

at concentrations of 0.05, 0.10, and 0.25 ppm and the samples were extracted and analyzed as described above, the mean percent recovery at each level was 93.5, 98.6, and 89.2, respectively. Typical control values for both β -naphthoxyacetic acid and β -naphthol were <0.05 ppm.

Both β -naphthoxyacetic and β -naphthol can be analyzed in strawberries with precision, accuracy, and reproducibility at levels ranging from 0.05 to 0.25 ppm or higher by high-resolution liquid chromatography. The method is fast and accurate and the chromatographic resolution of the chemicals is good in the presence of strawberry extractives.

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Assessment of Dipropylnitrosamine Levels in a Tomato Field Following Application of Treflan EC

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A tomato field was examined for residues of *N*-nitrosodipropylamine in air, soil, irrigation water, and crops following application of a herbicide formulation containing an *N*-nitrosodipropylamine impurity. No residues of *N*-nitrosodipropylamine were detected. Application of a general screening procedure for *N*-nitroso compounds in the irrigation water revealed no evidence for the presence of *N*-nitroso compounds in the water due to use of the *N*-nitrosamine-contaminated herbicide formulation.

The presence of carcinogenic nitrosamines in food has been studied since Barnes and Magee (1956) first associated acute liver necrosis with *N*-nitrosodimethylamine (NDMA). It is only recently, however, that pesticide application as a source of nitrosamines in food has been considered (Sen et al., 1975; Eisenbrandt et al., 1975; Wolf and Zepp, 1976; Elespuru et al., 1974). Although nitrosation of pesticide residues in the field has not been demonstrated, Schmeltz et al. (1977) postulated a pesticidal genesis for the nitrosodiethanolamine they found in tobacco. *N*-Nitrosamines have been found in pesticide formulations (Ross et al., 1977). Reported here is the examination of possible human exposure to dipropylnitrosamine (NDPA), resulting from application of one of these formulations, Treflan EC containing 154 ppm (w/w) NDPA (Treflan is a registered trademark of Elanco Products Company, Division of Eli Lilly and Company, for the emulsifiable concentrate formulation of α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine, trifluralin).

The study field, located in the Sacramento Valley approximately 2 miles north of Davis, Calif., was devoted to tomato cultivation with row irrigation. After the last manual cultivation, the field was treated with Treflan EC by soil incorporation. Treatment of the field was completed over a 2-day period. After treatment with Treflan EC, the field was plowed for row irrigation. Four days after Treflan EC treatment, irrigation was initiated. Treflan had been applied to the field in the two previous years.

MATERIALS AND METHODS

The Thermal Energy Analyzer gas chromatograph (TEA-GC) was constructed from a Thermo Electron Model 661 single-column gas chromatograph interfaced to a Thermo Electron TEA Model 502 detector. An 8-ft

stainless steel tube, 0.125 in. o.d. packed with 5% Carbowax 20M on Chromosorb W, HP was used as the chromatographic column. Argon was used as the carrier gas at a flow rate of 15 mL/min with a column temperature of 150 °C.

The high-pressure liquid chromatograph-Thermal Energy Analyzer (TEA-HPLC) was constructed from a high-pressure pump (Waters Associates, Model 6000A), an injector (Waters Associates, Model U6K), and a Thermo Electron TEA Model 502 LC detector fitted with the TEA-HPLC interface. A UV detector (Waters Associates, Model 440) was also used. Operating conditions on the HPLC were 2 mL/min of 1:1 dichloromethane (DCM) and *n*-hexane eluent with a μ -NH₂ column (Waters Associates).

Formulated Treflan was obtained from the applicator in the study field at the time of application. Authenticated NDPA was obtained from the U.S. National Cancer Institute. Solvents were obtained from Burdick and Jackson (Muskegon, Mich.) of a grade which had been distilled in glass.

The XAD-4 resin (Rohm & Haas Co., Philadelphia, Pa.) was cleaned prior to use by washing with aqueous sodium carbonate, followed by dilute hydrochloric acid. The resin was then subjected to 24-h sequential Soxhlet extractions with water, methanol, acetone, and DCM. The resin was dried at 100 °C for 1 h.

Air samples were collected by drawing air at a flow rate of 500 mL/min through a 0.5 in. o.d. by 7 in. long stainless steel tube which had been packed with XAD-4 resin. The sampling systems were battery operated. The valve used to regulate flow was calibrated with a Hastings Mass Flow Meter.

The XAD-4 resin was eluted with three sequential column volumes of DCM. The eluent was concentrated by solvent distillation at 55 °C using a Snyder column. Recoveries were performed by spiking the XAD-4 resin and drawing a typical sample volume through the resin. Recoveries at the 0.1 μ g/M³ level were 70%. Determi-

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nation was by TEA-HPLC and TEA-GC. During the study period wind speeds usually fell between 5 and 10 knots. Lows of 3 knots and highs of 15 knots were observed. An air temperature at 45 °C was observed but a more usual daily high was 40 °C. All samples were taken in study field at the down wind side.

