# EMISSION OF CHLORINATED HYDROCARBONS FROM SIMULATED FIRES IN RECYCLING WASTE STATION

Yli-Pirilä P<sup>1</sup>, Tarhanen J<sup>1</sup>, Pennanen T<sup>1</sup>, Rinne T<sup>2</sup>, Jäntti J<sup>3</sup>, Väisänen T<sup>3</sup>, Ruuskanen J<sup>1</sup>, Tillander K<sup>2</sup>

<sup>1</sup>University of Kuopio, Department of Environmental Sciences, P.O. Box 1627, Kuopio, FI-70211, Finland; <sup>2</sup>VTT Technical Research Centre of Finland, P.O. Box 1000, Espoo, FI-02044 VTT, Finland; <sup>3</sup>Emergency Services College, P.O. Box 1122, Kuopio, FI-70821, Finland

#### Abstract

The gaseous and particulate phase concentrations of PAH, PCBz, PCPh, PCB and PCDD/F were measured during a simulated large scale waste bale fires of solid recovered fuel (SRF) and recycling paper. Airborne samples during the fire and its extinction were collected in the smoke plume and in the field using high volume samplers equipped with glass fibre filters and PUF cartridges. The emissions of analyzed POPs varied depending on the incinerated waste type. The emissions were also different between the fire and the extinction phases. Uncontrolled burning of recycling paper bales produced higher emissions of PCPhs and PCBs. PAH emissions were similar for both materials. PCDD/F emissions were 20 to 40-fold higher in SRF than recycling paper waste. The total concentrations of PCBzs and PCPhs measured in the smoke plume varied between 1-11 ng/Nm<sup>3</sup> and 332-3703 ng/Nm<sup>3</sup>, respectively, and in field samples 0.5-7 ng/Nm<sup>3</sup> and 13-100 ng/Nm<sup>3</sup>, respectively. PCBs were detected only in paper burning experiment and the concentration varied between 355-485 ng/Nm<sup>3</sup>. The total amount of PCDD/Fs in smoke plume varied between 53-2322 pg/Nm<sup>3</sup> (4-138 TEQ pg/Nm<sup>3</sup>). In SRF field sample the amount was 84 pg/Nm<sup>3</sup> (7 TEQ pg/Nm<sup>3</sup>). The total PAH concentrations varied between 22-95 µg/Nm<sup>3</sup> and in field samples 0.4-4 µg/Nm<sup>3</sup>.

#### Introduction

As the municipal waste management has become more sophisticated, local recycling centres have become more common. In these centres, the waste is sorted, baled and stored for reuse. A fire in the recycling centre, for example in waste storage, could result in remarkable environmental local risks<sup>1</sup>. The combustion process in uncontrolled waste fire is incomplete because of unfavourable combustion conditions and materials, thus posing a risk for the formation of persistent organic pollutants (POPs)<sup>2,3</sup>. These compounds could be released to the environment via air or to soil in the extinction waters. Furthermore, the firemen and local inhabitants could be exposed to hazardous compounds during a fire and its extinction of such waste fires. Unfortunately, information on these emissions currently available is sparse, especially from large scale fires<sup>4</sup>.

The POP emissions from waste fires could be partitioned either to gaseous or particulate phases. The partitioning affects the residence time and transport of those emissions in the atmosphere. Thus, it is important to study also the gas-particle ratio of the compounds<sup>5</sup>.

In this study, recycling waste fires were simulated in large scale. Two types of waste, solid recovered fuel (SRF) and recycling paper were used. The emissions of POPs were measured both directly from the smoke plume and downwind from the fire.

## **Materials and Methods**

Large scale simulations of waste bale storage fires were carried out. In field experiments, the incinerated SRF consisted of one large stock of 4 by 6 metres and recycling paper respectively of a pair of 2 by 8 metres bale lines. The airborne samples from smoke plume were collected 5-10 metres from the fire centre during uncontrolled fire and its extinction. Field samples were taken 20-30 metres downwind of the fire place in both experiments. The volume of collected air samples in these fire experiments varied from 9 to 39 m<sup>3</sup> and in field samples from 23 to 31 m<sup>3</sup>. The field samples were integrated samples over the whole experiment time including active fire and its extinction, whereas the samples from the smoke plume were taken separately for the fire and the extinction.

The samples were analysed for polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes (PCBzs), polychlorinated phenols (PCPhs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Details of the analysis are described elsewhere<sup>2,3</sup>. WHO-2005 toxic equivalent factors were used to derive the PCDD/F toxic equivalent (TEQ) values.

## **Results and Discussion**

The results from large scale field measurement of SRF and recycling paper fires are summarized in Table 1. The airborne emissions analysed varied depending on the type of the incinerated waste. The emissions differed during the fire and the extinction. Uncontrolled burning of recycling paper bales showed to produce higher emissions of PCPhs and PCBs. PAH emissions were similar for both materials. PCDD/F emissions were 20 to 40-fold higher while burning SRF.

The total emissions of 16 PAHs were 22-95  $\mu$ g/Nm<sup>3</sup> for SRF and 29-72  $\mu$ g/Nm<sup>3</sup> for recycling paper. Although the emissions were at the equal level, the emission peaked for SRF during the extinction, whereas for paper, the highest concentrations were measured during the active fire. Concentrations of PAHs were 20 to 50-fold higher than previously observed from municipal waste landfill fires<sup>3</sup>.

