by nitrosation of the steam distillate from whole corn, but the origin of the compound in nitrosated corn remains obscure.

The toxicology of nitroalkanes has not been extensively studied, but nitroalkanes are strong irritants, particularly for the upper respiratory tract and the gastrointestinal tract (Machle et al., 1940). Conjugated nitro olefins are stronger irritants than nitroalkanes and at least one nitro olefin, 3-nitro-3-hexene, is carcinogenic (Deichmann et al., 1965). We found nitrohexane in both local and Colombian corn that had been nitrosated. People in the area of high risk for stomach cancer in Columbia, however, are exposed to higher levels of nitrate and nitrite and, hence, potentially to higher levels of nitrosation products than people from low risk areas (Cuello et al., 1976; Tannenbaum et al., 1979).

Nitrite levels up to 3.6 mM have been found in gastric juice samples from individuals in the high risk area (Tannenbaum et al., 1979). We are currently investigating the nitrosation of corn and other food products at similar nitrite concentrations.

Finally, we have shown that nitroalkanes represent a new class of compounds that may be present in certain foods or form in the gastric environment in the presence of nitrite and which give a positive TEA response. Nitroalkanes may consequently interfere in the analysis of *N*-nitrosamines. However, since the molar response of nitrohexane is low, our sample containing 5 mg/kg of nitrohexane would give approximately the same size peak as a sample containing 0.1 mg/kg of a nitrosamine with the same molecular weight. Use of an auxiliary method such as UV photolysis would distinguish the two classes of compounds. Work is under way to identify other products formed following deliberate nitrosation of foods.

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Determination of Volatile Nitrosamines in Crops and Soils Treated with Dinitroaniline Herbicides

Sheldon D. West* and Edgar W. Day, Jr.

Volatile nitrosamines have been reported to be contaminants in several dinitroaniline herbicides. Since these nitrosamines are known to be carcinogenic in laboratory animals, it became necessary to analyze crops and soils treated with these herbicides for the presence of nitrosamine residues. In the procedures described, plant tissue was extracted with methanol, and soil was extracted with methanol/water (3:1). Sample extracts were purified by liquid–liquid extraction and alumina column chromatography. Measurement was accomplished by means of a gas chromatograph–thermal energy analyzer. The sensitivity of the methods was 0.2, 0.05, and 0.01 ppb for *N*-nitrosodi-*n*-propylamine in crops, soil, and water, respectively. No detectable nitrosamine residues were observed in any crops treated with the herbicides trifluralin, benefin, or oryzalin.

The development of the thermal energy analyzer as a sensitive and selective detector for *N*-nitroso compounds (Fine et al., 1973) led to the discovery that certain pesticide products contained trace quantities of volatile nitrosamines (Fine et al., 1976; Ross et al., 1977). Among these was the herbicide Treflan, a registered trademark of Elanco Products Co., Division of Eli Lilly and Co., for the her-

Lilly Research Laboratories, Division of Eli Lilly and Company, Greenfield, Indiana 46140.

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bicide trifluralin, α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine, which was reported to contain 154 ppm of *N*-nitrosodi-*n*-propylamine (NDPA). This and many other nitrosamines have been shown to be potent animal carcinogens (Druckrey et al., 1967) and the volatile nitrosamines have been suggested as potential sources of environmental carcinogens for humans (Lijinsky and Epstein, 1970).

The NDPA is present in Treflan by virtue of a side reaction between nitrosating agents and dipropylamine during an amination step of the manufacturing process. An examination of several dinitroaniline herbicides and other products which utilize secondary amines in their manufacturing process has revealed the presence of volatile nitrosamines (Cohen et al., 1978; Wright and Bontoyan, 1978; Day et al., 1979). Since these products are applied to soil and crops, it was of interest to analyze these substrates for the presence of the nitrosamine contaminants.

