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Concentrations of Pentachlorophenol in Atmospheric Samples from Three Canadian Locations, 1994

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Pentachlorophenol (PCP) was introduced in 1936 as a wood preservative and, later, as a disinfectant (Worthing and Walker 1987). PCP use in Canada is regulated by the Pest Control Products Act and, since 1981, uses have been restricted to minimize human exposure through diet, dermal contact and inhalation.

Recently, Thompson and Treble (1994) reported on PCP concentrations in the urine of humans in Saskatchewan, Canada who were not occupationally exposed. All urine samples (87), which were collected May to August 1993, contained concentrations of PCP exceeding 0.2 µg L^{-1}. The mean PCP concentration in all samples was 1.6 µg L^{-1}. Similar results have been reported in studies of non-occupationally exposed components of the U. S. A. population. Average PCP concentrations in the urine of the general population have been reported to be 4.9 µg L^{-1} (Cranmer and Freal 1970) and 3.4 µg L^{-1} (Cline et al. 1989). In a study carried out as part of the National Health and Nutrition Examination Survey in which 6000 urine samples were analysed, the mean PCP concentration was 6.3 µg L^{-1} (DHHS 1994).

Although inhalation exposure could account for some of the PCP detected in the urine of Saskatchewan residents, there is no information available on the levels of PCP in ambient air in that province and only limited information for the rest of Canada. Environment Canada (1989, 1990) reported the results of the Detroit Incinerator Monitoring Program in which a range of chlorinated organic compounds, including PCP, was monitored at two sites in Ontario, one being an industrialized urban site in Windsor and the other a rural site on Walpole Island. The mean concentration of PCP for these two sites was 0.63 ng m^{-3}. In the U. S. A., the EPA (1980) estimated atmospheric concentrations of PCP using air models. A cumulative concentration estimate based on all emission sources was 0.15 to 136 ng m^{-3}.

This paper reports ambient concentrations of PCP in air at two sites in Saskatchewan and one site in the Northwest Territories. Due to the high incidence of PCP in human urine reported by Thompson and Treble (1994), 7-d air samples, collected at these three sites from early May to late July 1994 as part of a study investigating the long-

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range transport of herbicides, were re-analyzed for PCP content to determine whether atmospheric contamination could account for some of the PCP detected in the urine samples.

MATERIALS AND METHODS

As part of the investigation of possible long-range atmospheric transport of several herbicides commonly used in prairie agriculture, air samples were collected from three Canadian sites: Yellowknife in the south-central Northwest Territories; Waskesiu in Prince Albert National Park in central Saskatchewan; and Regina in south-central Saskatchewan. Sampling occurred from May 4 to July 20, 1994. Each sample consisted of approximately 2100 m^3 of air aspirated by a high-volume sampler (Model PS-1, General Metal Works, Village of Cleves, OH) which operated continuously for 7 d. The sampling unit consisted of a 102-mm diameter borosilicate filter in front of a 60-mm i.d. x 90-mm glass cylinder which contained polyurethane foam (PUF; 50 mm), XAD-2 resin (25 mL), and PUF (25 mm) in series. The PUF/XAD-2 resin sandwich was retained inside the glass cylinder by a stainless steel mesh. The borosilicate filter and the sampling unit for each air sample were Soxhlet extracted together for 16 hr using 600 mL of acetone. The acetone extract was evaporated to approximately 5 mL using a rotary evaporator (water bath 40°C) and transferred to a 40-mL centrifuge tube together with three 4-mL acetone rinses of the evaporating flask. The acetone extract was then evaporated to ~ 0.5 mL using a stream of nitrogen gas and methylated by the addition of ethereal diazomethane solution (4 mL; Grover et al. 1985) for 75 min. Hexane (2 mL) was added to the methylated extract and the extract evaporated to ~ 1 mL with a stream of nitrogen gas. The addition of hexane and subsequent evaporation was repeated three more times to completely remove diethyl ether from the extract. The extract was then subjected to Florisil column cleanup (Grover et al, 1985) and the column eluate concentrated to 1.0 mL.

In the present study, $^{13}C_6$-PCP methyl ether (100 ng in 100 µL of hexane) was added as an internal standard to each of the concentrated column eluates of these air samples and the eluates re-concentrated to 1 mL using a gentle stream of nitrogen gas prior to gas chromatographic analysis.

