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Laboratory and Field Studies on the Fate of 1,3,6,8-Tetrachlorodibenzo-*p*-dioxin in Soil and Sediments

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The fate of ^{14}C-ring-labeled 1,3,6,8-tetrachlorodibenzo-*p*-dioxin (TCDD) was studied in sandy loam soil under field conditions and in silty-clay pond and lake sediments under laboratory conditions. Dissipation of 1,3,6,8-TCDD from small field plots was relatively rapid with 44% of the applied radioactivity lost after 131 days posttreatment. In sediment, 80% of the radioactivity could still be accounted for as intact chemical after 675 days under static aerobic conditions (10 and 25 °C) or after 310 days under a nitrogen or air purge. Transformation of 1,3,6,8-TCDD to degradation products and unextractable radioactivity in soils and sediments was very slow. Unidentified polar products represented a maximum of 2.5% of extractable ^{14}C in field soils and 7.0% in sediments. DDT incubated in sediments under the same conditions had half-lives of <310 days.

INTRODUCTION

The fate of the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) isomer in soils and sediments has been studied extensively in laboratory and field experiments (Kearney et al., 1972; Ward and Matsumura, 1978; Tsushimoto et al., 1982; Nash and Beall, 1980). There has been much less study of the persistence and degradation of other dioxin isomers in soils and sediments. The 1,3,6,8-TCDD isomer is the principal tetrachlorodioxin contaminant in 2,4-D ester formulations (Cochrane et al., 1982) and diphenyl ether herbicides (Tamagishi et al., 1981). This isomer has also been reported to be a major component of total TCDD congeners in fly ash from a municipal incinerator (Buser et al., 1978) and in particulates from wood combustion (Nestrick and Lamparski, 1982).

The 1,3,6,8-isomer is reported to be much less toxic than the 2,3,7,8-isomer based on its ability to induce aryl hydrocarbon hydroxylase activity and on an LD_{50} (rat) of >100 mg/kg (Esposito et al., 1980). The fate of this compound is nevertheless of interest because of its possible widespread introduction to terrestrial and aquatic ecosystems as a herbicide and fly ash microcontaminant. 1,3,6,8-TCDD has been identified in fish from agricultural areas of Japan where diphenyl ether herbicides were used (Tamagishi et al, 1981) and in fish from Lake Michigan (Stalling et al., 1983).

The purpose of this study was to examine the fate of 1,3,6,8-TCDD by using ^{14}C-labeled compound in soils and sediments from the Canadian prairies, a region in which 2,4-D esters contaminated with this isomer were used in large quantities until recently, and to compare results with published reports on the 2,3,7,8-isomer.

MATERIALS AND METHODS

Chemicals. [^{14}C]1,3,6,8-TCDD (U-ring-labeled) was obtained from New England Nuclear, (Boston, MA) and purified before use by reverse-phase TLC by using a solvent system of acetone–water (95:5). The final product (>99.5% radiochemically pure, sp act 1701 Bq/μg) was dissolved in hexane–ethyl acetate (1:1) for addition to soils and in acetone for addition to sediment incubations. [^{14}C]*p,p'*-DDT (Amersham Radiochemicals, Oakville, Ont.)

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(sp act 3101 Bq/μg) was purified by the same procedure.

Field Microplot Studies. Small soil plots (10 × 10 cm) were staked out in a sandy loam soil of the Asquith Association classified as a Dark Brown Chernozemic, orthic Dark Brown (White City, Sask.). The soil contained 10% clay, 25% silt, 65% sand, and 4.6% organic matter. Soil pH (1:1 slurry) was 7.6. The soil surface was dry but moist underneath. Each plot was treated with 0.76 mL of a hexane–ethyl acetate solution containing 36.83×10^3 Bq of 1,3,6,8-TCDD (21.65 μg/100 cm^2 plot) in a zig–zag pattern. After the solvent had evaporated the soil surface was scratched lightly with the tines of a kitchen fork to a depth of 0.5 cm and then tamped down to reduce wind erosion. Plots were sampled (in duplicate) after 20, 56, 131, 321, and 495 days by excavating 0–5- and 5–10-cm layers as described by Smith (1971). After sampling, soil was air-dried, weighed, ground through a sieve (30 mesh), and mixed for 20 min in a soil mixer. The soil was then stored at −20 °C until analysis.