Published methods utilizing colorimetric (Tate and Alexander, 1975) and flame ionization gas chromatographic techniques (Pancholy, 1976; Dressel, 1977) lacked the required sensitivity and selectivity. Fine et al. (1975b) described a method for the determination of sub-ppb amounts of nitrosamines in foodstuffs using a mineral oil distillation technique and measurement with a gas chromatograph–thermal energy analyzer (GC–TEA) system. Ross et al. (1978) used a modification of this procedure to analyze for NDPA in tomatoes harvested from a Treflan-treated field. The same authors described a dichloromethane extraction procedure for soils, in addition to the mineral oil procedure, followed by GC–TEA measurement which was sensitive to 1 ppb. The distillation method yielded good results at the 0.2-ppb level for tomatoes, but was not tested below the 1-ppb level in soil. The dichloromethane extraction procedure did not yield acceptable results at the 1-ppb level.

The mineral oil distillation method is somewhat cumbersome for the efficient processing of a large number of samples. Consequently, solvent extraction procedures have been developed for the routine determination of the volatile nitrosamines NDPA and BENA (*N*-nitroso-*N*-*n*-butyl-*N*-ethylamine) in crops, soils, and water, and the resulting techniques are reported herein. The procedures involve an initial extraction, followed by a liquid–liquid partition and alumina column cleanup. Measurement is accomplished by GC–TEA. Analytical results are reported for water samples collected from areas treated with Treflan and for soil and crop samples from fields treated with the dinitroaniline herbicides Balan [benefin, *N*-butyl-*N*-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine] and Surflan (oryzalin, 3,5-dinitro-N^4,N^4-dipropylsulfanilamide), and Treflan.

MATERIALS AND METHODS

Safety Note. Volatile nitrosamines are hazardous chemicals which should be handled with extreme caution. Contact of nitrosamines with skin and clothing must be avoided. Concentrated nitrosamine solutions should be handled in a glovebox under negative pressure, and diluted standard solutions should be stored in a hood.

Chemicals and Apparatus. The preparation of reference standards, solvents, and adsorbent were described in the previous paper (Day et al., 1979) as were the gas chromatograph–thermal energy analyzer conditions. Sodium chloride (5%) was prewashed with dichloromethane to remove traces of TEA-responsive impurities.

Extraction. *Water.* A 500-mL aliquot of water was extracted by shaking with three 100-mL portions of dichloromethane. The extracts were dried and combined by draining through sodium sulfate into a 500-mL boiling flask. The sodium sulfate was washed with 20 mL of 1-chlorobutane (which served as a "keeper solvent" during the concentration step), and the extract was concentrated to about 0.5 mL with a rotary vacuum evaporator (Rinco) and a 40 °C water bath. Sample extracts were not permitted to evaporate completely to dryness. The residual solution was quantitatively transferred to a 2-mL volumetric flask and diluted to volume with 1-chlorobutane for GC–TEA measurement.

Soil. Two variations of a similar extraction procedure were employed for soils. In initial studies, a 50-g portion of well-blended soil was shaken with 200 mL of methanol/water (3:1) for 30 min on a shaker table at 300 rpm. The mixture was centrifuged for 5 min at 2500 rpm and a 100-mL aliquot (50% of the extract) was transferred to a 250-mL separatory funnel containing 100 mL of 5% NaCl solution.

To lower the limit of detection, a 200-g sample was shaken with 200 mL of methanol/water (3:1) for 30 min on a wrist-action shaker. The mixture was passed through a Whatman no. 1 filter by vacuum and the filter cake was washed with two 25-mL portions of extracting solvent. The filtrate was transferred to a 500-mL separatory funnel containing 200 mL of 5% NaCl solution. (To analyze for the herbicide itself, a 10.0-mL aliquot of either of these two extracts was taken at this point and processed separately.)

In either of the above cases, the resulting aqueous methanol solution was extracted with three 40-mL portions of dichloromethane. Each extract was drained through a bed of sodium sulfate and combined in a 250-mL boiling flask. The sodium sulfate was rinsed with 30 mL of 1-chlorobutane and the rinsings combined with the dichloromethane extracts. The combined extracts were concentrated to about 5 mL on a rotary vacuum evaporator.