All samples were analyzed using a Hewlett-Packard Model 5890A gas chromatography (GC) interfaced to the Model 5970B mass selective detector (MSD) which was operated in the selected ion monitoring mode. The GC-MSD system was controlled with the Model 5895A data station and the GC was equipped with a 25-m x 0.2-mm i.d. Ultra- 1 capillary column (Hewlett-Packard; film thickness of 0.11 µm). Two µL of each sample extract were injected onto the GC column using a HP7673A autosampler. The split-splitless injector was operated in the splitless mode and maintained at a temperature of 230°C. The helium carrier gas flow was 25 cm s^{-1}, and the column temperature program consisted of an initial temperature of 70°C for 1 min followed by a temperature increase of 5°C min^{-1} to 270°C and hold for 1 min. The capillary interface between the GC and MSD was maintained at 280°C throughout

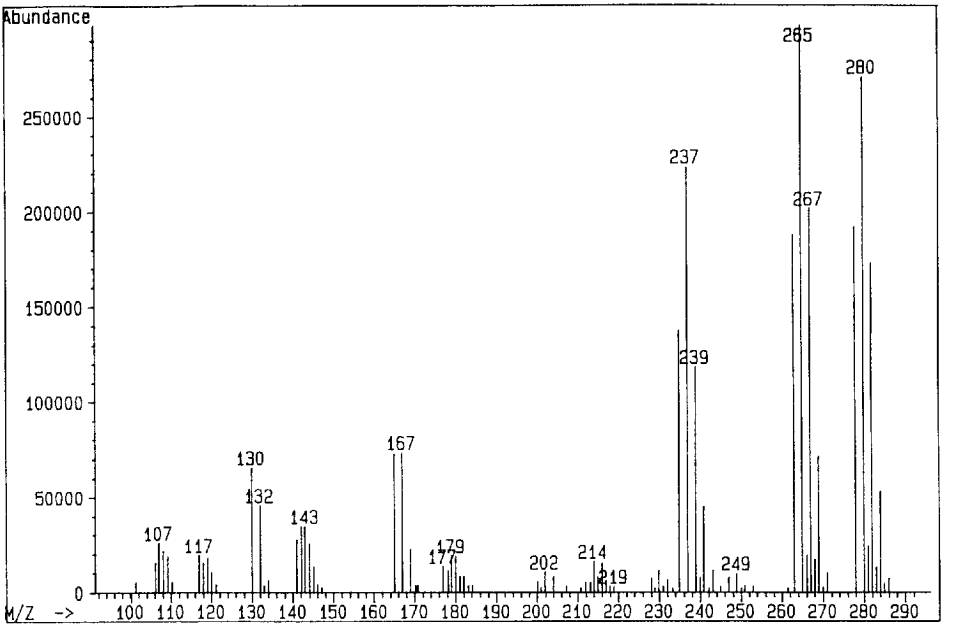

Figure 1. Electron-impact mass spectrum of PCP methyl ether (40 ng) obtained with the mass selective detector

each run. Under these operating conditions, the retention time for the methyl ether of PCP was 25.73 min.

The electron impact mass spectrum of PCP methyl ether produced parent ions (M) as well as ions corresponding to the loss of a methyl group (M-15) and the loss of an acetyl group (M-43) (Figure 1). Two ions from the parent cluster (m/z 278 and 280) and the most intense fragment ions [m/z 265 (M-CH_3; base peak) and m/z 237 (M-CH_3CO)] were monitored for native PCP and one ion (m/z 288; parent peak) for ^{13}C-isotopically labelled PCP. Utilizing $^{13}C_6$-PCP methyl ether as an internal standard, quantitation of PCP methyl ether was from a four-level (0.5, 1.0, 2.0 4.0 ng) calibration curve (based on peak areas from the m/z 280 peak) which was linear and passed through the origin ($r^2 = 0.999$). The minimum quantitation level was 0.25 ng for each 2 µL injection. This was equivalent to 125 ng per air sample or an ambient air concentration of 0.06 ng m^{-3}.

RESULTS AND DISCUSSION

PCP has been reported to be present in the atmosphere also as its methyl ether; that is, as pentachloroanisole (PCA) (Erickson et al. 1989; Hoff et al. 1992). Using pine needles as a monitoring tool, Erickson et al. (1989) reported PCA as a widespread air pollutant in Sweden at levels approximately twice those in the rest of Europe. In 1992, Hoff et al. reported concentrations of PCA detected in air samples collected

over an annual cycle at a rural site in southern Ontario in Canada. In that study, the annual mean concentration of PCA was 28 pg m^{-3} with the maximum concentration being 130 pg m^{-3}. PCA may also have been present in the air samples analysed in the present study. However, since diazomethane was used as the derivatizing agent, the analytical methodology did not permit differentiation between PCP present in the atmosphere as the phenol or as the anisole.