Laboratory Sediment/Water Studies. Pond and lake sediments (equivalent to 10 g of oven dry weight) were added to culture flasks and respirometer flasks along with dechlorinated water to give sediment/water ratios of 1:10 and 1:20, respectively, as described by Muir and Yarechewski (1984). Pond sediment was obtained from a farm pond with no history of direct pesticide treatment. Lake sediment was obtained from Tobin Lake, a reservoir on the Saskatchewan River. Both sediments were stored at −50 °C until use. Pond sediment consisted of 75% clay, 24% silt, 1% sand, and 6.3% organic matter and had a pH of 7.6. Lake sediment contained 79% clay, 21% silt, and 6% organic matter.

Sediment/water systems were equilibrated for 21 days (22.5 °C). Sediments to be incubated under nitrogen aeration were amended with cellulose (1% by weight) to provide an additional source of carbon. Additional culture flask incubations were autoclaved (30 min) to examine degradation under sterile conditions. Acetone solutions of 1,3,6,8-TCDD were added to each flask to give water concentrations of 10 ng/mL in culture flasks and 5 ng/mL in respirometers. In order to compare degradation of 1,3,6,8-TCDD with other compounds, [^{14}C]DDT was added to additional flasks to give water concentrations of 5 ng/mL. All flasks were held in a controlled environment room (22.5 or 10 °C) with a photoperiod of 16 h of light and 8 h of darkness. Culture flasks were loosely capped (Teflon lined screw caps) and will be referred to as static incubations since only passive exchange with air occurred. Nitrogen aerated flasks were darkened continuously by covering with aluminum foil. Respirometer flasks were connected to a manifold which delivered air (CO_2 free grade) or nitrogen (zero grade, <5 ppm O_2) presaturated with water at 1–2 mL/min. Effluent gas was passed through a polyurethane foam plug to trap nonpolar volatiles and through a CO_2 trapping agent (2-methoxyethylamine, Amersham Radiochemicals, Oakville, Ont.).

Culture flasks were removed after 40, 80, 160, 370, and 675 days of static incubation of 1,3,6,8-TCDD and DDT. Respirometer flasks, foams, and CO_2 traps were removed after 40, 160, and 310 days. Redox potentials in water and sediment (0–1-cm depth) were recorded prior to removing sediment from each flask by using a Pt/Calomel electrode.

Extraction of Soil and Sediment. Duplicate subsamples (25 g) of soils from microplots treated with [^{14}C]1,3,6,8-TCDD were extracted with hexane–acetone (1:1) in a Soxhlet apparatus (24 h). The hexane–acetone extract was diluted with water to recover the hexane phase. The aqueous phase (adjusted to pH 2) was further extracted with dichloromethane (DCM). The combined hexane and DCM phase was dried by passing through a column of anhydrous Na_2SO_4, evaporated to about 1 mL on a rotary evaporator, and taken up in ethyl acetate. Aliquots of the ethyl acetate phase were diluted with a xylene–based scintillation fluor and assayed by liquid scintillation counting (LSC). Samples were counted for 10 min on a Beckman 7500 scintillation counter.

The ethyl acetate phase was evaporated to dryness and the residue dissolved in methanol. The methanol phase was "cleaned up" by chromatography on a reverse-phase cartridge (C-18 Sep-Pak, Waters Scientific, Mississauga, Ont.) and radioactivity was eluted with 5 mL of methanol. Subsamples of the extracted soil residuum and of unextracted soil (0.3 g) were combusted on a Packard 306 oxidizer to determine total radioactivity in samples before and after extraction. The $^{14}CO_2$ was collected in 2-methoxyethylamine and diluted with scintillation fluor in the instrument.