Rows were irrigated by filling from a master trench. Water samples were taken at the clear well for the pump servicing the field and in irrigation ditches at the far end of the field from the filling point.

Water samples (500 mL) were extracted sequentially with three 65-mL portions of DCM. DCM was dried over sodium sulfate and then concentrated by solvent distillation at 55 °C with a Snyder column. The final 1 mL concentrate was used for introduction into the TEA-GC and TEA-HPLC (Fine and Rounbehler, 1976). Recovery was $65 \pm 5\%$ at the detection limit of 0.02 $\mu\text{g/L}$ (ppb).

Tomato samples were taken within 1 week of harvesting the study field. A single composite sample was prepared by random picking within the field area from which soil and water samples had been taken and replicate determinations performed.

NDPA in tomatoes was determined by a modification of the mineral oil vacuum distillation procedure of Fine and his co-workers (Fine et al. 1975a). The tomato sample (100 g) was placed in a 500-mL boiling flask and 4 mL of 0.1 M sodium hydroxide and 100 mL of mineral oil (USP) were added. The flask was attached to the vacuum distillation apparatus with twin liquid nitrogen cold traps. A rotary vacuum pump was essential, since a 1.5–1.0 Torr vacuum was required. The cold trap temperature was maintained at $-192\text{ }^\circ\text{C}$ with liquid nitrogen and the boiling flask heated to 100 °C over an approximately 40-min period. The distillate from both cold traps was combined in a 125-mL separatory funnel with three aliquots of 10 mL of DCM used to rinse the connecting tubing and the cold traps. After addition of 4 mL of 0.1 M hydrochloric acid to the combined distillate, the aqueous and DCM layers were separated. The aqueous layer was extracted with two additional 7-mL portions of DCM. The combined DCM extracts were dried by passing through 3 g of anhydrous sodium sulfate, and the sodium sulfate was washed sequentially with two 3-mL portions of DCM. The DCM was collected in a Kuderna-Danish concentrator, 0.2 mL of 2,2,4-trimethylpentane was added, and the concentrator was heated at 55 °C until the volume was reduced to approximately 0.5 mL. The final volume was measured and an aliquot injected on TEA-GC or TEA-HPLC. The recovery of NDPA at 0.2 ppb was 89%.

A composite soil sample was prepared at each sampling interval by removing 0–6 in. cores from random sites in the study field. Samples were taken beneath the tomato plants. Soil samples (50 g) were mixed with 60 mL of DCM for 20 min using a magnetic stirrer. The slurry was filtered through anhydrous sodium sulfate and concentrated by distillation to 0.5 mL with a Snyder column. Determination was performed with TEA-GC and TEA-HPLC. Distilled water was added to those soil samples not taken during irrigation to make them the same gross consistency as the samples taken during irrigation. As additional confirmation of the solvent extraction procedure, aliquots of these same samples were analyzed by the mineral oil vacuum distillation procedure. Recoveries were obtained by addition of 24- and 100- μL aliquots of NDPA in DCM solution (2 $\mu\text{g/mL}$) to control soil samples. After addition of NDPA solution, the soil sample was mixed thoroughly and allowed to stand at room temperature for 15 min. With the solvent extract, 80% recovery was

Table I. Determination of NDPA in Soil and Tomatoes from a Field Treated with Treflan EC

| Sample | NDPA found, ng/g |
|-----------------------------------|------------------|
| Pretreatment soil | ND ^a |
| Soil, immediately after treatment | ND ^a |
| Soil, 1 day after treatment | ND ^a |
| Soil, after irrigation completed | ND ^a |
| Tomatoes, harvest | ND ^b |

^a ND, nondetectable at a detection level of 1 ng/g.

^b ND, nondetectable at a detection level of 0.2 ng/g.

Table II. Determination of NDPA in Air Above a Field Treated with Treflan EC

| Sample | Sample size, m ³ | NDPA found, ng/m ³ |
|--|-----------------------------|-------------------------------|
| Control, 1 ft above ground | 0.08 | ND ^a |
| During application, 1 ft above ground | 0.19 | ND |
| After application and cultivation, 1 ft above ground | 0.23 | ND |
| During initiation of irrigation, 1 ft above ground | 0.68 | ND |
| 4 ft above ground | 0.68 | ND |
| During irrigation, 1 ft above ground | 0.32 | ND |
| | 0.59 | ND |
| At completion of irrigation, 1 ft above ground | 1.29 | ND |
| | 1.29 | ND |

^a ND, none detected at a detection limit of 50 ng/m³.

