

# TOXA (po)

Concentrations of pentachlorophenol and some related compounds in seasonally collected atmospheric samples from five Canadian locations.

**D. T. Waite**, Environment Canada, 300-2365 Albert St., Regina, SK, S4P 4K1, Canada, N. P. **Gurprasad**, Environment Canada, Edmonton and **M. B. Constable**, Environment Canada, Edmonton.

## 1 - INTRODUCTION

The compound pentachlorophenol (PCP) was introduced in 1936 as a wood preservative and, later, as a disinfectant (1). PCP use in Canada is regulated by the Pest Control Products Act. Uses have been restricted, since 1981, to minimise human exposure through food, contact and inhalation. In 1994 Thompson and Treble (2) reported a high incidence of PCP in the urine of Saskatchewan residents not occupationally exposed to this chemical. Air samples collected, in summer, on composite polyurethane foam (PUF)/XAD-2 resin plugs as part of an unrelated atmospheric investigation, were reanalysed for PCP to determine if atmospheric contamination could account for some of the chemical measured in the urine samples. All samples contained detectable quantities of PCP (Environment Canada unpublished data). The current study was undertaken to determine if there is a seasonal trend in the atmospheric abundance of pentachlorophenol and to ascertain if the related compounds hexachlorobenzene (HCB) and some dioxins were also present.

There exists a large body of literature on the movement and toxicity of PCP. Much of this deals with soil and groundwater contamination. The dangers due to volatility of PCP in indoor situations were noted by Roberts (3) and by Spengler and Sexton (4) who referred to California regulations on the use of treated wood in building interiors. PCP was monitored in air and in workers' urine in the unpublished California study they quoted. Roberts also quoted a United States Environmental Protection Agency position paper as saying that PCP may be 100% absorbed by inhalation (5 from 3). Cline et al. (6) reported elevated concentrations of PCP in urine and serum from United States residents of treated log houses and related this to inhalation of the chemical. Hattemer-Frey and Travis (7), however, considered that most exposure to PCP in the continental United States came from food sources. PCP has been reported from rain in Hawaii (8) and in the urine of humans in the continental United States (9). There seems, though, to be little information about background PCP concentrations in the Canadian atmosphere. Environment Canada (10, 11) reported a mean PCP concentration of 0.63 ng m<sup>-3</sup> in air samples taken from two Ontario sites, Windsor (urban) and Walpole Island (rural).

In the current study PCP was analysed from high volume atmospheric samples collected from five Canadian locations during three seasons (summer, fall and winter) to examine the seasonal variation in atmospheric concentrations. It has been reported (12, 13) that, in rats, PCP in urine may result from

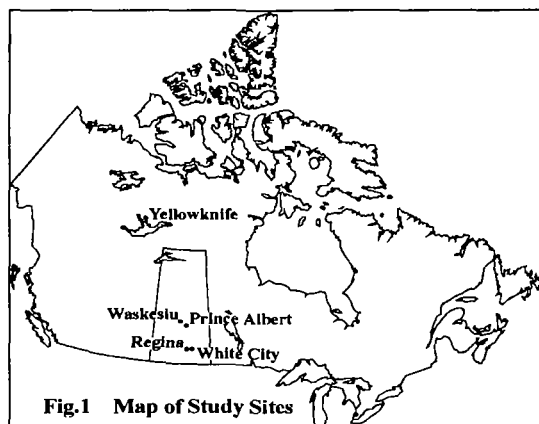
the metabolization of HCB. Various dioxins, an often reported contaminant of PCP (e.g.14). For these reasons the samples were also analysed for HCB and some dioxins.

## 2 - METHODS AND MATERIALS

### 2.1 Study Sites and Field Methods

Table 1 Atmospheric samples were collected from five Canadian sites (Fig. 1):

Site Name	Location	Description
Yellowknife	Northwest Territories	Small city located in boreal forest , mining industry
Prince Albert	Central Saskatchewan	Small city in park land near boreal forest, pulp and paper, lumber industries
Waskesiu	Central Saskatchewan	Within the Prince Albert National Park in boreal forest
(Regina) Research Station	Southern Saskatchewan	Agricultural research station in rural setting just outside Regina
White City	Southern Saskatchewan	An outdoor storage facility for hydro/utility poles treated with wood preservatives, east of Regina City



Sampling occurred for three sequential weeks during the following periods: July 17 to August 7, 1995; October 16 to November 6, 1995 ; and, January 15 to February 5, 1996. Each sample consisted of approximately 2100 m<sup>3</sup> of air aspirated, by a high-volume sampler (Model PS-1, General Metal Works, Village of Cleves, OH), through a 102 mm diameter borosilicate filter and then a composite

# TOXA (po)

polyurethane foam (PUF)/XAD-2 resin plug (PUF plug) contained in a glass cylinder. The samplers were operated continuously for 7 days for each sample.

