

Norwegian Spruce Needles: A Monitoring Technique for PCDD/Fs During and After a Tire Fire

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1. Introduction

Chlorinated pollutants have become a major environmental concern over the past few decades. One class of compounds which has been the subject of much scientific and public concern are the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). This particular group of compounds has been brought to the forefront world-wide as a result of various accidental contamination incidents such as Seveso Italy¹⁾, Times Beach Missouri²⁾, and Vietnam³⁾.

Some manufacturing and combustion processes involving the use of other chlorinated substances such as polychlorinated phenols⁴⁾, chlorinated benzenes^{5,8)}, chlorinated diphenyl ethers⁶⁾, and polychlorinated biphenyls^{7,8)} were found to inadvertently produce PCDD/Fs as by-products. Combustion sources, such as waste incinerators or domestic furnaces fueled by coal, oil or wood have also been well documented as sources of PCDD/F formation^{9,10)}. In countries like Britain and Germany, where some waste incinerators and domestic furnaces are fueled by coal, studies have shown that considerable amounts of PCDD/Fs were present both in ash samples as well as in soot found in the chimney stacks^{9,10)}.

Accidental fires that involved transformers and capacitors containing PCB oil, were discovered to produce the more toxic PCDF isomers (i.e. those having the 2,3,7,8-chlorine substitution)^{7,8)}. A different combustion source was discovered on February 12, 1990, when some thirteen million tires were set ablaze at a tire recycling site in west central Ontario.

The rubber manufacturing industry uses several different types of polymers to process rubber for products like tires, cable and wire coatings, industrial hoses and belts. One such process involves the vulcanization of a chlorinated compound, 2-chloro-1,3-butadiene, generically known as chloroprene (chlorobutadiene)¹¹⁾. A study¹²⁾ was conducted to determine whether or not short chain chlorinated hydrocarbons, which are used in many industrial processes including the production of rubber, were potential precursors of PCDD/Fs formations. The findings of that study indicated that short chain chlorinated organic compounds, involving the use of a catalyst and heat, did indeed lead to the formation of PCDD/Fs.

The Ontario Ministry of the Environment was called in to monitor the situation and to determine the overall environmental impact of the fire. Tire fires of this magnitude have been known to burn for many months. The thick black plume of smoke could be seen for miles and since not much was known about tire fires and their overall impact, various

techniques such as analyzing water runoff, ground water, oily runoff from the tires, soil, air, and vegetation, were employed for monitoring the situation during and after the fire. As a precautionary measure, special containment ponds were set up for both the runoff water and the oil from the melted tires. Once these samples were analyzed to determine what was present in the water and oil, then appropriate disposal measures were taken.

This paper examines the effects to vegetation, in particular Norwegian Spruce Needles, as a biological indicator for PCDD/Fs during and after a tire fire. The sampling of vegetation allowed studies to be conducted to determine not only the immediate but also the long term environmental impact on the area. Many questions arose out of this dreadful situation. How long would it take for the surrounding areas to recover from the fire? Will the situation improve or will it remain unchanged?

Studies have been conducted using higher plants, like the conifers, as an environmental monitoring tool for various compounds like pesticides, chlorophenols, PAHs, PCBs, HCBs and PCDD/Fs¹³⁻¹⁵). The success in using conifer needles is attributed to the structure of the needles themselves. They consist of an outer coating made up of lipophilic waxes which are ideal for trapping airborne material such as soot from a fire. The surface of plant foliage consists of small pores called stomata that open and close allowing atmospheric gases, like carbon dioxide, to enter and exit the plant. The fact that these higher plants are stationary year round and are so wide spread on a global basis, makes them a good monitoring indicator for environmental pollutants.

There have been many investigations in to the method of transport of hydrophobic pollutants, such as PCBs and PCDD/Fs within plants^{13,16,17}). The results from these findings have indicated that there is very little translocation of hydrophobic pollutants moving from the soil to the roots and travelling up through the plant. This method of transportation of these compounds cannot account for the degree of concentration found on the foliage. However, there are two processes which can explain these concentration effects: airborne deposition as well as surface volatility of the compounds themselves. Hydrophobic compounds can volatilize from the soil, providing there is sufficient enough vapour pressure. These pollutants are then re-absorbed by the foliage of the plant via, the waxy coating and the opening of the stomatas^{13,16,17}). Hence, conifer needles are excellent natural trapping devices for both airborne particulates as well as pollutants which are in their gaseous state.