PCBz emissions (5 ng/Nm<sup>3</sup>) were detected in SRF only during extinction. For recycling paper, the total concentration varied between 1-11 ng/Nm<sup>3</sup>. PCPh emissions were high in recycling paper fire (1690-3703 ng/Nm<sup>3</sup>) compared to SRF (332-1084 ng/Nm<sup>3</sup>). During the active fire, the emission was nearly 10-fold and during the extinction nearly 2-fold higher than in the SRF experiment. PCBs were detected only in paper burning experiment and the concentration varied between 355-485 ng/Nm<sup>3</sup>. The total emissions of PCDD/Fs were in the range of 2157-2322 pg/Nm<sup>3</sup> (119-138 TEQ pg/Nm<sup>3</sup>) for SRF and 53-102 pg/Nm<sup>3</sup> (4-7 TEQ pg/Nm<sup>3</sup>) for recycling paper. Thus, the concentrations of PCBs and PCDD/Fs from SRF and recycling paper fires were in same order of magnitude than previous landfill studies<sup>2,3</sup>.

A field sample represents the surrounding working air where the smoke plume from fire has been already diluted. During the recycling paper experiment, wind direction varied much more than during the SRF experiment and it might have caused lower results.

Analysis	Phase	SRF			Recycling paper		
		fire	extinction	field	fire	extinction	field
PAH ( $\mu g/Nm^3$ )	gas	9.9	31.2	3.0	11.9	22.7	0.3
	particulate	12.4	63.5	1.0	60.5	6.7	0.1
PCBz (ng/Nm <sup>3</sup> )	gas	n.d.	4.8	n.d.	0.5	3.7	6.0
	particulate	n.d.	n.d.	0.5	0.1	7.0	1.0
PCPh (ng/Nm <sup>3</sup> )	gas	286.4	995.2	98.8	3444.0	1667.9	12.6
	particulate	45.4	88.5	0.8	259.4	21.8	0.4
PCB (ng/Nm <sup>3</sup> )	gas	n.d.	n.d.	n.d.	124.8	314.8	1.0
	particulate	n.d.	n.d.	n.d.	359.6	40.1	n.d.
PCDD/F (pg/Nm <sup>3</sup> )	gas	63.8	87.8	0.7	3.0	n.d.	n.d.
	particulate	2092.9	2234.6	82.9	98.5	53.2	n.d.
PCDD/F (pg TEQ/Nm <sup>3</sup> )	gas	3.9	5.4	0.1	0.2	n.d.	n.d.
	particulate	115.0	132.9	7.1	6.9	3.6	n.d.

Table 1. Summary of the gaseous phase and the particulate phase concentrations of PAH, PCBz, PCPh, PCB and PCDD/F. N.d. denotes "Not detected".



Figure 1. Distribution of PAHs in gaseous phase during a fire (a) and extinction (b).

Figure 1 shows the distribution of PAHs in gaseous phase. For SRF, the gas-particle distribution of total PAH emission was 44 % in gaseous phase and 56 % in particulate phase during fire and 33 % / 67 % during extinction, respectively. For recycling paper the distribution was 16 % / 84 % during fire and 77 % / 23 % during extinction, respectively. In field samples distributions were similar for both of the waste types: SRF 75 % / 25 % and paper 77% / 23 %.



Figure 2. Distribution of PCBs in gaseous phase during fire and extinction of recycling paper.

Although the use of non-carbon copying paper containing PCBs have been forbidden for decades, it is still evident that recycled papers contain small amounts of PCBs similar to those used for the non-carbon copypaper<sup>6</sup>. In our experiments PCBs were detected only in recycling paper incineration. During the fire, PCBs were almost all bound to particulate phase and during the extinction gas phase fractions of TCB and TeCB were emphasised. Small amounts of PeCB and HeCB were found, but only in particulate phase (Fig. 2). These results reveal that some of these recycling paper bales contained old archive papers and these archive papers included a commercial PCB product such as Aroclor 1242.



Figure 3. Distribution of PCDD/F congeners during a fire (a) and extinction (b).

Figure 3 shows the distribution of PCDD/F congeners in fire gases. Emissions in both cases were emphasized to dioxins and the most abundant toxic congeners were 1,2,3,4,6,7,8-HpCDD and OCDD. Distribution is similar as previously studied in landfill fires<sup>2</sup>. Congener distributions did not differ during fire and during extinction.

The results of the current study demonstrate the gas-particle partitioning of POPs in the smoke plume and in the surroundings of the fire. In the future, the results could be utilised in the modelling of the dispersion of the emissions from fires in waste centres and landfills.

The emissions from uncontrolled fires of stored waste bales can be considered a potential occupational and environmental risk.

## Acknowledgements

This project was funded by VTT Technical Research Centre of Finland, Finnish Fire Protection Fund, Paperinkeräys Oy, Jätekukko Oy, Federation of Finnish Financial Services, University of Kuopio and Emergency Services College.

#### References

- 1. Blomqvist P., Persson B. and Simonson M. Fire Technology 2007; 43: 213.
- 2. Ruokojärvi P., Ettala M., Rahkonen P., Tarhanen J. and Ruuskanen J. Chemosphere 1995; 30: 1697.
- 3. Ruokojärvi P., Ruuskanen J., Ettala M., Rahkonen P. and Tarhanen J. Chemosphere 1995; 31: 3899.
- 4. Nammari D., Hogland W., Marques M., Nimmermark S. and Moutavtchi V. Waste Management 2004; 24: 9.
- 5. Lohmann R., Gioia R., Eisenreich S. and Jones K. Atmospheric Environment 2007; 41: 7767.
- 6. Storr-Hansen E. and Rastogi S. Bull. Environ. Contam. Toxicol. 1988; 40: 451.