## 2.2 - Laboratory Extraction and Analysis

The PUF plugs were Soxhlet extracted for 20 hours with 500 ml acetone. The acetone extract was concentrated to dryness and then made up to a 5 ml final extract volume with toluene for GC/MSD analysis of hexachlorobenzene (HCB) and four dioxins (penta, hexa, hepta and octa chloro-). For pentachlorophenol analysis, one ml of the toluene final extract was evaporated to dryness and treated with 2 ml of diazomethane solution for 30 minutes to derivatize the phenol to the methyl. The diazomethane solution was evaporated to dryness and the extract was made up to 1 ml final volume with toluene for pentachlorophenol GC/MSD analysis.

All analytes were analysed using a HP5971 GC/MSD in the selective ion monitoring (SIM) mode. The column used was a Rtx-5, 30 m long, 0.25 micron film thickness and 0.25 mm ID. Helium was used as carrier gas. The GC temperature programming was: initially hold at 100° C for 1 minute then ramp to 220° C at 20° C/min then at 5° C/min to 300° C. Hold at 300° C for 5 minutes. Injection and transfer line temperature were 300° C and 280° C, respectively. Detection limits were set at 250 ng per sample or approximately 0.1 ng m<sup>-3</sup> of air, for all compounds reported.

## 3 - RESULTS AND DISCUSSION

Table 2 Seasonal concentrations of pentachlorophenol in the atmosphere at six Canadian locations. The concentrations (ng m<sup>-3</sup>) are the average of three consecutive 7-day samples.

Site	July 17 - Aug. 7	Oct. 16 - Nov. 6	Jan. 15 - Feb. 5
Yellowknife	3.4	trace	trace
Prince Albert	5.0	0.3	n.d.
Waskesiu	0.9	n.d.	trace
Research Station	0.5	trace	n.d.
White City	619.0	19.6	1.1

trace = confirmed presence but below level of quantitation

n.d. < 0.1 ng m<sup>-3</sup> (less than detection)

In the July samples, PCP was found at all sites (Table 2). The highest concentrations were, expectedly, at the utility pole storage facility in White City. Concentrations were 100x the next highest samples. The concentrations in the two city sites, Yellowknife and Prince Albert, were similar and about 10x greater than the two rural sites, Waskesiu and the Research Station. Concentrations of PCP in the October samples were consistently lower than in July by about an order of magnitude (10x). Concentrations were reduced to trace or non detectable levels in January except at White City. This probably reflects the effect of temperature on the volatilisation of PCP. Temperatures in October were generally cool but in January they were -20 to -30 ° C with frequent blizzard conditions.

Higher concentrations of PCP were expected at the White City site where PCP treated utility poles are stored. The concentrations in the two rural sites, Waskesiu and the Research Station, may represent background levels in the south to central region of the province. The concentrations at the two city sites, elevated above this background, may result from local use of treated wood for construction, utility poles, landscaping etc.

All the samples were analysed for hexachlorobenzene (HCB) and four dioxins (penta, hexa, hepta and octa chloro). Traces of HCB were found in July samples from Yellowknife, Prince Albert and the Research Station sites but not from the other sites or from the other seasons. It appears that the concentration of HCB is not correlated with the presence of PCP in these air samples. Actual HCB concentrations were too low to draw conclusions about trends in distribution. No dioxins were detected in any sample. This does not mean that dioxins may have been present but only that they were below the  $0.1 \text{ ng m}^{-3}$  detection level.

Summer concentrations of PCP can not be explained on the basis of Canadian use patterns. Sales volume in Canada are confidential but are about two orders of magnitude (100x) lower than the popular herbicide 2,4-D. Almost 4 million kg of 2,4-D were sold in Canada in 1990 with more than half of that being used in Saskatchewan and the two adjacent prairie provinces (Environment Canada unpublished data). Concentrations of 2,4-D in air at the Research Station site in 1989 and 1990, during the growing season (herbicide use period) were: maximum  $4.2 \text{ ng m}^{-3}$  and median values of  $0.2$  and  $0.1 \text{ ng m}^{-3}$  respectively (Environment Canada unpublished data). Average concentrations of PCP at the rural sites exceeded median 2,4-D values and average urban PCP concentrations exceeded the maximum concentration of 2,4-D recorded over two growing seasons. The relatively high concentrations of PCP may result from higher environmental mobility and greater persistence of this compound or may reflect some influence from global transport or a combination of both.