Sediment and water containing [^{14}C]1,3,6,8 TCDD and *p,p'*-DDT were separated by vacuum filtration (Whatman No. 1 paper). Total ^{14}C in water was determined directly by diluting 2-mL aliquots with scintillation fluor and assaying by LSC. The water was subsequently discarded since it contained very low levels of radioactivity. Sediment was refluxed (16 h) with acetonitrile (150 mL) and centrifuged (1000 × g) and the supernatant decanted. The sample was reextracted in the centrifuge bottle by shaking with additional acetonitrile on a wrist-action shaker (20 min). The acetonitrile was evaporated leaving an aqueous residue (20–30 mL) which was diluted to 50 mL with water and extracted with DCM. DCM extracts were subsequently chromatographed on reverse-phase cartridges as described for soil.

Thin-Layer Chromatography. Sample extracts containing [^{14}C]1,3,6,8-TCDD were spotted on reverse-phase (Whatman KFC18) (System I) and silica gel plates (System II). Chromatograms were developed with acetone–water (95:5) for System I and hexane–diethyl ether (10:1) for System II. R_f's for 1,3,6,8-TCDD and *p,p'*-DDT on System I were 0.54 and 0.71, respectively. On System II R_f's for the same compounds were 0.58 and 0.50, respectively.

Radioactive spots were located by exposing the plates to X-ray film (Kodak NS2T) for 2 to 3 weeks. Spots were then scraped, the radioactivity dissolved in acetone, and an aliquot assayed by LSC to determine total radioactivity under each spot.

Additional Studies. The combustion efficiency of 1,3,6,8-TCDD in soils was estimated by fortifying soil (5–10-cm depth from microplots) with [^{14}C]1,3,6,8-TCDD at 18 or 180 ng/g (4 replicate 0.5-g samples at each concentration). Samples were combusted and the $^{14}CO_2$ analyzed by LSC.

Trapping efficiency of polyurethane foam plugs for 1,3,6,8-TCDD was estimated by using the procedure of Grover and Kerr (1981).

RESULTS

Field Microplot Studies. Total ^{14}C in field soils (0–5-cm depth) from microplots averaged 94% of the quantity initially added at 20 days posttreatment and had decreased to 56% by 131 days (Figure 1). Results expressed as ng/g equiv of 1,3,6,8-TCDD are in Table I. In samples taken at 321 days about 80% of the radioactivity originally added to the plots was accounted for while an average of only 26% remained at 495 days. The results at 321 and 495 days were not entirely consistent with those from the three earlier sampling times perhaps because of the prolonged exposure of the small bare soil plots. Some variability

Table I. Concentrations of ^{14}C Radioactivity (as 1,3,6,8-TCDD Equiv) in Soil from Field Microplots

time, days	plot no.	depth, cm	extracted,[a] ng/g	unextractable,[b] ng/g	direct combustion,[b] ng/g
20	1	0–5	16.7	1.3	16.5
		5–10			0.15
	2	0–5	25.9	2.1	20.9
		5–10			0.13
56	1	0–5	16.1	4.9	19.6
		5–10			0.42
	2	0–5	20.2	6.5	25.2
		5–10			0.21
131	1	0–5	11.2	1.3	12.3
		5–10			0.17
	2	0–5	15.6	1.5	16.8
		5–10			1.10
321	1	0–5	21.1	2.5	24.4
		5–10			0.40
	2	0–5	27.7	3.4	30.3
		5–10			0.31
495	1	0–5	1.85	0.37	1.56
		5–10			<0.02
	2	0–5	11.8	2.17	11.9
		5–10			0.18

[a] All results are from duplicate extractions or combustions on each replicate. [b] Samples determined by combustion were corrected for combustion efficiency by dividing by 0.92.

