

OCCURRENCE OF DIOXINS AND FURANS IN AIR AND VEGETATION SAMPLES FROM A TIRE FIRE IN ONTARIO, CANADA

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ABSTRACT

A disposal site containing between twelve and fourteen million tires burned for seventeen days in February, 1990. During the course of the fire and the subsequent clean-up, environmental samples were collected and analyzed for polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). Air samples produced complex incineration patterns with a large number of isomers detected; total toxic equivalents (TEQ) at 3km downwind of the fire were an order of magnitude lower than those at 1km downwind. Concentrations on vegetation declined rapidly with distance from the burn site suggesting only a very localized impact.

INTRODUCTION

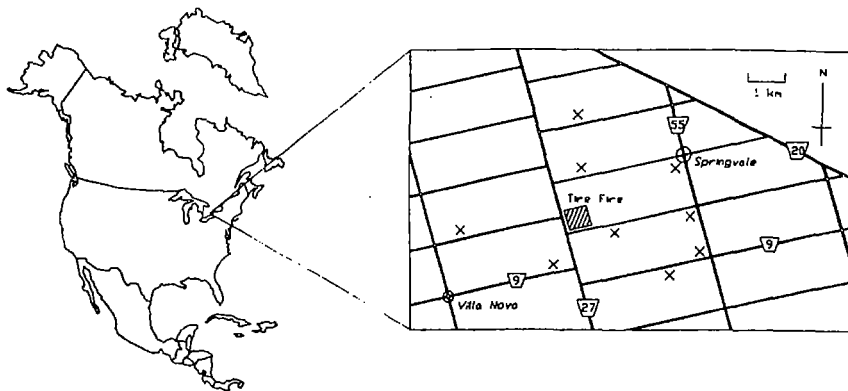
There have been several large tire fires in North America in the past few years, for example; Winchester, VA; Somerset, WI; and Hudson, CO as well as a number of smaller fires (Howard, 1988; Weston, 1989). Typically, volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) have been measured both in the plume and downwind but no results have been reported for PCDDs and PCDFs (NIOSH, 1984; Stofferahn and Simon, 1987; Weston, 1989). In southwestern Ontario in mid-February 1990, a fire was set in a disposal site containing between twelve and fourteen million used tires (Fig. 1). Environmental monitoring in the vicinity of this fire provided an opportunity to obtain data on this topic. This paper reports concentrations of PCDDs and PCDFs in air and vegetation samples collected during and after the fire.

EXPERIMENTAL

Air Sampling

Ambient air samples were collected with a high-volume sampler modified to accept a polyurethane foam (PUF) vapour trap behind a teflon-coated glass fibre particulate filter. Details are provided elsewhere (Tashiro et al., 1989). Sampling sites were changed as required to provide near-fire samples (1km downwind) and samples at the limit of the evacuation zone (3km downwind). On at least one occasion, samples were collected simultaneously at 1km upwind and 1km downwind. Sampling times were 24 hours during the fire and 48 hours after the fire was extinguished.

FIGURE 1. Location of the Hagersville Tire Fire and Air Sampling Sites.



Vegetation Sampling

Foliage samples from Norway spruce (*Picea abies*) were initially collected at 12 sites in the vicinity of the fire as well as at various distances from the fire site. Following the discovery of the presence of PCDDs and PCDFs in the sample collected nearest the fire, foliage from several additional species was collected at various distances from the fire. These species included Colorado blue spruce (*Picea pungens*), white cedar (*Thuja occidentalis*), eastern white pine (*Pinus strobus*), Japanese yew (*Taxus cuspidata*), several junipers (*Juniperus* spp.), and euonymus (*Euonymus fortunei*) in addition to the Norway spruce. The PCDD and PCDF content is being monitored to determine rate of loss from the foliage of the spruce.

Analysis

All samples were spiked with a mixture of $^{13}\text{C}_{12}$ -labelled PCDDs prior to extraction. Air samples (PUF and filter) were Soxhlet extracted with toluene for 18 hours. Vegetation samples were ground or cut into smaller portions and then Soxhlet extracted overnight with 20% acetone in hexane. Vegetation samples required extra preparation prior to the modified Dow cleanup. The vegetation hexane extracts were treated with a small amount of water to remove the acetone, washed with sulphuric acid and dried over sodium sulphate. At this stage all extracts were concentrated to 5-10 mL and processed using a modified Dow column cleanup. All samples were analyzed on a 60 m DB-5 column by GC/MS/MS using a Finnigan TSQ70 in the reaction ion monitoring mode. Detection limits for air samples ranged between

a minimum of 0.002 pg/m³ for H₄CDD and a maximum of 0.2 pg/m³ for H₃CDF and OCDF. Detection limits in vegetation samples ranged between 10 ppt for TCDD and 20 ppt for OCDD.

RESULTS

Results from the ambient air sampling are shown in Table 1 as international toxic equivalents (TEQ) for both PCDDs and PCDFs separately and the combined total. The fire was extinguished after 17 days. At sites 1km downwind of the fire the total TEQ was one order of magnitude higher than at 3km downwind. The highest total TEQ of 2.5 pg/m³ represents 50% of the provincial interim guideline of 5 pg/m³ (annual average).

TABLE 1. Dioxin and Furan Toxic Equivalents in Ambient Air Downwind of a Large Tire Fire (pg/m³).

Days After Fire Started	1km Downwind			3km Downwind		
	D	F	Tot	D	F	Tot
8/9	0.34	2.2	2.5	0.039	0.23	0.27
9/10	0.18	1.4	1.6	0.03	0.13	0.16
10/11	not sampled			0.037	0.2	0.24
12/13	0.095	0.66	0.76	0.014	0.032	0.046
13/14	0.01	0.012	0.022	not sampled		
15/16	0.029	0.093	0.12	not sampled		

D is dioxin; F is furan; Tot is combined dioxin and furan

On the second last day of the fire, the total TEQ at 1km downwind was 0.12 pg/m³ and at 1km upwind was 0.089 pg/m³. By this time, congener group concentrations in ambient air had declined to sub-picogram levels typical of those reported elsewhere in North America (e.g. Hunt and Maisel, 1989; Smith et al., 1989; Steer et al., 1989).

The concentrations of PCDDs and PCDFs measured in foliage samples are shown in Table 2. There is some variation among plant species with respect to the relative amounts of the various congeners present. In most cases, there is a much lower concentration of PCDDs and PCDFs at Site 2 in comparison to Site 1 indicating a rapid decrease in contamination with distance from the fire.

TABLE 2. Concentrations (pg/g) of PCDDs and PCDFs in evergreen foliage exposed to smoke from a large tire fire.

Species Site	Spruce		Cedar		Yew	Juniper	Euonymus
	1	2	1	2	1	1	1
<u>Dioxins</u>							
T ₁ CDD	83	ND	ND	ND	31	ND	15
P ₂ CDD	85	7	ND	ND	11	8.3	3.9
H ₈ CDD	42	25	ND	ND	17	24	16
H ₇ CDD	35	50	140	ND	41	74	61
O ₈ CDD	51	96	510	ND	56	290	150
<u>Furans</u>							
T ₁ CDF	580	9.4	300	28	190	220	160
P ₂ CDF	200	19	41	ND	26	43	66
H ₈ CDF	66	17	ND	ND	ND	16	20
H ₇ CDF	ND	ND	ND	ND	ND	ND	ND
O ₈ CDF	ND	ND	ND	ND	ND	17	ND

Sites 1 and 2 are approximately 100 m west and 200 m south respectively from the centre of the fire.

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