The parent (m/z 278 and 280) and fragment [m/z 265 (M-CH_3) and 237 (M-CH_3CO)] ions selected to confirm the presence of PCP in the air samples precluded interferences from the $^{13}C_6$- (and any $^{13}C_4$-labelled impurity) isotonically labelled PCP methyl ether. Three peak area ratios (m/z 237/265, m/z 278/265 and m/z 280/265; Table 1), based on the m/z 265 base peak, were initially used for confirmation purposes. The presence of PCP in an air sample was considered to be confirmed if i) a peak appeared at the same retention time (± 0.02 min) as the $^{13}C_6$-PCP methyl ether in the reconstructed chromatograms of all four ions monitored for native PCP and ii) at least two of the peak area ratios were within ± 30% of the analogous ratios obtained for standard solutions of PCP methyl ether. A maximum window of ±30% (EPA 1992) was chosen because of the high volume (~ 2100 m^3) of the air samples. The window, which was approximately an order of magnitude greater than the standard deviations associated with the ratios derived from standard solutions of PCP methyl ether (Table 1), allowed for variations due to matrix effects; for example, the presence of matrix compounds at the retention time (± 0.02 min) of PCP methyl ether which produced one or more of the ions used to confirm the presence of PCP.

Table 1. Mean peak area ratio values (± standard deviation) resulting from duplicate analyses of amounts (0.5, 1.0, 2.0 and 4.0 ng) of PCP methyl ether used to construct the calibration curve.

Mean peak area ratio		
237/265	*278/265*	*280/265*
0.60 ± 0.02 (± 3%)	0.50 ± 0.02 (±4%)	0.83 ± 0.01 (± 1%)
237/280	*265/280*	*278/280*
0.72 ± 0.03 (± 4%)	1.19 ± 0.01 (± 1%)	0.61 ± 0.02 (± 3%)

All sample extracts met the criterion for confirmation that a peak within± 0.02 min of the retention time of $^{13}C_6$-PCP methyl ether be present in the reconstructed chromatograms of all four ions monitored for native PCP (Figure 2). However, none of the Regina samples (n = 11) and only three of the Waskesiu samples (n = 5) met the requirement that two of the three peak area ratios fall within ± 30% of the mean ratios obtained using standard solutions of PCP methyl ether. The m/z 237/265, m/z 278/265 and m/z 280/265 peak area ratios for all Regina samples were consistently

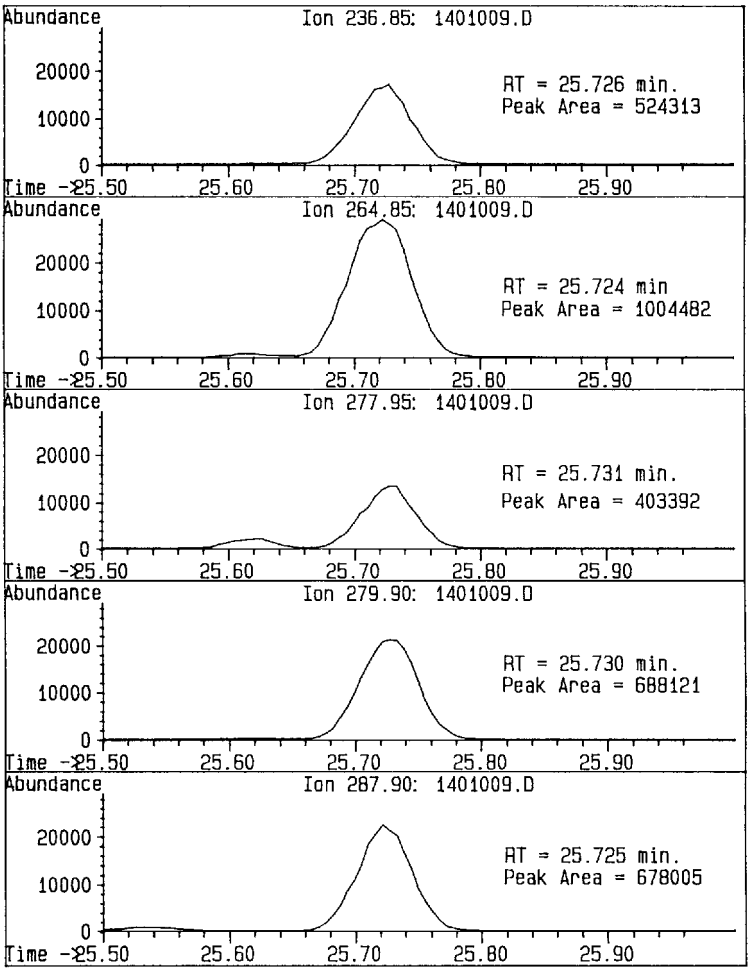

Figure 2. Reconstructed chromatograms of all four ions monitored for presence of PCP in air samples. The chromatograms are for the air sample collected at Yellowknife, May 11 - 17, which contained 0.42 ng m^{-3} of PCP.

