FORMATION AND EMISSION OF CDDs AND CDFs FROM ACCIDENTAL COMBUSTION OF AUTOMOBILE TIRES

T.S. Thompson, R.E. Clement, R.S. Mercer, and J.A. Townsend
Ontario Ministry of the Environment, 125 Resources Road, P.O. Box 213
Rexdale, Ontario, Canada M9W 5L1.

ABSTRACT

Aqueous and oily runoff resulting from the combustion of automobile tires was analyzed for chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs). A series of CDDs and CDFs were identified. The total levels of CDDs and CDFs were in the low parts-per-billion range for the oil samples, while the maximum concentrations in runoff water were several hundred parts-per-quadrillion. The concentration of 2,3,7,8-TCDD was only a small fraction of the total CDDs found in the water and oil samples.

INTRODUCTION

The formation of chlorinated dioxins and furans during combustion processes has been well documented [1]. CDDs and CDFs have been found to be byproducts in accidental fires involving dielectric fluids containing polychlorinated biphenyls (PCBs) and/or chlorinated benzenes [2]. In this study, we will present data which demonstrates the formation of chlorinated dioxins and furans as a result of the combustion of automobile tires.

In mid February 1990, a large fire began at a tire dumpsite located in Ontario, Canada. The site contained approximately 14 million used tires and the blaze soon spread to involve most of the tires stored onsite. Large volumes of water were employed in an attempt to douse the fire and the resulting runoff water was collected in several huge reservoirs to prevent possible contamination of groundwater in the area. The runoff oil resulting from the burning tires was also collected. Samples of the oil and runoff water were submitted to the Ministry of the Environment's Dioxin Laboratory for analysis of CDDs and CDFs. The results of some of these analyses will be presented.

METHODOLOGY

All oil and water samples were fortified with a solution containing 5 isotopically labelled CDD surrogate standards. Water samples (one litre) were extracted with dichloromethane and subsequently fractionated using the multi-column liquid chromatographic procedure devised by Lamparski [3]. Oil samples (approximately 1.5 grams) were diluted with hexane and fractionated using the same procedure as for the water samples. The final extracts for the oil samples were reduced to 50 microlitres while the final extract volumes for the aqueous samples were 10 microlitres.

The CDD/CDF analyses were carried out using a Finnigan MAT TSQ70 triple sector quadrupole GC-MS-MS system. All analyses were performed using a 60 metre DB-5 fused silica capillary column (0.25 mm i.d. with 25 micron stationary phase film thickness). The MS-MS was operated in the multiple reaction monitoring mode. Ions characteristic of the tetra- through octachlorinated dioxins and furans were selected in addition to ions characteristic of chlorinated diphenyl ethers.

RESULTS AND DISCUSSION

CDDs and CDFs were identified in all four of the oil samples which were analyzed. The levels of the CDDs were found to range from 8.0 to 11.4 ppb while the total levels of the CDFs ranged from 0.85 to 1.1 ppb. OCDD was the predominant compound identified in all four samples with levels ranging from 2.5 to 3.7 ppb (approximately 30 percent of the total CDD concentration). The most toxic isomer, 2,3,7,8-TCDD, was found to range from 18 to 53 ppt in the samples analyzed. While the concentrations of the individual CDD congener groups tended to slightly increase with increasing degree of chlorination, the lower chlorinated CDF congeners dominated the distribution of the furan isomers. The relative distribution patterns of the CDD and CDF congener groups were similar for all four samples.

Several runoff water samples were collected and analyzed. Tetra- through octachlorinated dioxins were identified in the runoff water while tetra- and pentachlorinated furans were the predominant CDFs found to be present. The concentrations of the dioxins ranged from several hundred parts-per-quadrillion to a few parts-per-trillion with OCDD comprising approximately 30 percent of the total CDD concentration. The total concentrations of the individual CDD congener groups tended to increase with increasing chlorination. The concentration of 2,3,7,8-TCDD was typically in the low ppq range and therefore contributes relatively little to the total level of the CDDs present in the water. In the case of CDFs, the total concentrations of the individual congener groups were generally in the low ppq range. Unlike the series of dioxin isomers found in the water samples, the concentration of the CDF congener groups tended to decrease with increasing degree of chlorination. Although the congener distribution profiles within a given congener group remained fairly constant for

both the dioxins and furans, the relative concentrations of the congener groups appeared to vary somewhat from sample to sample. This was probably due to the fact that numerous samples were collected and analyzed at different stages throughout the two month period of the tire fire.
While the oily runoff material was collected and transported offsite for future treatment and disposal, the runoff water was treated onsite and subsequently discharged. A water treatment plant facility was setup onsite and the small batches of the water were initially processed to determine the efficiency with which toxic compounds, including CDDs and CDFs, could be removed. A series of untreated and treated water samples were analyzed for their CDD/CDF content. The treated water was not found to contain detectable levels of either CDDs or CDFs (typical detection limits were in the low ppq range). The treatment process was deemed to be satisfactory and treatment was begun on the million litres of runoff water which had been collected. Raw and treated water samples were collected and analyzed periodically to ensure that the efficiency of the process was being maintained.

Although the longterm environmental effects of the tire fire are not known, the potential damage was minimized by collecting and treating the oil and runoff water that were generated. A massive cleanup effort is ongoing, which includes groundwater monitoring for the CDDs/CDFs. The Hagersville fire was the first in which dioxins and furans were identified as byproducts from the burning of discarded tires. There are numerous used tire dumpsites located throughout North America and therefore the possibility of similar incidents exists. This investigation shows that when such fires occur, it is important to prevent runoff from contaminating groundwater supplies with toxic combustion byproducts such as the CDDs and CDFs.

REFERENCES

1. O. Hutzinger, M.J. Blumich, M.v.d. Berg, and K. Olie; **Chemosphere**, 14(6/7), 581, 1985.
2. P.E. des Rosiers; **Chemosphere**, 16(8/9), 1881, 1987.
3. L.L. Lamparski, T.J. Nestrick, and R.H. Stehl; **Anal. Chem.**, 51(9), 1453, 1979.