Crops. Crop samples or plant tissue was finely ground and thoroughly mixed to provide homogeneous samples. A representative 50-g portion was weighed into a 1-qt Mason jar and sufficient methanol was added to yield a total liquid volume of 200 mL after the moisture content of the crop was given consideration. For example, if the moisture content was estimated to be 60–90%, 160 mL of methanol was added. The mixture was blended on an Omni-mixer for 15 min or shaken on a shaker table for 30 min at 300 rpm. Following brief centrifugation, a 100-mL aliquot of the supernatant extract was transferred to a 250-mL separatory funnel containing 100 mL of 5% NaCl solution. The aqueous methanol solution was shaken with 30 mL of hexane and the hexane discarded. The aqueous portion was then extracted with dichloromethane and the extract was concentrated as described above for soil.

Column Chromatography. *Standardization of Alumina.* The elution characteristics of the nitrosamines on the 4% deactivated alumina were ascertained before samples were analyzed. A 250 mm × 14 mm i.d. glass column was packed with 13 mL (11.5 g) of alumina and topped with a 1–2-cm layer on sodium sulfate. The column was washed with 30 mL of 1-chlorobutane, and 0.05 μg of NDPA was placed on the column in 5 mL of 1-chlorobutane. After the liquid was drained to the top of the column, 100 mL of 1-chlorobutane was added and the eluant was collected in 10-mL fractions. Each fraction was concentrated to 2.0 mL and analyzed by GC–TEA to determine the elution pattern of the nitrosamine. The NDPA eluted in the 20–80-mL fractions on a properly

Table I. Recovery and Sensitivity for Nitrosamines in Water, Soil, and Crops

sample	nitrosamine	ppb added	sample size	no. of runs	% recovery range	% recovery av	detection limit, ppb
water	DMNA	0.6	500 mL	15	22-46	33	0.02
		0.1	500 mL	6	64-75	69	0.01
		0.02	500 mL	6	58-91	77	0.01
	NDPA	1.1	500 mL	20	60-94	77	0.01
		0.1	500 mL	6	80-100	90	0.01
		0.02	500 mL	6	82-97	92	0.01
	BENA	1.3	500 mL	15	65-86	76	0.01
soil	NDPA	0.5	50 g	14	70-97	81	0.2
		0.5	200 g	10	67-90	75	0.05
		0.04	250 g	6	73-114	86	0.02
	BENA	0.5	50 g	2	96-96	96	0.2
soybeans	NDPA	0.5	50 g	6	53-68	63	0.2
cottonseed	NDPA	0.5	50 g	2	60-63	61	0.2
others[a]	NDPA	0.5	50 g	5	49-61	55	0.2
peanuts	BENA	0.5	50 g	3	66-76	73	0.2
lettuce	BENA	0.5	50 g	2	61-65	63	0.2

[a] Others include carrots, cauliflower, cotton seedlings, volunteer alfalfa, and mung been sprouts.

Table II. NDPA in Water Samples

location	description	NDPA, μg/L
Hernando, MS	pond surrounded by field treated with Treflan for four consecutive years	ND[a]
Florence, SC	pond surrounded by field treated with Treflan for five consecutive years	ND
Walls, MS	Well, 425 M deep, in field treated with Treflan for several years	ND
Panama City, FL	irrigation well, 150 M deep, in field treated with Treflan for nine consecutive years	ND
Lafayette, IN	Wabash River, 5 kM upstream from Eli Lilly outfall, 4/18/77	ND
Lafayette, IN	Wabash River, 10 kM downstream from Eli Lilly outfall, 4/18/77	ND

[a] ND = none detected at test sensitivity of 0.01 μg/L.

prepared alumina column. (Benzene may be used in place of 1-chlorobutane, if desired.)

