Parathion Residues in Environmental Samples from Untreated Areas

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Reports about the persistence of parathion (ethyl-parathion) in soil are not surprising in view of the findings that this chemical forms strong complexes with organic matter and clay.

Persistence of the compound over periods of months (IAWATA et al., 1973) and years (STEWART et al., 1971., WOLFE et al., 1973) implies that translocation from its site of application takes place. During the last three years the following observations were made on extracts not intended for parathion quantitation (except 1), and obtained from samples taken in the cranberry producing area of southeastern Massachusetts.

1. An interlaboratory check of analytical procedures using fortified homogenates of Mya arenaria and Fundulus sp. revealed a background of 0.01 and 0.04 ppm parathion in fish by means of GLC on SE-30/AFID, and DC-200/flame photometric detector, respectively. Under the same analytical conditions the residues in shellfish were 0.01 and 0.03 ppm. The specimens had been collected early in May 1973.

2. In April 1974, homogenates of Mya arenaria from Falmouth Inner Harbor (Falmouth, Mass.), and Phinney's Harbor (Bourne, Mass.) were found to contain 0.02 and 0.03 ppm parathion (SE-30/AFID). TLC analysis produced spots with the R_F of parathion, whose eluates caused parathion peaks during GLC analysis (SE-30/AFID). GC/MS analysis produced an M^+ 291, and m/e 109 and 139 were the first and second peaks. Large amounts of di-n-butyl-phthalate emerged from the column (SE-30) together with parathion.

Bulletin of Environmental Contamination & Toxicology, Vol. 15, No. 5 © 1976 by Springer-Verlag New York Inc.

3. Extracts of two rainbow trout from a hatchery receiving drainage from cranberry bogs (Wareham, Mass.), analyzed in December 1974, were found to contain 0.015 ppm parathion on SE-30, and 0.017 ppm on OV-17.

4. Extracts of eight soil samples taken in April 1975, at distances up to five miles from the nearest cranberry bog, were analyzed on SE-30 and OV-17 with AFID. On both columns the quantities of parathion were estimated 0.001 (0.001 - 0.002) ppm. TLC analysis of four extracts, and GLC analysis of the eluates confirmed the presence of parathion.

To support the validity of these observations, two soil samples and one shellfish sample were analyzed for parathion with emphasis on confirmation.

MATERIALS AND METHODS

The soil samples consisted of 200 g top soil (0 - 1 in.) taken in July 1975 from a wooded hill in a residential area about four miles away from the nearest application site. They were extracted in two portions with hexane - iso-propyl alcohol (2:1).

Six oysters were taken in June 1975 at Sippican Harbor (Marion, Mass.) at a distance of about two miles from the nearest application site. Sixty-two grams of meat and liquor were extracted according to GAUL et al., 1972,(Section 212.13a). The extracts of soil and fish were subjected to the same cleanup procedure, (GAUL et al., 1972, Section 211.14d).

TLC analysis was carried out using 20 x 20 cm plates coated with 0.25 mm aluminum oxide for TLC (Camag). The plates were prewashed with the same solvent system used for developing, activated at 130°C, stored at 105°C, and developed with 10% acetone in hexane using a Brinkmann sandwich apparatus. Spots were visualized with iodine vapors, eluted with hexane, and the eluates analyzed by GLC.

For GLC a Varian 2700 Moduline with thermoionic detector (Rb_2SO_4) was used. The instrument was equipped with two 1/8 in. x 5 ft. stainless steel

columns, one packed with 3% SE-30 on 100/120 Varaport 30, and the other one with 3% QF-1 on the same type of support. Temperature settings were: Injector 195° C, detector 210° C. Carrier gas N_2 19 ml/min. At attenuation 16, 0.1 ng parathion produced peaks of about 30% FSD (SE-30) and 20% FSD (QF-1).

The p-values were determined according to GAUL et al., 1972, (Section 621) using equal volumes of heptane and ethanol.

Previous recoveries of parathion from homogenates were 83% at 0.1 ppm, and from soil 81% at 0.1 ppm. The reported quantities were not corrected. Solvent blanks were carried through extraction, cleanup and TLC.

RESULTS

Parathion residues in soil were 1.3 ppb on SE-30, and 1.0 ppb on QF-1. The residue content of the homogenate was 41 ppb on QF-1, and 38 ppb on SE-30. These quantities were obtained using 50% ether eluates. The 6% and 15% eluates did not produce peaks on either column with the retention time of parathion.

The raw extracts were spotted on TLC plates. The residue amounts from soil were too small to produce spots, but eluates of the parathion zone (R_F 0.38) produced peaks on both columns. To obtain acceptable peaks, the attenuation had to be lowered to 8. This required GLC analysis of eluates of the adsorbent, and solvent injections were necessary to eliminate residual effects.

The 50% eluates were used to determine p-values. The expected value was 0.3, and the calculated values for soil were 0.278 on SE-30, and 0.313 on QF-1, and for shellfish 0.286 on SE-30 and 0.293 on QF-1.

Caution is advised against relying on SE-30 for quantitation because an unidentified compound, found in several alewives (used in another study) produced an unsymmetrical peak on SE-30 when used as described in this study. The apex was 1.09 - 1.14 relative to parathion (malathion 0.93). In larger quantities, or

at slightly higher column temperature, the peak appeared with the retention time of parathion but always with a tendency to tailing. The unknown was contained in the 50% eluate and did not produce peaks on QF-1.

CONCLUSION

The presence of parathion in samples from areas not treated with the chemical suggest that parathion residues are translocated in the environment.

ACKNOWLEDGMENTS

The study was supported by Hatch 346 FY 1974. We are grateful to Mr. Arnold Carr and Mr. Richard Harlow for procuring the shellfish samples.

LITERATURE

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