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Oxychlordane Residues in Soil

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Oxychlordane, 1,2-dichlorochlordene epoxide (Figure 1) is a metabolite of the insecticide chlordane found in a number of animal species including pigs, rats, dogs (BROOKS 1974) and starlings (NICKERSON and BARBEHENN 1975). In addition, the occurrence of oxychlordane has been reported in alfalfa (WILSON and OLOFFS 1973), milk and cheese from cows (LAWRENCE et al. 1970), human adipose tissue (BIROS and ENOS 1973) and human milk (STRASSMAN and KUTZ 1977).

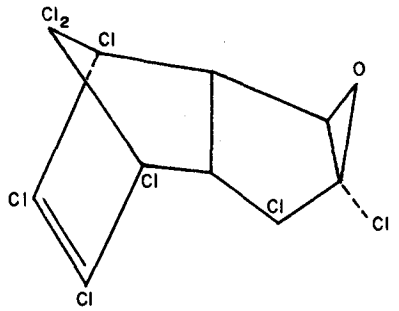

FIGURE 1. STRUCTURE OF OXYCHLORDANE

In this communication, we report the finding and confirmation of oxychlordane residues in soil samples collected at a number of US Army installations between the years 1975 - 1978 under the Department of the Army Pesticide Monitoring Program (DAPMP). This paper presents data on 1) installations and land use stratifications where oxychlordane residues were found; 2) electron-capture gas chromatography retention times for oxychlordane and other associated chlordane products relative to aldrin on four different chromatographic columns and; 3) gas chromatography - mass spectrometry (GC/MS) confirmatory techniques.

MATERIALS AND METHODS

Sample Collection and Extraction

Soil samples were collected under the DAPMP from selected US Army installations throughout the United States. Soil sampling and collection techniques used are detailed in two USAEHA

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technical reports (ROAN 1975, VINOPAL et al. 1977). Sample preparation, extraction and cleanup procedures are detailed in another USAEHA technical report (VINOPAL et al. 1976). Extraction procedures used in the DAPMP are a modification of the methodology used by STEVENS et al. (1970) and WIERSMA et al. (1972). Average recovery obtained from soil for oxychlordane was 78 % and the analytical limit of detectability in soil was 0.008 ppm (VINOPAL et al. 1976).

Gas Chromatography

Soil samples were routinely screened and analyzed for oxychlordane using Tracor MT-220, MT-222 and Model 560 gas chromatographs equipped with linearized (MT 222 and Model 560) and non-linearized (MT 220) Ni^{63} electron-capture detectors. A 6 ft x 4 mm I.D. glass column packed with either 1.5 % OV-17/1.95 % QF-1 on 80/100 mesh Gas Chrom Q or 1.5 % SP 2250/1.95 % SP-2401 on 100/120 mesh Supelcoport was used as the basic working column. Routine gas chromatographic operating temperatures were: oven - 195°C-205°C, inlet - 225°C - 230°, detector- 300°C - 325°C. Argon/methane carrier gas flows were set at 50-60 ml/min. Quantitation of oxychlordane peaks was accomplished using Spectra - Physics Auto Lab System IV or SP-4000 chromatography data systems. Confirmatory gas chromatographic columns used are as follows: 4 % SE-30/6 % QF-1 on 80/100 mesh Gas Chrom Q, 5 % OV-210 on 80/100 mesh Gas Chrom Q, and 3 % OV-1 on 100/120 mesh Gas Chrom Q.

GC/MS

Combined gas chromatography/mass spectrometry studies were performed using a Hewlett-Packard Model 5992 B GC/MS system. A 6 ft x 2 mm I.D. glass column packed with 1.5 % OV-17/1.95 % QF-1 on 80/100 mesh Gas Chrom Q was used. Gas chromatographic operating conditions were: oven temperature - 185°C, inlet temperature - 225°C, helium carrier flow - 25 ml/min. Mass spectrometer operating parameters were as follows: electron multiplier voltage - 2800, scan speed - 4 samples/0.1 amu, mass peak detection threshold - 5000, gc peak detection threshold (triggered on total abundance) - 3000.

