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# Multidetector Gas Chromatographic Determination and Confirmation of Airborne Triallate Residues in Saskatchewan

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Accumulative triallate samples were collected daily from May to November by using an air sampling train with polyurethane foam as the adsorbent material. A cleanup procedure was developed to improve the analysis of extracted triallate [*S*-(2,3,3-trichloroallyl) diisopropylthiocarbamate] by gas chromatography, using an electron capture (EC) detector and an alkali flame ionization detector (AFID). The limit of detection for airborne triallate was set at 0.5 ng $m^{-3}$ (12.7 ng $m^{-3}$ = 1 part per trillion triallate in the air). The maximum concentrations of triallate were found during the peak spraying season in May, being up to 200 ng $m^{-3}$ in 1978 and 100 ng $m^{-3}$ in 1979. The triallate concentrations in the air gradually decreased to 20 ng $m^{-3}$ or less by midsummer, with some increase again in the fall, corresponding to the limited fall application of the chemical. After freeze up of the soil in early November, the triallate levels in the air fell below the detection limit. In general, the dramatic increases in triallate concentrations in the air during summer usually followed a rainfall event.

The presence of atmospheric residues of phenoxy herbicides, such as 2,4-D (2,4-dichlorophenoxyacetic acid), in the cereal growing regions of Canada and the United States is well documented (Farwell et al., 1976; Grover et al., 1976). It is also recognized that the major route of their input into the atmosphere is drift and vaporization losses during and immediately following their application (Grover et al., 1972, 1973). This short "release" period, combined with their relative nonpersistence in the environment (Loos, 1975), has no doubt limited the residence time of these herbicides in the atmospheric compartment to periods during or immediately after their application.

In contrast, however, the postapplication volatilization losses of soil-incorporated herbicides, such as trifluralin ($\alpha,\alpha,\alpha$-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine), to the atmospheric compartment may be a continuing process, extending over the entire growing season (White et al., 1977). Triallate, a soil-incorporated herbicide, with a vapor pressure similar to that of trifluralin (Grover et al., 1978), is used extensively in the Canadian prairies and the great plains of the United States to control wild oats (*Avena fatua* L.) in cereal and oilseed crops. The present study reports the levels and duration of triallate residues in the air in the Regina Plains, a high-use area.

## MATERIALS AND METHODS

**Location and Duration of Sampling.** The field monitoring sites were at Regina in 1978 and 1979 and at Indian Head in 1979, both located in the cereal growing region of southern Saskatchewan. The sampling train was usually started in the first week of May each year and continued up to the freezing of the soil surface in early November to mid-November.

**Sampling Procedure.** Accumulative triallate samples were collected on 24-h basis on weekdays and 72-h basis on weekends by using polyurethane foam as the solid adsorbent. The sampling train consisted of (1) a glass tube with an inverted cone-shaped inlet set at 2 m from the ground, (2) an adsorbent chamber containing one or two, 45 mm diameter by 50 mm long, polyurethane foam plugs, (3) a calibrated flow meter (Gilmont Instruments, Inc., Great Neck, NY), and (4) an electric vacuum pump (Gelman Instrument Co., Ann Arbor, MI). The adsorbent chamber, flow meter, and pump were set in a Steven's screen weather box, to protect the system from sunlight, rain, etc. The air flow rate during sampling was set at 25 L $min^{-1}$ with a needle valve and was checked during each foam plug change.

The adsorbent chamber contained only one foam plug in 1978. However, recovery studies indicated that two foam plugs in series were required to retain all of the entrapped triallate vapor, especially when weekend samples were run over the 72-h period at this high flow rate (Grover and Kerr, 1981). Consequently, two plugs in series were used in 1979 sampling. The exposed foam plugs for each sampling period were transferred to individual glass jars equipped with Teflon-lined screw-cap lids and the jars stored in a freezer until analysis.

**Extraction, Cleanup, and Analysis.** During 1978, the entrapped triallate vapor in each foam plug was Soxhlet extracted with 250 mL of *n*-hexane for 2 h. In 1979, when two plugs in series were used, the first plug was extracted with 300 mL of *n*-hexane for 2 h, after which it was replaced with the second plug and the extraction continued for another 2 h. The volume of the extracts was then reduced to ~1 mL by using a rotary evaporator.