Detectable concentrations of PCP are, then, present in the atmosphere in Saskatchewan and the Northwest Territories in summer and fall months. It is possible that some of the PCP found in Saskatchewan human urine samples (2) may be derived from inhalation. Very low and infrequent traces of hexachlorobenzene were found and it is unlikely that inhalation and metabolism of this compound accounts for PCP in the urine samples, even though this has been reported in the literature (12, 13) as a possible source. No dioxins were detected even in samples from the site where treated wood is stored, possibly because of the relatively high detection limits for these compounds.

**Acknowledgments** We would like to thank C. Teichroeb, R. Finlayson, B. Moldenhauer, E. Cabalo, M. Gilchrist, P. Tarleton, R. Cherepak, K. Mack (and the Prince Albert Water Survey staff) and S. Harbicht for technical assistance and the Saskatchewan Power Corporation for their cooperation. Funding was provided by Environment Canada Toxic Chemicals Fund with additional support from Prince Albert National Park.

# TOXA (po)

## 4 - REFERENCES

- 1 - Worthing, C. R. and S. B. Walker (eds). 1987. The pesticide manual. eighth edition. British Crop Protection Council, Lavenham Press, Lavenham, Suffolk. 1981p.
- 2 - Thompson, T. S. and R. G. Treble. 1994. Preliminary results of a survey of pentachlorophenol levels in human urine. *Bull. Environ. Contam. Toxicol.* 53:274-279.
- 3 - Roberts, H. J. 1984. Untitled letter to *Science* 223 (4631):6
- 4 - Spengler, J. D. and K. Sexton. 1984. untitled letter to *Science* 223(4631):8.
- 5 - EPA. 1981. Wood preservative pesticides: creosote, inorganic arsenicals, pentachlorophenol. Position Document no 2/3, Environmental Protection Agency, Washington, D. C.
- 6- Cline, R. E. , R. H. Hill, D. L. Phillips and L. Needham. 1989. Pentachlorophenol measurements in body fluids of people in log homes and workplaces. *Arch. Environ. Contam. Toxicol.* 18:475-481.
- 7 - Hattemer-Frey, H. A. and C. C. Travis. 1989. Pentachlorophenol: environmental partitioning and human exposure. *Arch. Environ. Contam. Toxicol.* 18:482-489.
- 8 - DHHS. 1994. Toxicological profile for pentachlorophenol (update). U. S. Department Health Human Services, Public Health Service, Agency Toxic Substances disease Registry. Atlanta, GA. TP-93/13.
- 9 - Cranmer, M. and J. Freal. 1970. Gas chromatographic analysis of pentachlorophenol in human urine by formation of alkyl ethers. *Life Sci.* 9:121-128.
- 10- Environment Canada. 1989. Detroit incinerator monitoring program. Data report #3. Windsor air sampling site, July 1987 - September 1988. Walpole Island air sampling site, January 1988 - September 1988. Conservation and Protection PMD 89-8. Ottawa, Ont.
- 11 - Environment Canada. 1990. Detroit incinerator monitoring program. Data report #4. Windsor air sampling site, sampling site, September 1988 - October 1989. Walpole Island air sampling site, August 1988 - October 1988. Conservation and Protection PMD 90-8. Ottawa, Ont.
- 12- Koss, G., W. Koransky and K. Steinbach. 1976. Studies on the toxicology of hexachlorobenzene. Part 2: identification and determination of metabolites. *Arch. Toxicol.* 35:107-114.
- 13 - Rizzardini, M. and A. G. Smith. 1982. Sex differences in the metabolism of hexachlorobenzene by rats and the development of porphyria in females. *Biochem. Pharmacol.* 31:3543-3548.
- 14 - Buser, H. R. and H. P. Bosshardt. 1976. Determination of polychlorinated dibenzo-p-dioxins and dibenzofurans in commercial pentachlorophenols by combined gas chromatography -mass spectrometry. *J. Am. Assoc. Anal. Chem.* 59:562-569.