Table II. Proportion of 1,3,6,8-TCDD and Unidentified Products in Extracts of Field Soils Determined by TLC–Autoradiography

		% of total ^{14}C under each spot		
day	plot no.	TCDD	2[a]	immobile
20	1	99.7	<0.1	0.3
	2	99.9	<0.1	0.1
56	1	99.8	<0.1	0.2
	2	99.9	<0.1	0.1
131	1	97.5	2.5	<0.1
	2	98.9	1.1	<0.1
321	1	98.4	1.3	0.2
	2	99.2	0.7	0.1
495	1	99.4	2.2	3.4
	2	98.3	0.7	1.0

[a] R_f of 0.66 on System I and 0.08 on System II.

between replicate plots especially at 20 and 495 days (Figure 1, Table I) may also be due to effects of wind and precipitation.

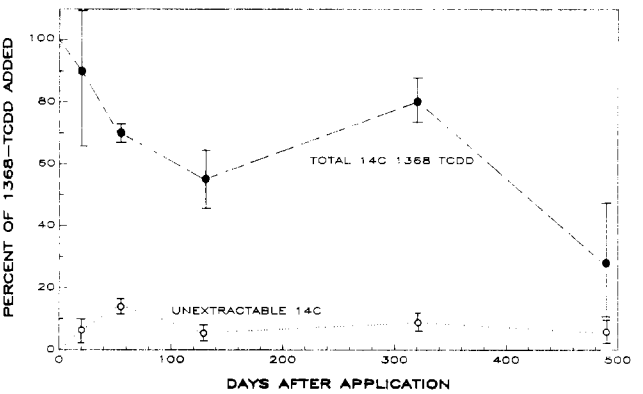

Figure 1. Persistence of total ^{14}C radioactivity and unextractable ^{14}C in field soils treated with 1,3,6,8-TCDD expressed as % of quantity added to each plot.

Negligible radioactivity was found in 5–10-cm depths throughout the experiment; the amount present probably reflects contamination during sampling by small amounts of soil from the upper layer (Table I). Unextractable radioactivity, determined by combustion of extracted soil, was generally low, ranging from 2 to 15% of total ^{14}C, and did not increase with time (Figure 1). Combustion efficiency of TCDD averaged 92.4 ± 2.3% at 18 ng/g and 95.7 ± 2.6% at 180 ng/g. Greater than 99% of the radioactivity that was extractable with acetone–hexane partitioned into the organic phase when the extract was diluted with water.

TLC–autoradiography of the DCM–hexane extracts revealed that >97.5% of the extractable radioactivity was in the form of intact 1,3,6,8-TCDD throughout the 495-day period (Table II). A single degradation product (R_f 0.08 in System II) representing 0.7–2.5% of total ^{14}C was observed in extracts at 131 and 321 days. At 495 days an increased proportion of the extractable radioactivity was immobile, especially on silica gel plates, and no degradation products could be resolved. The low levels of the degradation product precluded further identification.

Laboratory Sediment/Water Studies. Following addition to static incubations 1,3,6,8-TCDD partitioned almost entirely into the sediment phase. Levels of total ^{14}C in water were generally <1% for both pond and lake sediments with sediment/water ratios of 1:10 (static systems, Table III) and 1:20 (respirometers, Table IV). Unextractable radioactivity in sediments was also low, ranging from 3.1% in lake sediments to 8.6% in pond

Table III. Distribution of 1,3,6,8-TCDD and *p,p'*-DDT in Static Sediment/Water Incubations at 25 and 10 °C and in Autoclaved Sediments