Florisil (4 mL), deactivated with 5% water, was packed in a 7 mm i.d. glass column (Chromaflex No. 22, Kontes Glass Co., Vineland, NJ), containing *n*-hexane, and the excess hexane was drained slowly at the rate of 1 mL/min. The triallate residue was then quantitatively transferred to the column, by washing the extraction flask with five 2-mL portions of *n*-hexane, and the column eluted with 25 mL of 0.5% acetone in *n*-hexane. The first 10 mL of the eluate was discarded, the remaining eluate collected

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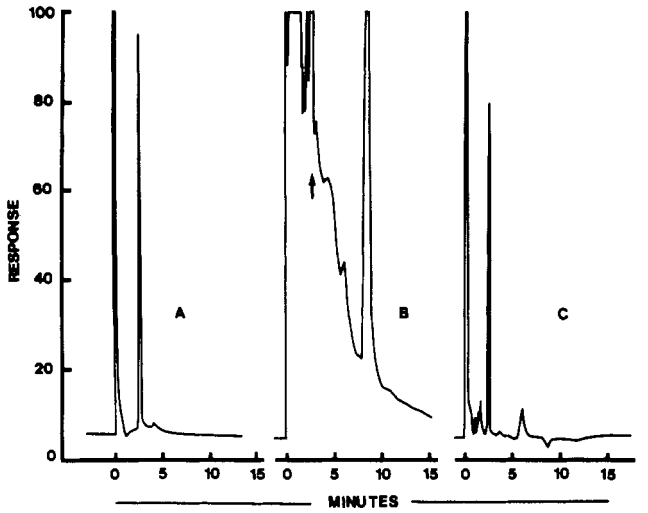


**Figure 1.** Chromatograms of triallate standard (A) and a 72-h air sample before (B) and after (C) Florisil cleanup.

and reduced to 10 mL, and an aliquot injected into a gas chromatograph for analysis.

The gas chromatograph used was a Tracor Model 560, equipped with a $^{63}Ni$, linearized electron capture detector. The glass column, 1.5 m by 4 mm i.d., was packed with 100–120-mesh Ultrabond 20M (RFR Corp., Hope, RI). The injector, column, and detector temperatures were 220, 165, and 350 °C, respectively. The flow rates of the carrier and purge gas, 5% methane in argon, were 40 and 20 mL/min, respectively. Under these temperature and carrier flow conditions, triallate had a retention time of 3.25 min. The concentration of triallate in the samples were calculated by comparing the sample peak heights with those derived from a standard curve constructed from analytical-grade triallate obtained from the U.S. Environmental Protection Agency, Research Triangle Park, NC. All data were corrected for trapping efficiencies whenever required.

**Confirmation.** All samples containing triallate were quantitatively confirmed by using an AFID in the N mode. The gas chromatograph used was a Hewlett-Packard Model 5730A equipped with a Model 18789A N-P AFID. The glass column, 0.91 m by 4 mm i.d., was packed with 10% OV-1 on 80–100-mesh Chromosorb W, HP. The injector, column, and detector temperatures were 225, 225, and 300 °C, respectively. The flow rate for the carrier gas, helium, was 40 mL/min whereas the gas flow rates for hydrogen and air in the detector were 3 and 50 mL/min, respectively. Under these conditions triallate had a retention time of 3.5 min.

In addition to the use of EC detector and AFID analysis, the identity of triallate in several samples was also confirmed by the GC–MS spectrometry technique. A Finnigan Model 3100 mass spectrometer connected to a Finnigan Model 9500 gas chromatograph by means of a jet separator was used. The mass spectrometer was interfaced with a Model 6100 computer-controlled data acquisition system. A 1.5 m by 4 mm i.d. glass column packed with 10% OV-1 coated on 80–100-mesh Chromosorb W HP was used for gas chromatographic separation. The mass spectra were recorded at 70 eV. The mass spectra of the field sample containing triallate were compared with that of the reference compound.