Sample Extracts. Concentrated soil and plant extracts (water extracts did not normally require the column chromatographic step) were placed on columns prepared as described above. Sample flasks were rinsed with two 5-mL portions of 1-chlorobutane, the rinsings added to the columns, and the eluates discarded. Another 10 mL of 1-chlorobutane was added to each column, and the eluates discarded. The nitrosamines were eluted from the columns with an additional 60 mL of 1-chlorobutane, which was then concentrated to about 0.5 mL with a rotary vacuum evaporator and a 40 °C water bath. The solvent was not permitted to evaporate completely to dryness. The residual solutions were quantitatively transferred to 2-mL volumetric flasks and diluted to volume with 1-chlorobutane for GC–TEA measurement.

Gas Chromatography. Volatile nitrosamines in sample extracts were measured on a GC–TEA set up as described above. Injection volumes of 5 or 50 μL were made for solutions containing a mixture of nitrosamine standards, and 50-μL injections were made for concentrated sample extracts.

RESULTS AND DISCUSSION

Extreme precautionary measures were required to eliminate interferences and avoid contamination during the processing of samples. Laboratory glassware and equipment were thoroughly rinsed with acetone prior to each step in the procedures. All solvents were redistilled prior to use. This was especially critical for dichloromethane, which was occasionally found after concentration to exhibit a TEA response near that of diethylnitrosamine. Sodium sulfate was washed with methanol and the 5% NaCl solution was prewashed with redistilled dichloromethane to eliminate interferences. Samples were processed under yellow fluorescent lighting to eliminate photodegradative losses of nitrosamines.

The procedures employed were applicable to both BENA and NDPA. It is probable that the described alumina column would permit the isolation and purification of other volatile nitrosamines as well. The use of rotary vacuum evaporators was suitable for the concentration of solutions containing NDPA and BENA providing the "keeper solvent" (1-chlorobutane or benzene) was added and solutions were not permitted to evaporate completely to dryness.

Untreated controls, fortified recoveries, and reagent blanks were assayed with each set of samples. Some recovery efficiencies are summarized in Table I. Water samples were frequently examined for *N*-nitrosodimethylamine (DMNA) in addition to NDPA and BENA. The recovery efficiencies for DMNA were substantially lower than for the higher molecular weight nitrosamines. Similar observations were made by Fine et al. (1975a). This was primarily due to the higher solubility of DMNA in water which made extraction more difficult. In addition, the greater volatility of DMNA probably resulted in more loss of the compound during concentration of sample extracts. Recovery efficiencies from soil were about the same as for water, but efficiencies were lower for crops because of the additional hexane washing step.

The detection limits of the procedures are also given in Table I and were dependent upon the substrate. For a 500-mL water sample, the limit was usually about 0.01 ppb (μg/L) for NDPA and BENA and 0.02 ppb for DMNA. With a 50-g soil or crop sample, the limit was 0.1–0.2 ppb, depending upon instrumental noise and background responses. The extraction of a 200–250-g soil sample lowered the detectability to 0.02–0.05 ppb.

The NDPA assay results for water from areas which received Treflan treatments and from the Wabash River

Table III. NDPA Assay Results and Theoretical Residues on Soils Treated with Treflan

location	no. of applic.	C_{NA},[a] ppm	rate, kg/ha	DAT[b]	soil depth, cm	NDPA, ppb theory[c]	NDPA, ppb obsd
Shirley, IL	10	150[d]	1.1	N/A	0-30	0.70	NDR[e]
Stoneville, MS	3	150	1.7	N/A	0-30	0.30	NDR
Midville, GA	13	150	0.84	N/A	0-20	0.91	NDR
Pinehurst, GA	5	150	0.56	N/A	0-25	0.25	NDR
Ft. Motte, SC	13	150	0.84	N/A	0-25	N/C[f]	NDR
Hayesville, SC	13	150	0.56	N/A	0-25	N/C	NDR
Columbia, SC	4	150	0.56	N/A	0-25	N/C	NDR
Slaton, TX	1	164	0.67	0	0-15	0.085	NDR
Slaton, TX	1	6	0.67	0	0-15	0.004	NDR
Branford, FL	1	159	1.1	0	0-15	0.14	NDR
Branford, FL	1	6	1.1	0	0-15	0.006	NDR
Yuma, AZ	1	134	0.84	46	0-7.5	0.10	NDR
Yuma, AZ	1	164	0.56	11	0-7.5	0.079	NDR
Yuma, AZ	1	164	1.1	176	0-7.5	N/C	NDR
Yuma, AZ	1	134	0.84	40	0-7.5	N/C	NDR
Parker, AZ	1	99	0.84	26	0-7.5	N/C	NDR
Parker, AZ	1	252	0.84	26	0-7.5	N/C	<0.2[g]
Posten, AZ	1	458	0.71	35	0-7.5	0.27	<0.2[h]