		% of added radioactivity in each fraction on each day[a]								
				160[b]		370		675		
fraction	compd	40	80	25 °C	auto	25 °C	10 °C	25 °C	10 °C	auto
				Lake Sediment						
extractable	TCDD	100.0	93.4	87.1	84.1	91.5	95.0	90.1	97.8	91.7
	DDT			48.6		37.4	36.8		31.9	
unextractable	TCDD	2.7	2.5	2.7	2.4	3.1	4.6	3.1	4.1	2.4
	DDT			36.8		42.9	51.6		62.5	
water	TCDD	0.1	0.5	0.5	1.0	0.4	0.4	0.6	0.1	1.1
	DDT			0.2		1.1	1.1		1.0	
				Pond Sediment						
extractable	TCDD	90.0	88.3	80.2	82.1	89.6	87.3	82.2	92.3	69.4
	DDT			58.3		26.6	37.7		33.2	
unextractable	TCDD	5.2	5.3	6.7	3.9	5.7	9.3	8.6	9.0	4.9
	DDT			31.5		41.7	42.9		58.3	
water	TCDD	0.2	0.6	0.6	0.8	0.4	0.6	0.6	0.1	2.1
	DDT			0.6		1.1	1.4		1.0	

[a] Auto = autoclaved sediment, 10 °C and 25 °C refer to incubation temperature. [b] DDT results from 224 days incubation in the same sediments.

Table IV. Distribution of 1,3,6,8-TCDD and DDT in Respirometer Flasks Incubations (25 °C)

fraction	compd	% of added radioactivity in each fraction on each day					
		40		160		310	
		air	N_2	air	N_2	air	N_2
		Lake Sediment					
extractable	TCDD	92.1	91.3	96.8	91.3	97.3	94.5
	DDT					49.5	49.7
unextractable	TCDD	3.9	4.7	4.2	3.7	5.2	4.2
	DDT					43.4	49.9
water	TCDD	0.5	0.6	0.6	0.5	0.4	0.5
	DDT					1.7	1.3
CO_2 trap[a]	TCDD	0.10	0.12	0.15	0.15	0.20	0.17
	DDT	0.17	0.18	0.28	0.29	0.53	0.44
		Pond Sediment					
extractable	TCDD	83.8	86.5	86.3	86.5	89.8	92.3
	DDT					62.0	53.5
unextractable	TCDD	5.6	3.8	8.9	6.6	11.1	7.3
	DDT					54.1	41.1
water	TCDD	0.5	0.5	0.5	0.4	0.5	0.6
	DDT					0.9	1.4
CO_2 trap[a]	TCDD	0.22	0.12	0.26	0.19	0.36	0.30
	DDT	0.36	0.12	0.60	0.18	0.84	0.38

[a] Cumulative ^{14}C in 2-methoxyethylamine solution over the duration of the experiment.

Table V. Redox Potentials in Sediment and Water during Incubation of 1,3,6,8-TCDD and p,p'-DDT under Static Conditions and in Respirometer Flasks

day	sediment/ system	E_h, mv			
		lake		pond	
		water	sediment	water	sediment
40	static	314	64	464	94
	air	324	294	344	224
	N_2	264	−156	164	−136
160	static	319	4	279	79
	autoclaved	294	184	224	204
	air	394	384	194	256
	N_2	264	344	194	−116
310	air	254	264	314	294
	N_2	324	−54	324	−54
370	static 25 °C	404	114	414	74
	static 10 °C	404	364	389	379
675	static 25 °C	314	329	364	379
	static 10 °C	364	384	369	374
	autoclaved	144	124	294	294

sediments for 1,3,6,8-TCDD at 675 days. By contrast, between 58.3 and 62.5% of total [^{14}C]p,p'-DDT in sediment remained unextractable by refluxing with acetonitrile after 675 days of incubation (10 °C), indicating considerable transformation of this compound.

