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Airborne Residues of Triallate and Trifluralin in Saskatchewan

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The presence of airborne residues of phenoxy herbicides, such as 2,4-D (2,4-dichlorophenoxyacetic acid) esters and triallate (S-(2,3,3-trichloro-2-propenyl)bis(1-methylethyl) carbamothioate) in cereal growing regions of the Canadian prairies are well documented (Grover et al. 1976, 1981). The airborne residues of 2,4-D esters were detected primarily during and immediately following their application whereas those of triallate were present both during application and continually thereafter throughout the growing season. In both of these cases, dissipation into the atmosphere was considered a major route for their removal from the targets. Trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine), another pre-emergent, soil-incorporated herbicide like triallate, is also extensively used in Saskatchewan. This study reports the levels and duration of triallate and trifluralin residues in air at two sites in Saskatchewan. One at Regina where triallate is primarily applied and the other about 300 km north of Regina at Melfort, in a region where both herbicides are extensively used.

MATERIALS AND METHODS

Accumulative air samples were collected on a 24-h basis for week days and a 72-h basis on weekends, using polyurethane foam plugs as the solid adsorbent. The sampling trains at both locations were started in the first week of May each year and continued until freezing of the soil surface in early- to mid-November. Each sampling train consisted of (1) a glass tube with an inverted cone-shaped inlet set at 2-m ht from the ground, (2) an adsorbent chamber containing two 45 cm dia by 50 cm long polyurethane foam plugs, (3) a calibrated flow meter, and (4) an electric vacuum pump, as described earlier (Grover et al. 1981). The adsorbent chamber was 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 exposed foam plugs for each sampling period were transferred to individual glass jars equipped with teflon-lined screw caps and the jars stored in a freezer until analysis.

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The foam plugs were Soxhlet extracted with 300 ml of n-hexane for 2 h each and the extracts passed through a Florisil column for clean-up and analyzed gas chromatographically using an electron capture detector (ECD), as described earlier (Grover et al. 1981). Under the temperature and carrier gas flow conditions described previously, the retention times for triallate and trifluralin were 3.3 and 3.9 min, respectively.

All air samples collected in 1981 which contained trifluralin and/or triallate were quantitatively confirmed by an alkaline flame ionization detector (AFID) in N mode, as described earlier for triallate (Grover et al. 1981). The retention times for the two herbicides, under the conditions described earlier, were 3.4 and 5.6 min, respectively.

In addition to the use of EC and AFID detectors in the GC mode, the identities of both trifluralin and triallate in several samples collected both in 1981 and 1982 were also confirmed by the gas chromatography-mass spectrometry (GC-MS) technique, using the Finnigan system described earlier (Grover et al. 1981).

RESULTS AND DISCUSSION

Because of the interferences due to contaminants encountered in the samples during EC GC analysis, a Florisil column clean-up was necessary. Column recoveries for trifluralin and triallate were in the 96 to 103% range, depending on the herbicide and the batch of Florisil used. The limits of detection for both herbicides were set at 0.05 ng m^{-3}, based on the presence of chromatographic peaks of four units above the base-line noise. There was good agreement in the analytical measurements, using the EC detector and AFID, for both trifluralin and triallate. The reproducibility data for trifluralin are presented in Table 1, the triallate data having been published earlier (Grover et al. 1981).

Table 1. Multidetector determination and confirmation of airborne trifluralin residues in selected samples.

	Residues, ng m^{-3}	
Sampling date	ECD	AFID
05 13 81	15.1	16.4
05 28 81	12.2	13.6
06 17 81	6.3	7.6
07 02 81	4.2	4.1
08 04 81	11.3	12.4

Consequently, only EC GC analysis was carried out on samples collected in 1982.

The identity of both herbicides in a number of samples collected in 1981 and 1982 was confirmed further by GC-MS. For triallate, a

