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Identification of Pentachloronitrobenzene in Ambient Air Extracts

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As a result of a study involving the determination of pentachlorophenol (PCP) in urine samples collected from the general population of residents of Saskatchewan (Thompson and Treble, 1994) it was decided that the potential for human exposure to PCP via inhalation warranted investigation. High volume ambient air extracts, which were initially collected for the determination of various herbicides including 2,4-D and triallate, were subsequently analyzed for PCP. During the analysis, it was determined that there were one or more components which were interfering in the determination of PCP by mass spectrometry using selected ion monitoring (SIM). The reconstructed ion chromatograms for the characteristic ions selected for the SIM analysis had several peaks appearing within the retention window scanned for PCP. Subsequent fill scan mass spectral analysis of these peaks revealed the presence of the fungicide pentachloronitrobenzene.

Pentachloronitrobenzene (PCNB), also known as quintozene or terraclor, is an organochlorine fungicide which is applied to seeds, soils, and plants. Dust or powder formulations containing PCNB are registered in Canada for use in soil applications for ornamental plants. PCNB is also registered in Canada for use as the active ingredient in a wettable powder for soil and plant applications on food (broccoli, brussel sprouts, cabbage, cauliflower) and feed crops, ornamental plants, and turf. Application of PCNB-containing products would be carried out manually or using some form of sprayer. There is no reported registered use of PCNB which would permit aerial application.

Caseley (1968) and Wang and Broadbent (1972) reported that the major mechanism for loss of PCNB from aerobic soil was via volatilization. The vapour pressure has been reported as 15.1 mPa at 25°C (Coring 1967). In a subsequent study (Wang and Broadbent, 1973) it was found that the microbial degradation of PCNB to pentachloroaniline (PCA) was the major route of loss for PCNB-treated soil samples which were flooded by water. Murthy and Kaufman (1978) also demonstrated that PCNB undergoes microbial degradation in anaerobic soil to form PCA. It was suggested that the PCA remained in the soil as a residue or was

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absorbed by plants. Depending upon the nature of the utilization of PCNB, it would not be unexpected for a portion of the applied fungicide to be lost to the atmosphere.

A series of extracts prepared from ambient air samples collected over May through July 1994 near Regina, Waskesiu and Yellowknife were re-analyzed for pentachloronitrobenzene. The results of these analyses are presented herein.

MATERIALS AND METHODS

Atmospheric samples were collected from three Canadian sites: near Yellowknife in the south-central Northwest Territories; Waskesiu in the Prince Albert National Park in the boreal forest of central Saskatchewan; and, near Regina in south-central Saskatchewan. Sampling occurred from May 4 to July 20, 1994.

Ambient air was sampled for periods of 7 days using a high volume sampler (model PS-1, General Metal Works, Village of Cleves, OH) equipped with a sampling unit consisting of a borosilicate filter (102-mm diameter) followed by a glass cylinder (60-mm i.d. x 90-mm) packed with a 50-mm plug of polyurethane foam (PUF), 25 mL of XAD-2 resin, and a 25-mm PUF plug in series. Approximately 2 100 m^3 of air was drawn through the sample train over each 7-day sampling period.

In brief, the filter and PUF/XAD-2 adsorbents were Soxhlet extracted together with 600 mL of acetone for 16 hours. The resulting extracts were concentrated to approximately 5 mL using a rotary evaporator equipped with a heated water bath (40°C). The extracts were derivatized with diazomethane (for the original purpose of analyzing acidic herbicides) and subjected to a Florisil column cleanup procedure previously described by Grover et al. (1985). The final extract volumes were adjusted to 1.0 mL. It should be noted that three randomly selected unexposed sampler units were processed in the same manner. The resulting extracts were used as laboratory blanks.

Samples were analyzed using a Fisons MD 800 GC-MS system in which a Carlo Erba gas chromatograph was interfaced to the quadrupole mass spectrometer by a direct capillary interface. The GC was equipped with a split/splitless injector which was operated in the splitless mode and maintained at a temperature of 22O°C. One microlitre of each extract was injected into the GC using a Fisons AS800 autosampler. A DB-5MS capillary GC column (15-m x 0.25-mm i.d.) having a stationary phase film thickness of 0.25 µm (J & W Scientific, Folsom, CA) was used for all analyses. The GC oven temperature profile consisted of an initial temperature of 120°C for 2 min followed by a temperature increase to 220°C at 8°C min^{-1}, and finally to 300°C at 20°C min^{-1}. The final temperature was held for 5 min. Under these chromatographic conditions, the PCNB eluted at approximately 8.6 min.