RESULTS AND DISCUSSION

Finding of Oxychlordane Residues

During the period 1975-1978, a total of 1,258 soil samples were collected and routinely analyzed for a variety of organochlorine and organophosphorus pesticides/pesticide metabolites (including oxychlordane) under the DAPMP. Of this number, 403 samples or 32 % of the total analyzed contained detectable residues of one or more products attributable to chlordane (i.e., technical chlordane, cis - chlordane, trans - chlordane, oxychlordane, heptachlor epoxide and heptachlor). Of the samples containing detectable residues attributable to chlordane, only 29 samples or 2.3 % of the total soil samples analyzed during 1975 - 1978

contained oxychlordane residues. On a year-by-year breakdown, 13 out of 697 samples analyzed in 1975 (1.9 %), 4 out of 272 samples analyzed in 1976 (1.5 %), 6 out of 130 samples analyzed in 1977 (4.6 %), and 6 out of 159 samples analyzed in 1978 (3.8 %) contained residues of oxychlordane. Soil samples representing eight geographically dispersed US Army installations (i.e., Ft Benning, GA; Ft Sam Houston, TX; Ft Dix, NJ; Ft Polk, LA; Ft Devens, MA; Ft Jackson, SC; Ft Lewis, WA; and Ft Knox, KY) and six different land use stratifications (i.e., pesticide storage area, residential area, cantonment area, recreational area, golf course area, and range/training area) were positive for oxychlordane. The majority (69 %) of the samples containing detectable residues of oxychlordane were from Ft Benning and Ft Sam Houston. Residues of at least one or more other chlordane associated products including technical chlordane, cis - chlordane, trans - chlordane, trans - nonachlor, heptachlor and heptachlor epoxide were found in all of the samples containing oxychlordane. Residues of heptachlor epoxide were found in more than half (59 %) of the samples positive for oxychlordane. It is interesting to note that in 9 out of the 10 soil samples containing oxychlordane, cis - chlordane and trans - chlordane the residue levels of cis - chlordane were greater than twice the levels of trans - chlordane. This finding provides evidence that formation of oxychlordane proceeded primarily via the trans isomer. Quantitatively, overall residue levels of oxychlordane found in the soil samples ranged from 0.008-0.11 ppm. The small percentage of occurrences of oxychlordane residues in relation to the total number of analyzed DAPMP soil samples, combined with the relatively low overall residue values found, may serve to explain why oxychlordane has not been previously detected in soil. Six of the soil samples containing residues of oxychlordane, representing three of the eight positive US Army installations, were selected for gas chromatographic or GC/MS confirmation studies. Descriptive information pertaining to these six samples is presented in Table 1.

TABLE 1. Descriptive Information on Soil Samples Selected for Oxychlordane Confirmation.

USAEHA Sample Number	Installation	Land Use Stratification	Collection Year	Oxychlordane Residues (ppm)
01253	Ft Dix	Golf Course	1975	0.01
01581	Ft Sam Houston	Recreational	1975	0.10
02544	Ft Sam Houston	Recreational	1976	0.07
03843	Ft Sam Houston	Recreational	1978	0.10
01925	Ft Benning	Pesticide Storage	1975	0.06
02027	Ft Benning	Recreational	1975	0.01

Confirmation of Oxychlordane Residues by Gas Chromatography.

Five of the soil samples listed in Table 1 (i.e., USAEHA Sample Nos. 01253, 01581, 02544, 01925 and 02027) were confirmed for

oxychlordane residues using alternate column gas chromatography. Sample chromatographic peaks which corresponded on the basic working column (i.e., 1.5 % OV-17/1.95 % QF-1 or 1.5 % SP 2250/1.95 % SP-2401) to oxychlordane and other chlordane associated products were further analyzed using three alternate columns (i.e., 4 % SE-30/6 % QF-1, 5 % OV-210, and 3 % OV-1). In Tables 2-5, sample retention time data (relative to aldrin) is given for oxychlordane and other quantifiable chlordane associated products) on the four chromatographic columns utilized. The data presented in these tables indicate that on all four columns the chromatographic behavior of oxychlordane (and other chlordane associated products) in all five samples corresponded very well with known reference standards.

TABLE 2. Retention Time Data (Relative to Aldrin) for Oxychlordane and Associated Chlordane Products - 1.5% OV-17/ 1.95% QF-1 (or 1.5% SP 2250/1.95% SP2401) Column[a]

Compound	Reference Standard	RRT Data (Aldrin = 1.00) Samples				
		01253	01925[b]	02027	01581[b]	02544[b]
oxychlordane	1.36	1.36	1.36	1.36	1.36	1.36
heptachlor epoxide	1.50	1.50	1.50	1.50	1.50	1.50
cis-chlordane	1.66	1.66	1.66	ND[c]	1.66	1.66
trans-chlordane	1.81	1.81	1.81	ND	1.81	1.81
trans-nonachlor	1.72	ND	ND	1.69	ND	ND

[a] Gas Chromatographic Analysis Conditions: Oven temperature - 200°C; Ar/Me carrier flow - 50 ml/min.
[b] These samples also contained quantifiable amounts of heptachlor.
[c] Below quantifiable limits in sample.