More than 80% of radioactivity in pond sediment and 87% in lake sediment, in both static and respirometer incubations, was extractable by refluxing with acetonitrile. Extraction efficiencies did not decrease with time and were higher at 31, 370, and 675 days than at 160 days (Table III and IV). Less than 1% of acetonitrile extractable radioactivity remained in the aqueous phase after partitioning with DCM. Recoveries of total ^{14}C from p,p'-DDT incubations under the same conditions ranged from 48–58% at 160 days to 31–33% at 675 days. Incubations of 1,3,6,8-TCDD at 10 °C had higher proportions of extractable radioactivity than those at 25 °C. Autoclaved samples had similar levels of extractable radioactivity as other samples but lower levels of unextractable radioactivity after 675 days of incubation (Table III).

Aeration with air or nitrogen created different redox conditions in sediments (Table V) but had little effect on extractability of radioactivity in incubations of 1,3,6,8-TCDD or p,p'-DDT over a 310-day period (Table IV). Redox potentials (E_h) in air-purged respirometers ranged from 264 to 384 mv in sediment indicating that aerobic conditions prevailed. Under N_2 aeration E_h values ranged from −54 to −136 mv which is indicative of extremely low oxygen conditions (Stumm and Morgan, 1981); however, water above the sediment had positive redox potentials so that conditions were not strictly anaerobic. Redox potentials in static incubations gradually increased from 64–94 mv at day 40 to 326–379 mv at 675 days indicating that aerobic conditions generally prevailed in these systems.

Radioactivity from 1,3,6,8-TCDD in CO_2 traps was similar under aerobic conditions and under N_2 purge (Table IV). By 310 days, less than 0.4% of total [^{14}C]TCDD added to respirometers had been collected in 2-methoxyethylamine. $^{14}CO_2$ from DDT treated respirometers reached a cumulative total of 0.8% of added radioactivity. The actual form of radioactivity in CO_2 traps was not measured. The presence of volatilized parent compound was unlikely since recoveries of 1,3,6,8-TCDD by polyurethane foams averaged 81.2 ± 1.0%. Radioactivity collected by foams amounted to <0.2% of [^{14}C]TCDD added to each flask and was not tabulated.

Most of the [^{14}C]1,3,6,8-TCDD added to respirometers and static incubations could be accounted for in sediment, water, or volatilized radioactivity. Overall accountability for respirometers ranged from 95–98% in lake sediments to 90–98% in pond sediments (Table IV).

TLC of sediment extracts revealed that virtually all of the DCM extractable ^{14}C was in the form of parent compound in both static and respirometer incubations throughout the study (Table VI). The highest proportion of degradation products was observed at 40 days for both sediments in static incubations. Two products having R_f's 0.03 and 0.06 (System II) were detected (Table VI). After 160 days these products were undetectable (<0.1% of extractable ^{14}C) and no other products were observed. Fewer products were observed with the same sediments under air or N_2 purge, although traces of the more mobile product (Spot 2, Table VI) were observed in both sediments at 160 and 310 days. No degradation products were observed in the analytical standard of 1,3,6,8-TCDD which was chromatographed at the same time.

DISCUSSION

The loss of [^{14}C]1,3,6,8-TCDD from field soils was much greater than from laboratory sediment/water incubations. Under field conditions the time for disappearance of 50%

Table VI. Proportion of 1,3,6,8-TCDD and *p,p'*-DDT and Unidentified Polar Products in Sediment Extracts by TLC-Autoradiography