The mass spectrometer system was operated in the electron impact ionization mode with an electron energy of 70 eV. The mass spectrometer parameters (i.e., repeller and focusing lens potentials, etc.) were selected by automatically tuning the MS with respect to the reference compound perfluorotributylamine (PFTBA). The ion source temperature and direct capillary interface temperature were maintained at 200°C and 300°C, respectively.

In order to achieve the desired sensitivity, the MS was operated in the SIM mode. Four ions characteristic of PCNB were chosen (see Table 1). Based on peak areas from the m/z 295 parent peak, quantitation of PCNB was from a three-level (0.1, 0.25 and 1.0 ng) calibration curve which was linear and passed through the origin (r^2=0.998). The minimum quantitation level was 0.01 ng for each 1-µL injection which was equivalent to 10 ng per air sample or an ambient air concentration of 0.005 ng m^{-3} (based on a 2000 m^3 sample). Criteria for the positive identification of PCNB in an air sample extract were set as follows.

1. A peak must occur in the reconstructed ion chromatogram (RIG) for each m/z value at the same retention time (±0.05 min) as for an authentic standard of PCNB analyzed under identical GC conditions.

2. The relative peak areas in the four RICs must agree within ±15% of those obtained for an authentic standard of PCNB analyzed under identical GC-MS conditions (Table 1).

3. Laboratory blanks (extracts obtained from unexposed sampler units which were processed with the other sample extracts) must be demonstrated to be free of PCNB.

Table 1. Ions monitored in SIM analysis of PCNB.

m/z value	ion	relative ratio*
249	$C_6{}^{35}Cl_4{}^{37}Cl^+$	100
293	$C_6{}^{35}Cl_5NO_2{}^+$	50
295	$C_6{}^{35}Cl_4{}^{37}ClNO_2{}^+$	79
297	$C_6{}^{35}Cl_3{}^{37}Cl_2NO_2{}^+$	50

* Normalized to the base peak (average of 4 injections of PCNB standard).

RESULTS AND DISCUSSION

Analysis of the extracts from the three unexposed sampling units showed no confirmed residues of PCNB and no interferences with the m/z 295 peak. Thus, it was concluded that the sampling units did not significantly contribute to the PCNB concentrations tabulated in Table 2 for the three sampling sites. In the RICs for all samples from the Regina and Waskesiu sites in which PCNB was detected, peaks for the m/z 249,293, 295 and 297 ions were within ±0.05 min of the retention time obtained for PCNR standard solutions analyzed under identical GC conditions. For all of these samples, relative ratios fell within ±15% of that (100:50:79:50; Table 1) obtained using an authentic standard of PCNB. Thus, the criteria for positive identification as PCNB (i.e., correct GC retention time and normalized relative peak areas, and the absence of peaks in the laboratory blanks) were satisfied for all samples showing ambient air concentrations of PCNB. Figure 1 depicts the RICs for the ions monitored to confirm the presence of PCNB in an extract obtained from an ambient air sample collected in Regina (May 4-10). For this sample, the relative ratio of the integrated peak areas for the RICs corresponding to the m/z 249, 293, 295 and 297 ions was 100:54:85:54.

Table 2. Ambient air PCNB concentrations (ng m^{-3}) at three different locations (1994 collections).

DATE	REGINA	WASKESIU	YELLOWKNIFE
May 4 - 11	1.60	-	-
May 11 - 18	0.24	0.38	ND
May 18 - 25	0.29	-	-
May 25 - June 1	0.09	ND	ND
June 1 - 8	0.16	-	ND
June 8 - 15	0.12	ND	-
June 15 - 22	ND	-	ND
June 22 - 29	0.06	0.03	ND
June 29 - July 6	0.02	-	ND
July 6 - 13	0.04	ND	ND*
July 13 - 20	0.01	-	-

* Six-day sample collected from July 7 to13, 1994.
"-" No sampling carried out.