TABLE 3. Retention Time Data (Relative to Aldrin) For Oxychlordane and Associated Chlordane Products - 4% SE-30/6% QF-1 Column[a]

Compound	Reference Standard	RRT Data (Aldrin = 1.00) Samples				
		01253	01925	02027	01581	02544
oxychlordane	1.34	1.34	1.35	1.35	1.35	1.35
heptachlor epoxide	1.44	1.44	1.45	1.44	1.44	1.44
cis-chlordane	1.51	b	1.52	ND	1.51	1.51
trans-chlordane	1.66	1.66	1.66	ND	1.67	1.67
trans-nonachlor	1.66	ND	ND	1.66	ND	ND

[a] Gas Chromatographic Analysis Conditions: Oven temperature - 205°C; Ar/Me carrier flow - 70 ml/min.
[b] RRT for cis-chlordane in this sample could not be determined due to interference from large heptachlor epoxide peak.

TABLE 4. Retention Time Data (Relative to Aldrin) For Oxychlordane and Associated Chlordane Products - 5% OV-210 Column[a]

Compound	Reference Standard	RRT Data (Aldrin = 1.00) Samples				
		01253	01925	02027	01581	02544
oxychlordane	1.50	1.50	1.50	1.50	1.50	1.50
heptachlor epoxide	1.77	1.77	[c]	1.77	1.76	1.77
cis-chlordane	1.72	[b]	1.74	ND	[b]	[b]
trans-chlordane	1.87	[b]	1.87	ND	[b]	[b]
trans-nonachlor	1.73	ND	ND	[b]	ND	ND

[a] Gas Chromatographic Analysis Conditions: Oven temperature - 180°C; Ar/Me carrier flow - 55 ml/min.
[b] RRT for cis and trans-chlordane in Sample Numbers-01253, 01581 and 02544 and for trans-nonachlor in Sample No. 02027 could not be determined due to interference from large heptachlor epoxide peak.
[c] RRT for heptachlor epoxide in this sample could not be determined due to interference from large cis-chlordane peak.

TABLE 5. Retention Time Data (Relative to Aldrin) For Oxychlordane and Associated Chlordane products - 3% OV-1 Column[a]

Compound	Reference Standard	RRT Data (Aldrin = 1.00) Samples				
		01253	01925	02027	01581	02544
oxychlordane	1.29	[b]	[b]	[b]	[b]	[b]
heptachlor epoxide	1.27	1.27	1.26	1.27	1.26	1.26
cis-chlordane	1.47	1.47	1.46	ND	1.46	1.46
trans-chlordane	1.65	1.65	1.64	ND	1.64	1.64
trans-nonachlor	1.75	ND	ND	1.75	ND	ND

[a] Gas Chromatographic Analysis Conditions: Oven temperature - 180°C, Ar/Me carrier flow - 70 ml/min.
[b] Oxychlordane peak in all five samples co-chromatographed with larger heptachlor epoxide peak.

Confirmation of Oxychlordane Residues by GC/MS.

One of the soil samples listed in Table 1 (i.e., USAEHA Sample No. 03843) was confirmed for oxychlordane residues using GC/MS. This sample (collected in 1978) was from the same sampling site as Sample No. 01581 which was collected three years earlier. GC/MS spectral analysis at 70 eV of both an oxychlordane reference standard and the ion chromatographic peak corresponding to

oxychlordane in Sample No. 03843 revealed identical spectra. The standard and sample both exhibited relatively weak molecular ions at m/e 420, and fragmentation produced major daughter ions of m/e 385, m/e 235, m/e 185 (base peak) m/e 149, and m/e 115 in both standard and sample. These spectra were comparable to those obtained by LAWRENCE et al. (1970) and BIROS and ENOS (1973), except that their spectra snowed the base peak at m/e 115 instead of m/e 185 and they also noted a major daughter ion at m/e 270 which our spectra did not show in either standard or sample.

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