		% of TCDD as product[a]							
		parent		1		2		immobile	
time, days	system	lake	pond	lake	pond	lake	pond	lake	pond
40	static	84.8	94.6	4.4	1.3	7.0	2.4	3.8	1.7
	air	97.0	96.7	<0.1	<0.1	<0.1	<0.1	1.7	0.8
	N_2	99.5	94.1	<0.1	1.1	<0.1	<2.2	0.5	1.2
80	static	98.4	98.6	0.3	<0.1	0.6	0.5	0.7	0.7
160	static	99.0	99.1	<0.1	<0.1	<0.1	<0.1	1.0	0.9
	autoclaved	98.8	98.9	<0.1	<0.1	0.4	0.4	0.8	0.7
	air	97.0	99.2	<0.1	<0.1	0.1	0.1	2.8	0.7
	N_2	99.4	99.4	<0.1	<0.1	0.1	<0.1	0.7	0.6
310	air	94.6	97.4	<0.1	<0.1	0.1	0.2	5.3	2.1
	N_2	99.5	99.5	0.1	0.1	0.1	0.1	0.3	0.3
370	static 25 °C	99.0	98.4	<0.1	<0.1	0.1	0.1	0.9	1.5
	static 10 °C	97.8	99.0	<0.1	<0.1	0.2	0.1	2.0	0.9
675	static 25 °C	99.6	99.7	0.1	0.1	0.1	0.1	0.2	0.1
	static 10 °C	99.6	99.6	<0.1	<0.1	0.2	0.2	0.1	0.2
	autoclaved	99.5	99.6	<0.1	<0.1	0.3	0.2	0.1	0.1
		% of DDT as product[a]							
		parent		DDD		DDE		other products	
time, days	system	lake	pond	lake	pond	lake	pond	lake	pond
224	static	37.1	17.6	31.8	48.0	4.5	3.5	27.3	30.9
310	air	61.2	43.0	20.0	25.7	7.5	3.1	11.1	28.2
	N_2	5.1	3.6	43.5	40.6	2.2	3.1	49.2	52.7
370	static 25 °C	29.4	6.4	32.1	53.5	3.6	13.2	34.9	26.9
	static 10 °C	20.3	7.0	34.2	43.9	3.7	4.8	41.8	44.3
675	static 10 °C	19.9	6.7	47.7	63.8	3.7	5.2	28.8	24.3

[a] R_f of unidentified spot 1 0.03 and R_f of unidentified spot 2 0.06 in System II.

of TCDD could not be estimated precisely because of variability between results at 131 and 321 days but is in the 130–400-day range. By contrast all incubation conditions in sediment suggest 50% disappearance times of >600 days. More than 50% of DDT, incubated under the same conditions, had undergone transformation to DDD, DDE, and unidentified products by 310 days and a high proportion was also unextractable from sediment (Table IV). Many chlorinated pesticides, containing aliphatic substituted chlorines, are known to undergo rapid degradation in flooded soils (Sethunathan, 1973). The behavior of 1,3,6,8-TCDD in sediments appears similar to the tetrachlorinated PCBs which degrade extremely slowly in natural sediments (Carey and Harvey, 1978) and in sewage sludge (Tucker et al., 1975).

The reduction in radioactivity in field plots was not due to movement into the soil or to degradation of the 1,3,6,8-TCDD molecule. Losses of 1,3,6,8-TCDD may have occurred via volatilization from soil. Volatilization of 2,3,7,8-TCDD from grass turf has been observed under field conditions and in microcosms (Nash and Beall, 1980). Volatilization of chlorinated pesticides with low vapor pressures, such as dieldrin, from bare soil and plant surfaces has been shown to be a major path of loss under field conditions (Taylor, 1978). Other possible losses include wind and water erosion of soil. Studies with herbicides applied to microplots at the same site for periods of up to 95 weeks indicate that erosional losses are small when the chemical is incorporated into the soil, as was the case with 1,3,6,8-TCDD (Smith and Muir, 1984).

The unidentified polar products observed on TLC analysis of both soil and sediment extracts had similar characteristics to polar products observed in sediment and pure culture incubations of 2,3,7,8-TCDD (Ward and Matsumura, 1978; Quensen and Matsumura, 1983). Ward and Matsumura (1978) estimated that between 1 and 4% of the 2,3,7,8-isomer was degraded in laboratory sediment/water incubations over a 588-day period, a similar level to that observed in the present study. The higher level of degradation products in sediment extracts at 40 and 80 days than in later sampling times may reflect greater bioavailability of the 1,3,6,8-isomer to microorganisms soon after addition to the water in each flask. Quensen and Matsumura (1983) observed a similar pattern of degradation of 2,3,7,8-TCDD in a farm soil which they attributed to TCDD being available for cellular uptake before it became bound to soil. The initial high level of degradation products in static incubation systems may also be related to changes in microbial populations coinciding with changes in redox potential from anaerobic to aerobic (Table V). Although the identity of the degradation products could not be determined, the work of Klecka and Gibson (1980) with monochlorodioxins suggests that microbial degradation will yield hydroxy metabolites. Such products would likely be relatively mobile on TLC solvent System I and immobile in System II. By contrast, products of reductive dechlorination, e.g., trichlorodioxins, would have much greater R_f values than the products isolated from soil and sediments.