The unanswered question as to the stability of these compounds became so important, especially after accidents like Seveso. Studies have pointed towards four possible mechanisms by which these compounds could break down: volatilization, absorption, mechanical loss, or photolysis¹⁸⁻²⁰). Evidence has pointed towards photodegradation being the main cause of the breakdown. In these investigations, the rate of photolysis was found to be dependant on two criteria: the degree of chlorination of the dioxins and furans and the presence of a strong hydrogen donating compound. Lower chlorinated T₄CDD/Fs were found to decompose at a faster rate than the higher chlorinated O₈CDD/Fs. Also, chlorines in the 2, 3, 7 and 8 positions were found to decompose at a much faster rate than those within the same isomer group¹⁸⁻²¹). Strong hydrogen donors are known to be found in the composition of the waxy cuticles of the foliage. Herbicide sprays and surface water on plant foliage are also strong hydrogen donors.

2. Experimental

Sampling The samples represented trees from one site located about 100 meters west of the fire. The control sample #1 was collected on the same day as samples 2-4. Samples

2-4, which were covered with black soot, represented three separate trees that were collected on the day that the fire was extinguished. Samples 5-10 were composites of these same three trees collected at approximately one month intervals after the fire. All samples were collected and placed in aluminum foil and rolled into pouches. These pouches were then dipped in liquid nitrogen in order to make the needles brittle. The pouches were then crushed to free the needles from the twigs and the needles were placed in 250 mL amber jars covered with a foil lined lid and stored frozen.

Sample Extraction and Cleanup Approximately 5g samples were weighed into Soxhlet extraction thimbles containing 1cm of silica. Each sample was fortified with ^{13}C -labelled quantitation standard and covered with glasswool. The sample was then Soxhlet extracted overnight (16hrs) with 200mL of 20% acetone/hexane mixture. After allowing the sample to cool, the samples were transferred into 250mL separatory funnels. Acetone was removed from the sample mixture by the addition of 10mL of HPLC grade water and then shaking the sample for one minute. The bottom water-acetone layer was decanted to waste and the samples were next washed with 10mL of concentrated sulphuric acid. Care was taken to quickly release the built up pressure inside the separatory funnel. Any emulsion which was present was eliminated by the careful addition of 1mL of HPLC water with a pipet. The acid layer was discarded to waste and the acid wash was repeated if necessary. Hexane extracts were then filtered through anhydrous sodium sulphate to remove any remaining traces of acid or water. The samples were then concentrated and placed through a chromatographic column packed with a glass wool plug followed by; 1g of 10% silver nitrate/silica, 1g silica, 2g of 33% sodium hydroxide/silica, 1g silica, 4g of 44% sulphuric acid/silica, 2g silica, and 2g of anhydrous sodium sulphate. The columns were initially washed with 50mL of hexane. Samples were quantitatively transferred to the column and the sample fractions collected by eluting the columns with 100mL of hexane. The samples were concentrated and further cleaned up on a second chromatographic column packed with a plug of glass wool, 5g of basic aluminum oxide, and 2g anhydrous sodium sulphate. Columns were prewashed with 50 mL of hexane and the samples were transferred to the column. Sample columns were further washed with 100mL of hexane followed by 20mL of 10% CCl_4 /Hexane. The final sample fractions were collected by eluting the columns with 40mL of 100% dichloromethane. The samples were then transferred to vials and concentrated to dryness under a gentle stream of nitrogen gas.

Instrumental All the vegetation samples from this fire were run on a gas chromatograph-tandem mass spectrometer (GC/MS/MS) system which consists of a Varian 3400 gas chromatograph that is interfaced to a Finnigan MAT-TSQ 70 triple quadrupole mass spectrometer via a direct capillary inlet. The GC column used was a 60 meter DB-5 capillary column with an internal diameter of 0.25 millimeter and a stationary phase thickness of 0.25 microns. The injector temperature was maintained at 280°C for all the analyses. The GC oven temperature program was the following: initial temperature of 100°C held for one minute, ramped to 200°C at 30°C/min, ramped to 235°C at 3°C/min and held for 10 minutes at 235°C, and finally ramped to 300°C at 6°C/minute where it was held at 300°C for 17 minutes. More information as to the quantitation of PCDDs/PCDFs and the ions monitored using GC/MS/MS can be found in more detail elsewhere^{22,23}.