Since the PCNB trapping efficiency of the PUF sampling unit and the recovery of PCNB from the sampling unit by Soxhlet extraction remain unknown, the ambient air concentrations of PCNB detected at the Regina and Waskesiu sites (Table 2) are semi-quantitative. The highest concentration of PCNB (1.6 ng m^{-3}), together

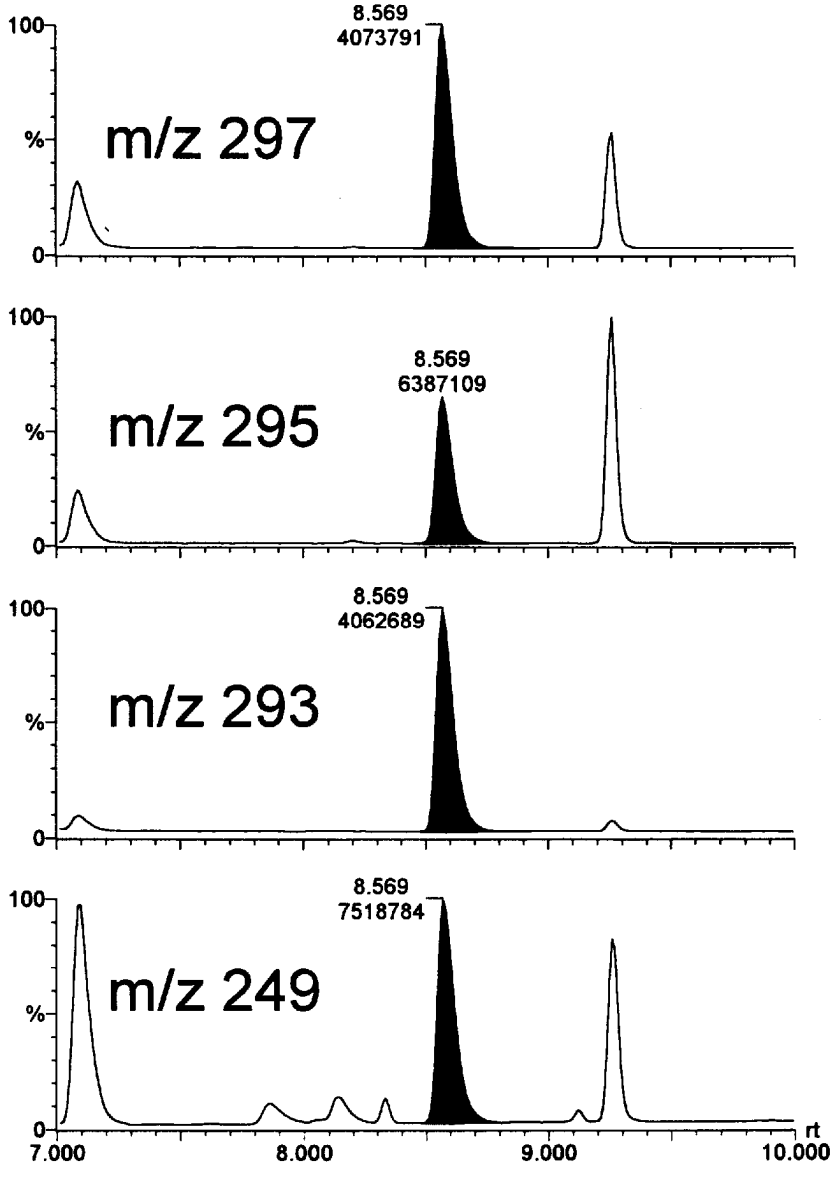

Figure 1. Reconstructed ion chromatograms for four ions monitored in SIM analysis of PCNB in a 7-day (May 4-10) ambient air extract from Regina.

with the highest frequency of occurrence (10 out of 11 samples), was detected in the Regina samples. PCNB concentrations in the Waskesiu samples were lower (maximum 0.38 ng m^{-3}) and occurred less frequently (2 out of 5 samples). No PCNB was detected in any of the 7 samples from Yellowknife. While the highest concentrations at Regina and Waskesiu were recorded in early and mid-May when agricultural activities are commencing for the summer, this chemical is not used on the cereal and oilseed crops most commonly grown in the region. The crops for which the chemical has registered uses in Canada include ornamentals, ginseng and turf, but these are not major crops grown in southern Saskatchewan (Anonymous, 1996).

Although the ambient air PCNB concentration data are semi-quantitative (Table 2) it is of interest to note that concentrations in the Regina samples were of the same order of magnitude as concentrations of several herbicides detected in the same samples. Dicamba, 2,4-D and triallate are used extensively within this region. For example, sales of 2,4-D in the prairie provinces (Manitoba, Saskatchewan and Alberta), for 1994, were in excess of 3,000,000 kg. Maximum concentrations of these three herbicides in the Regina samples were 0.1, 0.37 and 7.22 ng m^{-3}, respectively (Environment Canada, unpublished data). Even though the source of PCNB in the Regina samples is not evident, the relatively high concentrations detected may reflect the high photostability of this compound to sunlight irradiation (Crosby and Hamadmad, 1971).

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