Table III. Determination of NDPA in Irrigation Water in a Field Treated with Treflan EC

| Sample | NDPA found, $\mu\text{g/L}$ (ppb) |
|---------------------------------------|-----------------------------------|
| Untreated control | ND ^a |
| Before entering field | ND |
| After filling of irrigation ditch | ND |
| After filling of irrigation ditch | ND |
| 8 h after filling of irrigation ditch | ND |

^a ND, none detected at a detection limit of 0.02 $\mu\text{g/L}$.

observed at 4 ppb but only 45% recovery was obtained at 1 ppb. By vacuum distillation 60% recovery was obtained at 5 ppb.

RESULTS AND DISCUSSION

No NDPA was detected in the air, soil, water and tomato samples examined (Tables I, II, and III). Routes of human exposure to NDPA considered in this study are (1) inhalation, particularly by field workers, (2) ingestion in drinking water contaminated due to leaching by irrigation water, and (3) ingestion as a residue on the tomatoes cultivated in the field. Although there is no indication that any exposure occurred, maximum exposure due to each of these pathways was shown to be less than estimated levels of human nitrosamine exposure (Fine et al., 1977). For example, the field worker in an 8-h work day, inhaling 10000 L of air (Green, 1972) would be exposed to less than 1.0 μg of NDPA. This is below the exposure from ingestion of 100 g of bacon (0.5 μg of NDMA) (Scanlan, 1975) as is the exposure, if it occurs, from consumption of tomatoes grown in this field. Ingestion of one pound of these tomatoes would contain less than 0.1 μg of NDPA. Because no NDPA was detected in the irrigation water, leaching

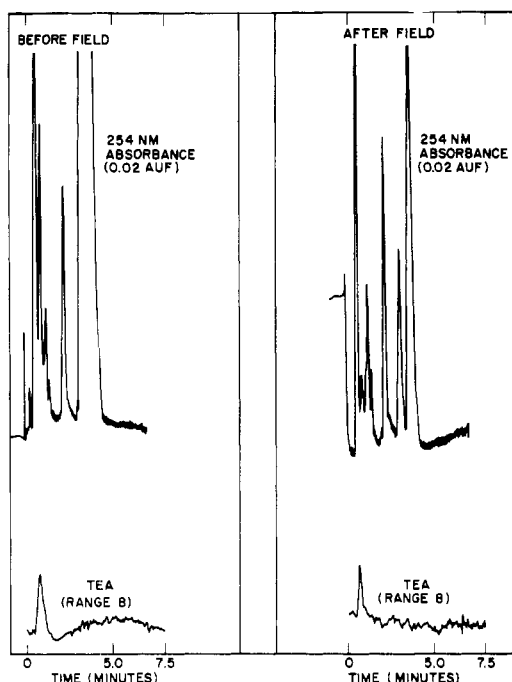


Figure 1. UV-HPLC and TEA-HPLC traces of irrigation water concentrate taken prior to passage through tomato field. UV-HPLC and TEA-HPLC traces of irrigation water concentrate taken after passage through tomato field.

would not be expected to lead to human exposure. Formulators and applicators could be exposed to higher quantities by direct contact with this formulation.

Soil was examined, not as a source of direct human exposure, but as a possible site of NDPA concentration and/or formation. Repeated application of NDPA to this field might result in buildup of soil concentrations eventually leading to human exposure through other routes. Another possible cause of NDPA built up in the soil is conversion of the persistent soil-bound trifluralin residues to NDPA. With 1 ppb lower limit of detection in the soil determinations, the NDPA added to the soil in the single application studies would not be detected simply due to dilution. The failure to detect NDPA in these soil samples indicated that neither soil buildup from past years, nor substantial formation of NDPA from trifluralin was occurring.

Examination of crops for increased nitrosamine levels due to application of pesticides is an immense task due to the large number of nitrosatable compounds which may arise from a single pesticide formulation. Treflan has at least six N-nitrosatable alteration products (Leitis and Crosby, 1974). An initial general screening procedure for increased nitrosamine levels following application of a pesticide formulation could obviate the necessity for some expensive N-nitroso pesticide residue studies. Although a variety of TEA responding non-N-nitroso compounds have been reported (Fan et al., 1977; Fiddler et al., 1977; Fine et al., 1975b; Krull et al., 1978; Stephany and Schuller, 1977), no false negatives have been observed with the TEA. The TEA may be applied for screening methodologies. For example, in Figure 1 we see the effect of exposure to a Treflan EC treated field on irrigation water. No new nitroso peaks appeared, indicating no increased background level of N-nitroso compounds in this extract. Direct injection of these extracts into the TEA confirmed

this result by giving no increased total response. This general screening procedure for increased N-nitroso compounds is limited by the exhaustiveness of the extraction employed.

Although these negative results provide no basis for defining the pathway of environmental degradation of dipropylnitrosamine, volatilization and subsequent photodegradation seem, a priori, of high probability considering the high temperature in the field and volatility of NDPA. Volatilization has been shown to be a major route of environmental dissipation for Treflan (Soderquist et al., 1975). Although it was not observed that NDPA built up in the top of rows, the wick effect of irrigation water does occur and could facilitate volatilization.

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