[a] Concentration of NDPA in the Treflan EC applied to the field. [b] DAT = number of days after treatment. [c] Theory values calculated from eq 2. [d] Assumed an average value of 150 ppm when actual value was unknown. [e] NDR = no detectable residue at a test sensitivity of 0.2 ppb. [f] N/C = not calculable from the data available. [g] One of three replicate samples exhibited an NDPA response equivalent to 0.19 ppb. [h] One of three replicate samples exhibited an NDPA response equivalent to 0.12 ppb.

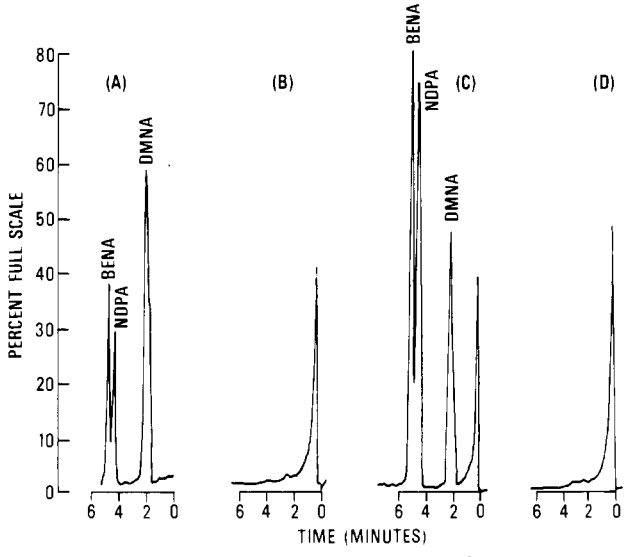

Figure 1. GC–TEA chromatograms from the determination of nitrosamines in a well water sample. (A) Standard solution containing DMNA, NDPA, and BENA at 0.078, 0.046, and 0.064 μg/mL, respectively, ×8. (B) Deionized water, 500 mL to 2.0 mL, ×8. (C) Recovery, 500 mL of water + 0.31 μg of DMNA, 0.54 μg of NDPA, and 0.64 μg of BENA, ×16. (D) Water from irrigation well, Panama City, FL, 500 mL to 2.0 mL, ×8. Volumes injected, 50 μL.

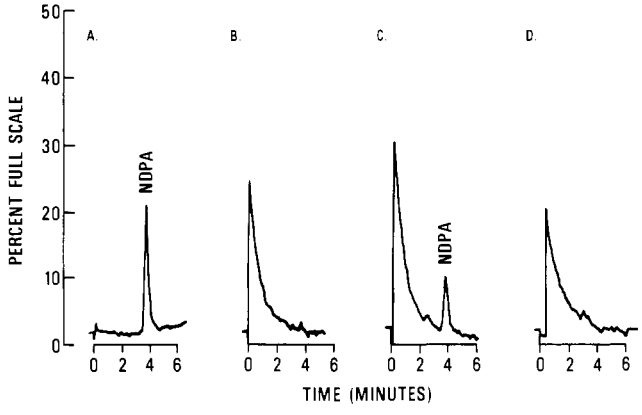

Figure 2. GC–TEA chromatograms from the determination of NDPA in a Treflan-treated soil. (A) Standard NDPA, 0.034 μg/mL, ×4. (B) Untreated soil, 50 g, 1/2 aliquot, ×2. (C) Recovery, 50 g of soil + 0.65 ppb NDPA, ×2; 87%. (D) Soil from field treated with Treflan containing 159 ppb NDPA, sampled immediately after application, 0–5 cm depth, 50 g, 1/2 aliquot, ×2. Volumes injected, 50 μL.