3. Results and Discussion:

Ten samples were submitted for PCDD/F analysis. The results appear in Table #1 and the concentrations were reported in picograms per gram of foliage (ppt). The result for

the control sample only showed one positive, O_8CDD , which was present at a level of 15ppt. The other PCDD/F congeners for the control were not detected. Background atmospheric deposition could account for the presence of O_8CDD in the control sample. The samples that were collected prior to extinguishing the fire showed positives for all congener groups except for the O_8CDF . There were also similarities in the isomeric distributions between the three samples. The results from Table 1 presented a trend towards the formation of higher concentrations of the lower chlorinated dioxins and furans and lower concentrations of the higher chlorinated dioxins and furans. Previous work done on short chain hydrocarbons as potential precursors to the formation of PCDD/Fs showed a similar trend¹². Listed in Table 1 is the overall totals for PCDD/Fs for each sample. The total concentration for furans was present at higher levels than the totals for the dioxins. This particular pattern from the tire fire is similar to those seen from other combustion sources as in the case of waste incinerators, coal powered plants, home furnaces and accidental PCB fires. The lack of O_8CDF being present in the tire fire samples was consistent with these other sources⁷⁻¹⁰.

A comparison of PCDD/F concentrations in various samples collected at monthly intervals after the fire was also examined from Table 1. A trend towards a steady decline in the levels of PCDD/Fs in the months following the fire was found with almost each successive month. There was only a slight increase within the PCDF levels for the months of July and September. This slight deviation could have been attributed to weather conditions.

Table 2 lists the total toxic equivalent (TEQ) values of the 2,3,7,8-substituted congeners. In both Tables 1 and 2, the pattern of decreasing levels follow the order of the lower substituted congeners declining at a much faster rate than the higher substituted congeners. The greatest decline can be seen during the spring-summer months when the amount of sunlight is the most intense. The results tend to correlate with other studies on the photodecomposition rates of PCDD/Fs²⁰. By comparing data from Tables 1 and 2, concentration values for those 2,3,7,8 substituted toxic congeners appear to decline at a much faster rate than those within the same isomer group. Again from Table 2, during the months of July and September, the levels of PCDD/Fs seem to fluctuate slightly upward in value. This slight increase could have been attributed to either volatilization of PCDD/Fs from surrounding soil near the trees or deposition of particulate caused by rain or wind.

4. Conclusions:

Overall, the data from the tire fire seems to correlate with similar findings to those found from other combustion studies. The results tend to confirm that the steady decline in concentration over approximately the eight month period was probably attributed to photodegradation as found in other work. Spruce needles, as a biological environmental indicator for such compounds as chlorinated dioxins and furans, allowed for not only immediate but also long term monitoring of a potentially hazardous situation.

5. References:

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Concentration (pg/g) of PCDD/Fs in Norwegian Spruce Foliage During and After a Tire Fire

TABLE#1

Sample Number	Norway Spruce Needles									
	1 Control	2	3	4	5	6	7	8	9	10
Sample Date	Feb 22 1990	Feb 22 1990	Feb 22 1990	Feb 22 1990	May 7 1990	June 6 1990	July 4 1990	Aug 9 1990	Sept 6 1990	Oct 30 1990
T ₄ CDD	ND(1)	170 ¹⁵	86 ¹⁵	230 ¹⁸	18 ¹³	ND(1)	ND(3)	ND(1)	ND(1)	ND(3)
P ₅ CDD	ND(2)	120 ¹²	61 ¹²	130 ¹²	27 ¹²	8.2 ⁵	6.2 ¹	2.3 ¹	4.0 ²	ND(3)
H ₆ CDD	ND(2)	90 ⁷	39 ¹	100 ⁷	27 ⁴	15 ³	ND(9)	7.8 ²	8.5 ²	ND(4)
H ₇ CDD	ND(3)	56 ²	32 ²	61 ²	22 ²	19 ²	24 ²	13 ²	13 ²	11 ²
O ₈ CDD	15	86	50	74	31	37	ND(30)	17	12	ND(10)
TOTAL PCDD	15	522	271	595	125	79.2	30.2	40.1	37.5	11
T ₄ CDF	ND(3)	1600 ²⁰	730 ¹⁹	1700 ¹⁹	100 ¹⁸	16 ⁵	29 ³	3.0 ¹	9.5 ³	ND(2)
P ₅ CDF	ND(3)	370 ¹²	190 ¹⁰	410 ¹¹	60 ¹¹	20 ⁷	31 ³	7.3 ³	18 ³	ND(3)
H ₆ CDF	ND(8)	140 ⁷	65 ⁵	140 ⁵	31 ⁴	12 ²	26 ²	8.4 ²	8.8 ²	ND(10)
H ₇ CDF	ND(5)	31 ⁴	9.3 ¹	26 ²	10 ²	4.7 ¹	7.6 ¹	3.8 ¹	3.6 ¹	ND(7)
O ₈ CDF	ND(9)	ND(10)	ND(10)	ND(10)	ND(3)	ND(3)	ND(10)	ND(5)	ND(6)	ND(10)
TOTAL PCDF	0	2141	994.3	2276	201	52.7	93.6	22.5	39.9	0

