Limiting the fly ash loading of EPA EX FA, containing 1.3 wt % carbon, to approximately 0.5g in 250 mL proved sufficient at preserving the partitioning to within 5-10% (bias towards the particle phase).

The overall partitioning determined from this solvent trap method at isothermal VR temperatures of 300 and 400 °C was determined in Task 3 and is reported in Table 1. Separate analysis of the collected fly ash in the trap and the solvent after sampling the emissions of the EFR revealed that 81% of the PCDDs/Fs formed were in the gas phase when the VR was kept at 300 °C. With the VR at 400 °C, 98% of the total PCDDs/Fs emitted was found in the gas-phase. However, as in most practical systems, a considerable amount of fly ash injected into the EFR remained on the wall of the reactor which has been shown previously to contribute significantly to the total PCDD/F yields<sup>8</sup>. When this fly ash was added to the collected fly ash in the trap, the percentage of gas-phase PCDDs/Fs in triplicate experiments at 300 and 400 °C decreased to 26 (+/-8%) and 79% (+/-6%), respectively. Of the total particle-bound PCDD/F formed (74%), approximately 90% was detected on the reactor wall fly ash (300 °C experiment). This latter finding adds definitive support for the significant contribution of fly ash deposits to overall PCDD/F emissions.

significant when conventional sampling techniques involving particle filters are used. This bias to the partitioning is both loading- and congener-specific as indicated in Figure 1 for 2-MCDF, 2378-TeCDF and OCDF, with bias to the particle phase with decreasing vapor pressure and increasing fly ash loading on the filter. No desorption of PCDDs/Fs spiked onto fly ash was observed in supplemental experiments until a temperature of 200°C. At this temperature, desorbed PCDDs/Fs (ca. 25% of the total recovered)

For comparison, a U.S. EPA Method 0023a sampling train was run for one experiment at 400°C in the VR. Separating the front half and back half of the sampling train resulted in 39% of the PCDDs and 55% of the PCDFs present in the XAD-2 resin (post filter). No discernable difference was observed in the overall yields reported by either method. Unfortunately, since the choice of experimental conditions resulted in nearly 90% of the total formation as hexa-octa PCDDs/Fs, homologue-specific information regarding partitioning was limited.

Table 1: Percentage of PCDDs/Fs on the Solid-Phase Particles (SP) and in the Gas-Phase (GP) as Determined by the Solvent Trap Method

VR Temperature [°C]	EFR Emissions		Total Formation	
	SP	GP	SP	GP
300	19	81	74	26
400	2	98	21	79

For “EFR Emissions”, only the particles collected in the trap are considered.  
For “Total Formation”, both particles collected in the trap and recovered from the reactor are included.

The results presented herein provide some explanation with regard to the difficulties in understanding and the general lack of agreement of some currently available literature data regarding the partitioning of PCDDs/Fs from combustion sources. Conventional sampling methods may introduce significant bias to the actual partitioning. This work has shown that uncollected fly ash (i.e., residuals in the cooler, post-boiler section of combustors) can greatly contribute to the overall PCDD/F emissions via the release of gas-phase PCDDs/Fs. If minimal adsorption occurs on entrained fly ash particles, as observed in the present contribution and in the work of Mätzing et al.<sup>8</sup>, without artificial enhancement of the particle number density (i.e., via the addition of activated carbon) a large fraction of the PCDD/F emissions are likely to be in the gas phase. These results can have significant implications on the development of control and monitoring technologies for SOCs from combustion sources.

## References

- Oser, H., Oudejans, L., Coggiola, M., Faris, G., Crosley, D. and Gullett, B. (2002) *Organohalogen Compounds.*, Vol. 59, 69-72.
- Mühlberger, F., Zimmermann, R. and Kettrup, A. (2001) *Anal. Chem.*, Vol. 73 (15), 3590-3604.
- Hunsinger, H., Kreis, S. and Vogg, H. (1996) *Chemosphere*, Vol. 32 (1), 109-118.
- Everaert, K., Baeyens, J. and DeGréve, J. (2003) *Environ. Sci. Technol.*, Vol. 37 (6), 1219-24.
- Wikström, E., Ryan, S., Touati, A. and Gullett, B. (2003) *Environ. Sci. Technol.*, Vol. 37 (9), 1962-1970.
- Test Method 0023a*. In SW-856 (NTIS PB88-239223) Office of Solid Waste and Emergency Response; Office of Solid Waste, USEPA: Washington, DC, 1996.
- Wikström, E., Ryan, S., Touati, A., Telfer, M., Tabor, D. and Gullett, B. (2003) *Environ. Sci. Technol.*, Vol. 37 (6), 1108-1113.
- Mätzing, H., Baumann, W., Becker, B., Klaus, J., Paur, H. and Seifert, H. (2001) *Chemosphere*, Vol. 42 (7), 803-809.