near the Treflan manufacturing facility at Lafayette, IN, are presented in Table II. No volatile nitrosamines were detected in any of these samples, nor in subsequent periodic samplings of the river, at a detection limit of 0.01 ppb. The chromatograms from the analysis of an irrigation well in Panama City, FL, are shown in Figure 1.

The analytical results for a number of Treflan-treated soils are presented in Table III. Chromatograms from the analysis of one of the soil samples from Branford, FL, are given in Figure 2. No nitrosamines were detected in any of the soil samples at a test sensitivity of 0.2 ppb. One of three replicate samples from two of the fields contained residues of slightly less than 0.2 ppb, as indicated in Table III. The Treflan applied to these fields contained the highest levels of NDPA (252 and 458 ppm). Estimates of amounts of NDPA which were theoretically applied to the fields are listed in Table III and were calculated from the following equations:

$$\text{theoretical NA residue (ppb)} = \frac{(C_{NA})(100/P_A)(R_A)(N_A)(1000\ \text{g/kg})}{(W_S/V_S)(D_S)(10^8\ \text{cm}^2/\text{ha})} \quad (1)$$

$$= \frac{(C_{NA})(R_A)(n)(d^2)(N_A)}{(P_A)(W_S)(1273)} \quad (2)$$

where C_{NA} = concentration of nitrosamine in formulated product, μg/g (ppm); P_A = percent of active ingredient in formulated product; R_A = rate of application of active ingredient, kg/ha; N_A = number of applications; W_S = total weight of soiled sampled, kg; V_S = total volume of soil sampled $[(n\pi d^2)(D_S)]/4$; n = number of core subsamples; d = diameter of core sampler, cm; D_S = depth of soil sampled, cm. The numerator in eq 1 calculates the micrograms of nitrosamine applied per hectare and the

Table IV. Results from Soil Surface Spray Experiments

exptl no.	trifluralin rate, kg/ha	trifluralin theory,[a] mg/pan	trifluralin found,[b] mg/pan	trifluralin % of theory	N-nitrosodipropylamine concn, ppm	N-nitrosodipropylamine theory,[c] μg/pan	N-nitrosodipropylamine found[b] μg/pan	N-nitrosodipropylamine found[b] ppb	N-nitrosodipropylamine % of theory
1	0.77	6.9	6.7	97	3.6	0.056	0.045	0.23	80
2	0.77	6.9	6.3	91	3.7	0.057	0.051	0.26	89
3	2.24	20.2	21.9	108	3.5	0.158	0.142	0.71	90
4	2.24	20.2	23.1	114	3.7	0.167	0.166	0.83	99
5	1.44	13.0	14.1	108	6.3	0.183	0.203	1.02	111
6	1.44	13.0	10.6	82	3.5	0.102	0.070	0.35	69

[a] Theory calculated from eq 3. [b] Average of three replicates. [c] Theory calculated from eq 4.

Table V. Volatile Nitrosamine Residues in Crops and Plants from Fields Treated with Dinitroaniline Herbicides

herbicide	rate, kg/ha	no. of applic.	crop	part	no. of samples	residue, ppb
Treflan	0.56-1.1	5-13	cotton	seed	5	NDR[a]
Treflan	0.56-0.84	1	cotton	seedlings	10	NDR
Treflan	0.56-2.2	1-10	soybeans	seed	6	NDR
Treflan	0.56-1.1	2	carrots	roots	4	NDR
				tops	4	NDR
Treflan	1.1	1	cauliflower	fruit	1	NDR
				leaves	1	NDR
Treflan	0.84	1	cotton	alfalfa (volunteer)	1	NDR
Surflan	0.56-1.1	1	soybeans	seed	6	NDR
Balan	1.7	2	lettuce	leaves	3	NDR
Balan	1.7	1	peanuts	nuts	1	NDR
				shells	1	NDR