## RESULTS AND DISCUSSION

Because of interferences due to contaminants encountered in the samples during EC GC analysis (Figure 1), especially in those collected over the 72-h period, a Florisil column cleanup procedure was developed which removed all of the background contaminants (Figure 1). Column recoveries were 102.8 ± 1.2%, based on six determinations. All chromatographic peaks, four units above the base-line noise (equivalent to 0.01 ng of triallate) and detected by both EC detector and AFID systems, were considered positive, thus giving a detection limit of 0.5 ng $m^{-3}$ for the daily samples. By use of the standard conversion calculations, this limit is equivalent to ~39 ppq, i.e. parts per quadrillion, 12.7 ng $m^{-3}$ = 1 ppt (Ledbetter, 1972).

Table I. Multidetector Determination and Confirmation of Airborne Triallate Residues in Selected Samples[a]

| sampling date | site | residues, ng $m^{-3}$ EC detector | AFID |
|---|---|---|---|
| 5/18-21/79 | Regina | 10.9 | 10.1 |
| 5/25-27/79 | Regina | 35.2 | 34.4 |
| 5/28/79 | Regina | 105.6 | 103.1 |
| 6/1-2/79 | Regina | 38.9 | 38.9 |
| 5/18-21/79 | Indian Head | 15.7 | 15.7 |
| 5/25-27/79 | Indian Head | 9.8 | 9.4 |
| 5/28/79 | Indian Head | 59.7 | 61.1 |
| 6/1-2/79 | Indian Head | 24.1 | 22.7 |

[a] Also confirmed by GC-MS spectrometry. $t$ = 1.397.

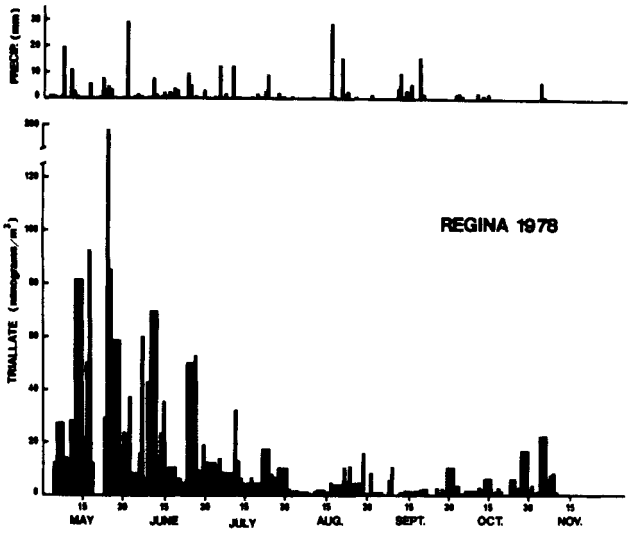


**Figure 2.** Histogram of triallate residues in air at Regina during 1978, including the precipitation pattern.

The reproducibility of analytical measurements, using the EC detector and AFID, proved to be excellent, the differences being insignificant when using the paired $t$ test (Table I), and provided in addition the confirmation of triallate in all samples by GC using the two detectors. The identity of the herbicide in a number of samples was confirmed further by gas chromatography–mass spectrometry. A GC–MS of the peak in the field sample with the same retention time as that of reference standard observed in the gas chromatograms showed a base peak at $m/e$ 86 and other ions at $m/e$ 268, 70, and 43. The spectrum was consistent with the mass spectrum of authentic triallate.

During 1978 sampling at Regina, the highest concentrations of triallate were found during May and early June, the maximum being 198 ng $m^{-3}$ (=16 ppt) on May 24 (Figure 2). This corresponded to the maximum use of this herbicide in this area, the peak application period being mid-May. After June, the levels of triallate in the air declined, in general, to less than 20 ng $m^{-3}$, with the lowest levels corresponding to the relatively dry periods (Figure 2). There was another peak period in late October and