Registry No. TCDD, 33423-92-6; DDT, 50-29-3.

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Effect of Antioxidants on the Volatiles of Roasted Sesame Seeds

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The aroma concentrates of roasted sesame seeds free from antioxidants (sesamin–sesamolin) as well as of roasted defatted sesame seeds mixed with sesamin–sesamolin were fractionated into neutral–acidic and basic fractions. The volatile components of each fraction were identified by the retention times of the authentic samples in gas–liquid chromatography–mass spectrometry. The major changes in components of the neutral–acidic fraction of the sesamin–sesamolin free sample were the amounts of 2,4-undecadienal (32.59%) and 2,4,6-dodecatrienal (18.61%) compared to those of the whole seeds (49.44% and 6.9%, respectively). However, irregular changes were observed for the pyrazine derivatives of the basic fraction. The predominance of the nutty flavor, thus, might be due to the increase of some individual pyrazine derivatives at the expense of some furan derivatives. However, the aroma components of the defatted white sesame seeds either with or without sesamin–sesamolin did not follow a definite pattern regarding the pyrazine derivatives.

INTRODUCTION

Animal and vegetable lipids contain many minor constituents which may be quite important to the odor and flavor characteristics of foods, although their total concentration provides less than 1% of total lipids present; the most important of these is the antioxidants.

It is known that the resistance of vegetable fats to oxidation rested on the presence of antioxidants which occur naturally in the tissue and which are present in the oil when it is pressed. These antioxidants inhibit the effect of prooxidants which accelerate the onset of rancidity. The uptake of oxygen and the onset of rancidity seems to be related to the unsaturation of the fat. The oxidation is not, however, a simple oxidation of the double bond.

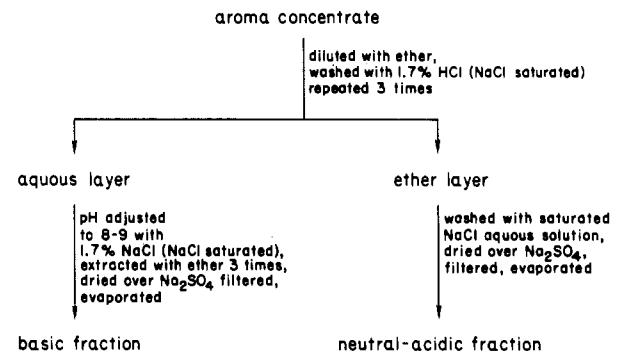
Analysis of the developed flavor of rancid fat shows that a very complex mixture of compounds is formed. Among them, heptanealdehyde formed the largest amount (Meyer, 1964).

On the other hand, these antioxidants undergo reactions with the amino acids present in the seed. This reaction is considered one of the most nonenzymatic browning reactions of food products. In neutral medium these reactions are stronger than those between glucose and amino acids (Segal et al., 1971).

Sesame seeds contain approximately 50% of edible oil which contains its characteristic antioxidant compounds (sesamin–sesamolin). These compounds are responsible for its stability and good quality.

The aim of the present work is to judge the role of the antioxidant (sesamin–sesamolin) on the development and changes of flavor compounds of roasted white sesame seeds.

Scheme I



MATERIALS AND METHODS

Materials. Local sesame seeds (*Sesamum indicum*) variety Giza-33 were obtained from the development of

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