[a] NDR = no detectable residue at a test sensitivity of 0.2 ppb.

denominator estimates the number of kilograms of soil per hectare at a given sampling depth. Equation 2 is a simplified form of eq 1 and was used to obtain the theoretical values in Table III. For example, 30 core samples were taken from the Midville, GA, field with a 1.91-cm diameter probe and yielded a total soil weight of 3.482 kg. Assuming the Treflan contained 44.5% trifluralin and 150 ppm of NDPA, the maximum theoretical concentration of NDPA in the field would be:

$$\frac{(150)(0.84)(30)(1.91)^2(13)}{(44.5)(3.482)(1273)} = 0.91 \text{ ppb}$$

The concentrations of NDPA which theoretically could have been present in the fields which received multiple applications are above the 0.2-ppb limit of detection of the method and would have been detected had the NDPA not dissipated. These data suggest that NDPA did not accumulate in soils which received consecutive annual applications of Treflan.

Reduction in the nitrosamine content in dinitroaniline herbicides to less than 10 ppm as a result of modified manufacturing procedures has resulted in the application of reduced amounts of contaminant to the soil. Two of the fields listed in Table III were treated with Treflan which contained 6 ppm NDPA, and the theoretical concentration of the nitrosamine in the soil was less than 0.01 ppb. Such concentrations are probable with the application and incorporation of Treflan and other dinitroaniline herbicides produced by Elanco since 1977. These levels are below the limit of detectability of the methods described. Nevertheless, it was of interest to determine the amount of nitrosamine reaching the surface of a field during the application of a herbicide containing less than 10 ppm of nitrosamine contaminant. To accomplish this, experiments were conducted in which 200 g of soil was spread evenly in a 30 × 30 × 2 cm pan and placed in the path of a tractor applying Treflan. The soil was placed in bottles immediately after application for transport to the laboratory. The entire sample was analyzed for NDPA and trifluralin content, and the results are presented in Table IV, along with the theoretical values. Chromatograms from the analysis of one of these soils are shown in Figure 3. The theoretical values were calculated from

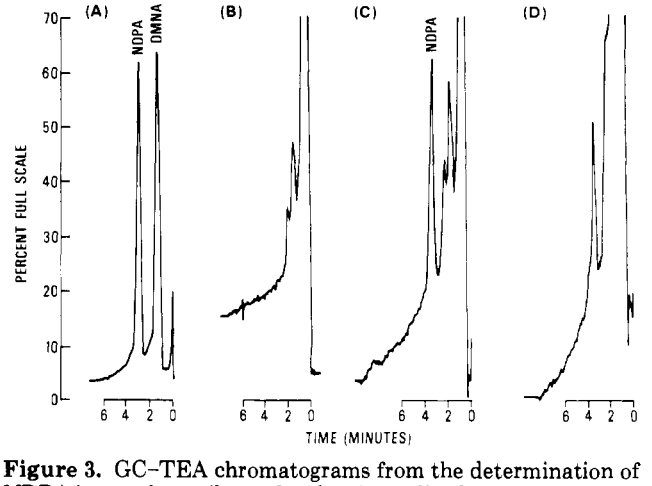

Figure 3. GC–TEA chromatograms from the determination of NDPA in a surface soil sample taken immediately after application of 1.44 kg/ha Treflan containing 3.5 ppm NDPA. (A) Direct standards DMNA (0.068 μg/mL) and NDPA (0.10 μg/mL), ×8. (B) Untreated soil, 200 g to 2.0 mL, ×4. (C) Recovery, 200 g of soil + 0.1 μg of NDPA (0.5 ppb) to 2.0 mL, ×4; 75%. (D) Sample, 200 g to 2.0 mL, ×4; 0.068 μg/pan (0.34 ppb) NDPA found. Injection volumes, 50 μL.