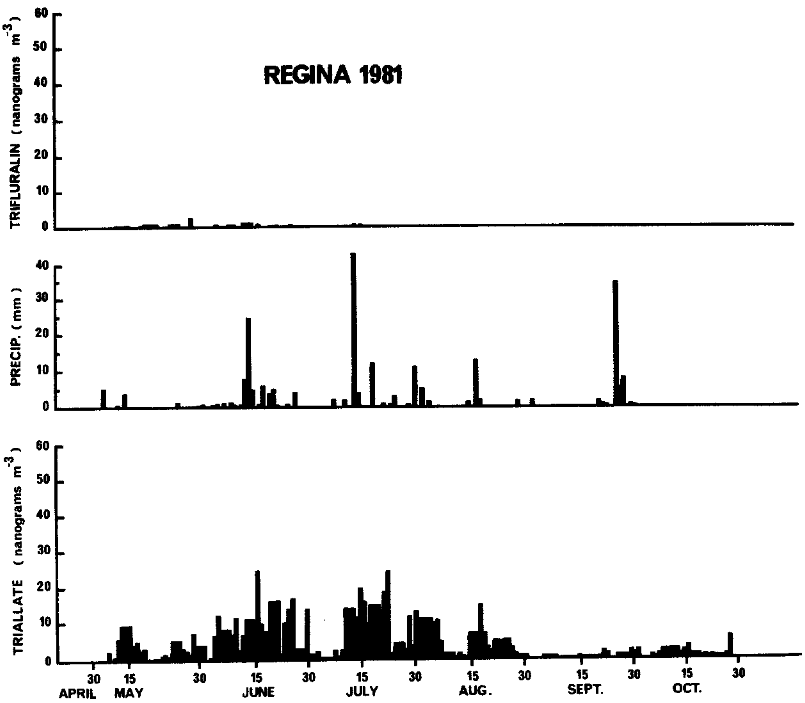

Figure 1. Histogram of triallate and trifluralin residues in air at Regina during 1981, and the precipitation data.

GC-MS peak in the field samples, with the same retention time as that of the reference standard observed in the gas chromatograph, showed a base peak at m/e 86 and other ions at m/e 268, 143, and 128. For trifluralin, ions m/e 335, 306, and 264 were monitored for confirmation. These spectra were consistent with the mass spectra of the authentic standards.

The spring of 1981 was a relatively dry period both at Regina and Melfort (Figures 1 and 2). At Regina, airborne concentrations of triallate were < 10 ng m^{-3} during the application and the immediate post-application period of May (Figure 1). However, with the onset of rainy periods in June and July, significant levels of triallate were released into the atmosphere, with maximum concentrations of 25 ng m^{-3} on June 15 and July 22. This is in contrast to the earlier data where major vapor losses occurred during and following the application period in May, with resultant atmospheric residue levels being as high as 198 and 104 ng m^{-3} for 1978 and 1979, respectively (Grover et al. 1981).

During 1981, the airborne residues of triallate at Regina were spread out throughout the summer period of June to August, with major peak periods corresponding, in general, to the rainfall

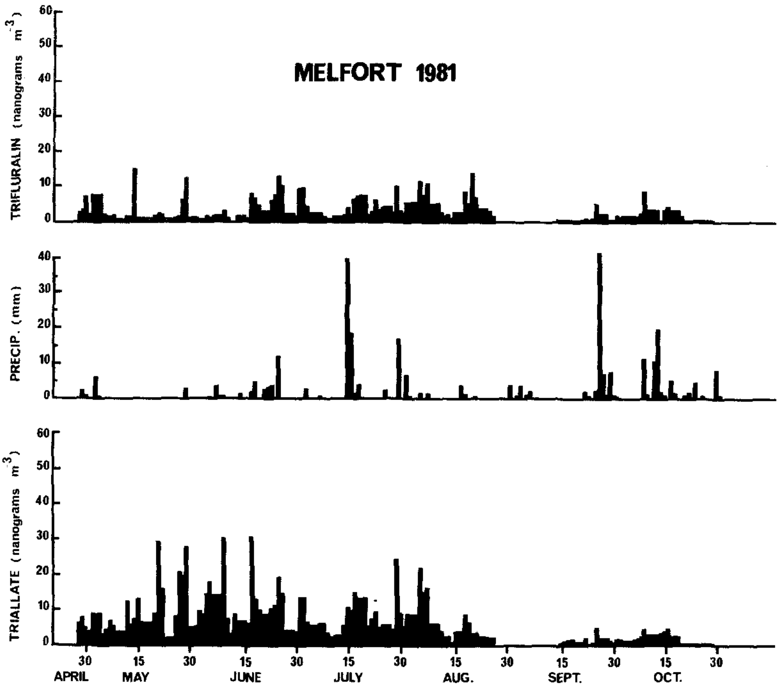

Figure 2. Histogram of triallate and trifluralin residues in air at Melfort, SK during 1981, and the precipitation data.

events. Airborne residues of triallate in October, the fall application period, were also low, again reflective of the prevalent dry conditions (Figure 1). Thus, the airborne residue data for 1981 at Regina may be considered typical of situations encountered during dry years. Airborne residues of trifluralin at Regina were minimal, with levels below 1 ng m^{-3}, when present (Figure 1). This situation would be typical of a region where little or no trifluralin is used.