- "ND" Not Detected. Detection limit in ppt given in brackets ().

- All concentrations expressed in ppt (parts-per-trillion; picograms (10⁻¹²grams) of PCDD/F per gram of sample).

- Superscripts indicated the number of isomers detected & values are corrected for recovery of isotopically labelled standards

TABLE#2

Total Toxic Equivalents (pg/g) of Norway Spruce Needles

	Norway Spruce Needles									
	1	2	3	4	5	6	7	8	9	10
2,3,7,8-T ₄ CDD	ND(1)	3.8	2.0	4.4	ND(1)	ND(1)	ND(3)	ND(1)	ND(1)	ND(3)
1,2,3,7,8-P ₅ CDD	ND(1)	9.1	4.1	10	2.4	ND(1)	ND(2)	ND(1)	ND(1)	ND(3)
1,2,3,4,7,8-H ₆ CDD	ND(2)	3.6	ND(2)	4.5	ND(1)	ND(2)	ND(9)	ND(2)	ND(2)	ND(4)
1,2,3,6,7,8-H ₆ CDD	ND(2)	6.4	ND(3)	8.6	ND(2)	ND(2)	ND(9)	ND(3)	ND(3)	ND(4)
1,2,3,7,8,9-H ₆ CDD	ND(2)	14	6.4	15	4.1	ND(2)	ND(10)	ND(3)	ND(3)	ND(4)
1,2,3,4,6,7,8-H ₇ CDD	ND(3)	25	14	27	9.3	8.1	10	5.6	5.5	4.8
O ₈ CDD	15	86	50	74	31	37	ND(30)	17	12	ND(10)
2,3,7,8-T ₄ CDF	ND(3)	ND(1)	ND(1)	ND(1)	ND(1)	ND(1)	ND(3)	ND(1)	ND(1)	ND(2)
1,2,3,7,8-P ₅ CDF	ND(3)	18	11	12	4.4	1.4	ND(3)	ND(1)	ND(2)	ND(3)
2,3,4,7,8-P ₅ CDF	ND(3)	35	16	41	6.1	3.1	5.0	1.4	2.4	ND(3)
1,2,3,4,7,8-H ₆ CDF	ND(6)	39	20	43	9.2	5.2	13	3.8	4.6	ND(10)
1,2,3,6,7,8-H ₆ CDF	ND(6)	14	6.4	16	ND(4)	ND(2)	ND(5)	ND(2)	ND(4)	ND(10)
2,3,4,6,7,8-H ₆ CDF	ND(7)	14	7.4	16	4.6	ND(3)	ND(8)	ND(2)	ND(3)	ND(10)
1,2,3,7,8,9-H ₆ CDF	ND(8)	ND(4)	ND(4)	ND(6)	ND(2)	ND(2)	ND(8)	ND(2)	ND(3)	ND(10)
1,2,3,4,6,7,8-H ₇ CDF	ND(3)	20	9.0	21	7.4	4.7	7.6	3.8	3.6	ND(5)
1,2,3,4,7,8,9-H ₇ CDF	ND(3)	ND(2)	ND(3)	ND(2)	ND(2)	ND(2)	ND(5)	ND(3)	ND(2)	ND(7)
O ₈ CDF	ND(9)	ND(10)	ND(10)	ND(10)	ND(3)	ND(3)	ND(10)	ND(5)	ND(6)	ND(10)
TOTAL TEQs	*0.02	36.39	16.90	41.36	6.45	*2.31	*2.81	*1.19	*1.76	*0.05

- A value of 0 was used in the TEQ calculations for congeners that were not detected.

- *Detection limits for individual congeners less than TEQ value.

- "ND" Not detected. Detection limit in ppt given in brackets ().