$$\text{mg of trifluralin/pan} = (9.02)(\text{kg/ha applied}) \quad (3)$$

$$\mu\text{g of NDPA/pan} = (\text{mg of trifluralin/pan})(\text{ppm NDPA}/445) \quad (4)$$

The amounts of trifluralin and NDPA applied in the six experiments averaged 100 and 90% of theory, respectively. This indicated that there was very little, if any, dissipation of NDPA during the application and that the contaminant was subsequently incorporated into the soil.

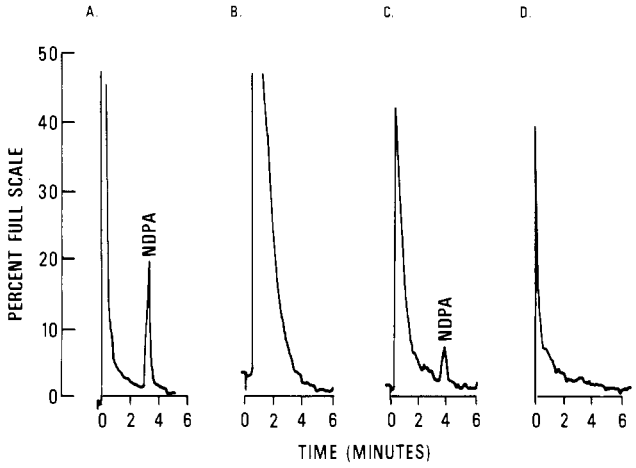

Figure 4. GC–TEA chromatograms from the determination of NDPA in cottonseed. (A) Direct standard NDPA, 0.034 μg/mL, ×4. (B) Control cottonseed, 50 g, 1/2 aliquot, ×2. (C) Recovery, 50 g of seed + 0.65 ppb NDPA, ×2, 62%. (D) Cottonseed from field treated with Treflan for 13 consecutive years, 50 g, 1/2 aliquot, ×2. Injection volume, 50 μL.

The results of nitrosamine residue assays on crops grown in fields treated with Treflan, Balan, or Surflan are given in Table V and a set of chromatograms from a determination in a cottonseed sample is presented in Figure 4. No volatile nitrosamines were detected in any of the samples at a test sensitivity of 0.2 ppb. Ross et al. (1978) reported similar findings on tomatoes harvested from a Treflan-treated field. These results were not unexpected in view of the absence of detectable amounts of nitrosamines in the soils from which these crops were harvested.

The apparent absence of nitrosamines in water, soil, and crops from fields receiving the contaminant is consistent with the findings of other investigators. Tate and Alexander (1975) and Dressel (1976) observed a microbial involvement in the disappearance of NDPA and other volatile nitrosamines. These chemicals are also known to undergo rapid photodegradation (Hanst et al., 1977; Burns and Alliston, 1971; Althorpe et al., 1970). Oliver et al. (1978) observed half-lives of 2–3 weeks for NDPA and DMNA in laboratory soil studies with most of the initial losses being due to volatilization following surface application. Following soil incorporation, degradation to CO_2 predominated over volatilization. Saunders et al. (1978) conducted field studies with [^{14}C]NDPA and obtained results similar to those of Oliver et al. Only a small amount of loss (1%) was attributed to leaching. Hence, the most likely mechanism of dissipation of the nitrosamine contaminant is volatilization followed by vapor phase photolysis (Hanst et al., 1971). Trifluralin itself is subject to dissipation in this manner (Soderquist et al., 1975). Plants have demonstrated the ability to absorb nitrosamines (Dean-Raymond and Alexander, 1976), but laboratory studies have demonstrated that nitrosamines absorbed by plants disappear rapidly (Dressel, 1976). Kearney et al. (1978) observed no detectable radioactivity in stems, leaves, and beans from soybean plants grown in soil containing 100 ppb of [^{14}C]NDPA.

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