The airborne residues of triallate at Melfort during 1981 was similar to that in Regina, indicative again of the dry spring for that region. The highest concentration was 30 ng m^{-3}, detected on May 20, June 8 and 16 (Figure 2).

In addition to triallate, the Melfort samples also contained trifluralin throughout the sampling period. The highest concentrations occurred on May 13, 28, June 24, and August 19, being 15, 12, 13, 14, ng m^{-3}, respectively. The pattern of residue distribution showed the effect of the dry spring, as was the case for triallate.

Airborne residues of both triallate and trifluralin during the fall application period at Melfort during 1981 were also detected

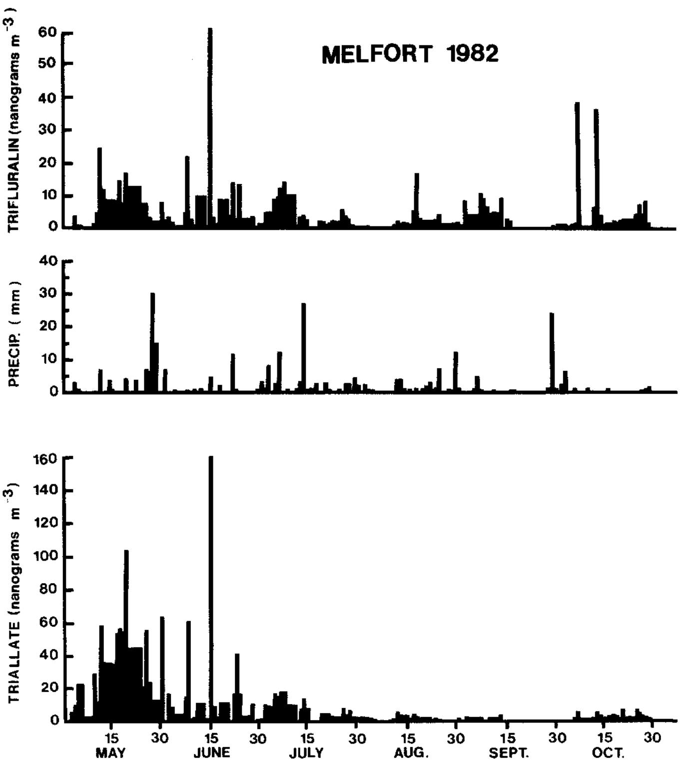

Figure 3. Histograms of triallate and trifluralin residues in air at Melfort during 1982, and the precipitation data.

from the September 15 to October 15 period (Figure 2), indicating that both herbicides were used in the fall in this region.

Air sampling at Melfort was continued for 1982, which was a wetter year than 1981. During 1982, the highest concentrations of both triallate and trifluralin at Melfort were found in mid-May to Mid-June, corresponding to the maximum use period of these herbicides in this region (Figure 3). The highest concentrations for the triallate were 114 and 160 ng m^{-3} on May 20 and June 15, whereas for trifluralin the highest concentrations were 25 and 63 ng m^{-3} on May 12 and June 15, respectively. After June 15, the levels of both herbicides in the air declined to < 20 ng m^{-3}, with lowest levels corresponding to relatively dry periods (Figure 3). Both of these herbicides were also detected in air samples collected between October 1st and 30th, the second application period. Airborne residues of trifluralin in samples collected in October 7 and 13, were 38 and 36 ng m^{-3}, suggesting an increased use of this herbicide in the fall of 1982. In general, the 1982 herbicide residue patterns at Melfort were similar to those observed in Regina during 1978 and 1979 (Grover et al. 1981). In all of these cases, the spring application periods had received normal rainfall amounts.

In conclusion, the airborne residue data for triallate and trifluralin collected at two sites in Saskatchewan suggest that:

Airborne residues of triallate are present both in the southern and central regions of the province, indicating its general use in both agricultural areas.

Significant airborne residues of trifluralin were present only at Melfort, indicating its general use in that area only. In addition, in spite of the prevailing northwesterly wind direction in this province, little or no trifluralin was detected at the southern site at Regina.

Airborne herbicide residues were highest during and following their application, provided soil moisture conditions were condusive to vapor activity, after which the residues declined to low level, with detectable losses corresponding to rainfall events.

When soil moisture conditions were dry during and following the application period, airborne residues corresponded to rainfall events over the remaining growing season. However, airborne concentrations did not reach the maximums observed under moist application periods/years. Thus, increased carryover of both of these herbicides can be expected in dry years.

Vapor transport is a major route for the dissipation of these herbicides from the treated areas with soil water as the limiting factor.

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