low and only one of the 33 ratios fell within the ± 30% window. This pattern of consistently low values for the peak area ratios was also observed with the Waskesiu samples and indicated that, at these two sites, there was a major interference with the m/z 265 ion. In contrast, all Yellowknife samples showed confirmed residues of PCP and all peak area ratios [0.56 ± 0.02, 0.45 ± 0.03 and 0.74 ± 0.04 for the m/z 237/265, m/z 278/265 and m/z 280/265 ratios, respectively (n= 9)] were well within ± 30% of the mean ratios obtained with standard solutions of PCP methyl ether (Table 1) indicating that little or no such interference was present in the extracts of these samples. As a consequence of the site specific interference, ion ratios were redetermined (Table 1) on the basis of the next most abundant ion, that being the m/z

280 parent ion (Figure 1).

When the m/z 280 ion was used as the basis for the peak area ratios, residues of PCP, as its methyl ether, were confirmed and quantitated in the extracts of all air samples from all three sites, with the exception of the sample collected during the week of May 25-31 at the Regina site. The m/z 265/280 peak area ratio was consistently high and fell outside the ± 30% window for the Regina and Waskesiu samples and, together with the peak area ratios based on the m/z 265 ion, indicated that matrix interference with the m/z 265 ion decreased in the order Regina > Waskesiu > Yellowknife. Extracts from three unexposed PUF/XAD-2 resin sampling units were also analyzed and the mean background interference (14 ng) was approximately an order of magnitude less than the minimum quantitation level (125 ng). Thus, it was concluded that interferences or PCP contamination from the sampling units did not contribute significantly to PCP residues detected in the field samples.

Ambient air PCP concentrations were consistently greatest at the Yellowknife site (Table 2). This was somewhat unusual because we have not been able to identify any significant sources of PCP contamination within the Yellowknife vicinity. Concentrations ranged from 0.43 to 3.68 ng m^{-3}, with a mean value of 1.53 ng m^{-3} (Table 2). This value is somewhat greater than that (0.63 ng m^{-3}) previously reported for two sites in Ontario (Environment Canada 1989, 1990). At the Regina site, concentrations of PCP ranged from 0.06 to 0.58 ng m^{-3} and the mean concentration over the 11-wk period was 0.30 ng m^{-3}. Similar concentrations were detected in samples from the Waskesiu site where fewer samples were collected. The PCP concentrations detected at the Regina site were generally of lower magnitude than corresponding atmospheric concentrations of triallate, a commonly used preemergence soil-incorporated herbicide which has a vapor pressure (25.7 mPa; Jury et al 1983) similar to that (20 mPa; Anon 1987) of PCP. For the period 1978-81, Grover et al (1981, 1988), using 24-hr air samples, reported that maximum atmospheric concentrations of triallate (up to 198 ng m^{-3}) at a site near Regina occurred during the spring application period. Throughout the remainder of the growing season, triallate concentrations generally ranged from 0.5 to ~20 ng m^{-3}, except for extended periods of no rainfall when concentrations fell below 0.5 ng m^{-3}.

The collection of the air samples at all three sites spanned much of the 1994 growing season and essentially all samples contained detectable concentrations of PCP (Table 2). It has been reported that PCP may be 100% absorbed by inhalation (EPA 1981 from Roberts 1984). Thus, it is possible that atmospheric sources of PCP contributed to the residues measured in urine from Saskatchewan residents (Thompson and Treble 1994) via inhalation exposure.

Table 2. Pentachlorophenol residues in air samples (~ 2 100 m^3) collected over 7 d (168 hr) from early May to late July, 1994 at three locations in Canada.

Date	Regina	Waskesiu	Yellowknife
	----------	ng m^{-3}	----------
May 4-10	0.18	-[a]	NS[b]
11-17	0.13	0.14	0.43
18-24	0.22	-	NS
25-31	0.39	0.30	2.32
June 1-7	0.39	-	0.64
8-14	0.26	0.02	1.79
15-21	0.06	-	0.92
22-28	0.58	0.43	0.93
29-July 6	0.22	-	1.10
July 6-13	0.37	0.27	1.94
13-20	0.45	-	3.68
Mean	0.30	0.23	1.53

[a]Samples were collected at this site only every second week.

[b]NS = no sample was collected during that week due to sampler malfunction.

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