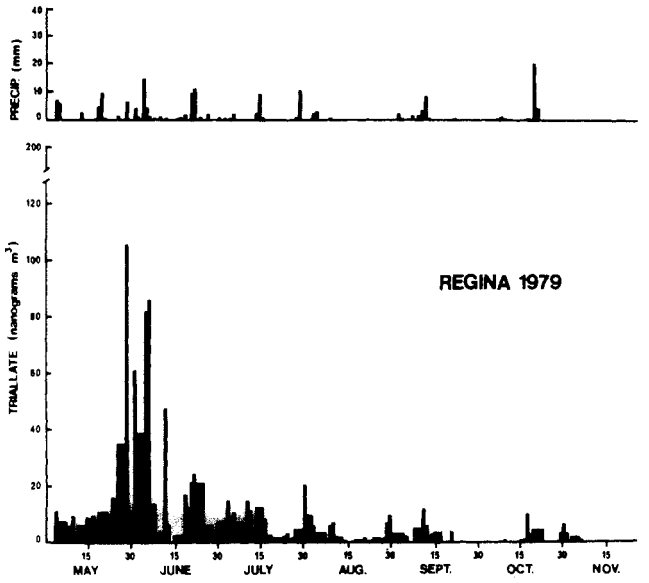


**Figure 3.** Histogram of triallate residues in air at Regina during 1979, including the precipitation pattern.

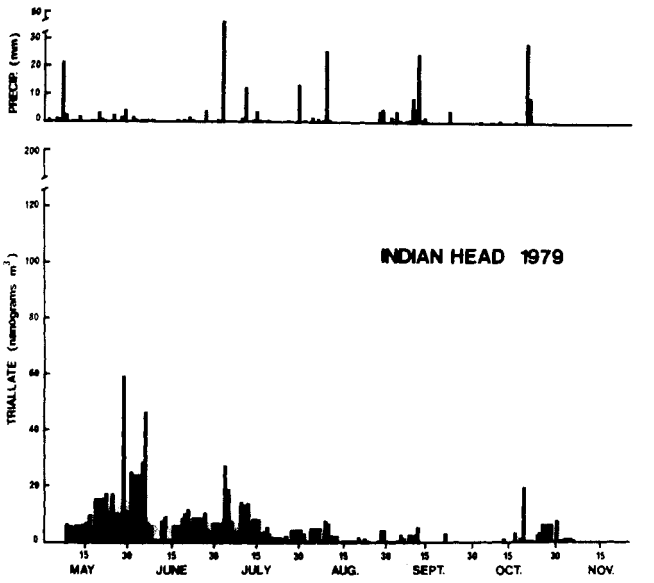


**Figure 4.** Histogram of triallate residues in air at Indian Head during 1979, including the precipitation pattern.

early November, again corresponding to the second application in the fall, which usually occurred from mid-October to late October. The high concentration levels in November followed the rainfall after the fall application. The triallate residues in the air fell below the detection limit after Nov 13, after which temperatures were continuously below freezing.

A similar trend was observed in 1979 air sampling, both at Regina and at Indian Head (Figures 3 and 4). The highest concentrations of triallate were found during May and June, the maximum concentrations being 104 and 60 ng $m^{-3}$ on May 28 at Regina and Indian Head, respectively. After June, the levels of triallate declined again, in general, to less than 20 ng $m^{-3}$, with lowest concentrations corresponding to relatively dry periods at both sites. The increase in air concentration of triallate in mid-October to late October at both sites paralleled the fall application period.

Triallate air concentrations were highest during and following the application and incorporation period, for both spring and fall treatments. Laboratory studies, using trifluralin (Spencer and Cliath, 1974) and triallate (Jury et al., 1980), and field studies with trifluralin (White et al., 1977) have also shown that major vapor losses of soil-incorporated herbicides occur during and following their application which represents primarily their initial depletion from the surface layers.

The sorption of both trifluralin and triallate has been shown to be a reversible process (Grover, 1974). During the summer months and especially during relatively dry periods, the concentrations of triallate in the air were lowest, indicating minimal vapor flux of the herbicide, presumably due to strong adsorption to the dry soil surfaces. The sudden increases in the triallate concentrations in the air, generally following the rainfall events, were no doubt due to the increased soil vapor flux after desorption of the herbicide upon soil rewetting. This phenomenon has also been observed for trifluralin (Harper et al., 1976).

In conclusion, vapor loss may be one of the major routes for the dissipation of triallate as well as other soil-incorporated herbicides with similar vapor pressures. Furthermore, the magnitude of atmospheric residues reported here may also reflect the concentration levels that are likely to be encountered in the atmospheric sink under the present usage pattern in this area.

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