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Organochlorine Pesticide Residues in Grain Storages of New South Wales

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One of the most problematic groups of pesticide is the organochlorine (or chlorinated hydrocarbon) insecticides. This particular class of pesticide has been used extensively for a wide range of agricultural and pest control purposes over many years. All pesticides in common use produce residues that persist for noticeable periods. The organochlorine insecticides are very stable substances which are only slowly degraded in the environment and can survive 10 to 15 years or more depending on soil, plant and weather conditions (Moriarty 1975; Edwards 1973; Fukuto & Sims 1971).

The use of organochlorine pesticides (OCPs) has been banned in many countries, but in Australia only DDT and its derivatives have been totally banned to date, the other organochlorine pesticides, dieldrin, heptachlor, aldrin and chlordane, have been deregistered for any agricultural or horticultural use but may still be purchased and used by licensed pest control officers (Agricultural Memo 1987). In recent times (May 1987) organochlorine pesticides have been found in Australia's export produce. Following the detection of these pesticide residues above the MRL (maximum residue level) in export produce an increased level of testing has been introduced.

This work forms part of an extensive overall screening programme which set out to ensure organochlorine pesticides did not find their way into further produce.

In the method described here swab samples of grain storage areas were screened for residues of the more persistent organochlorine pesticides and their breakdown products.

MATERIALS AND METHODS

All solvents and reagents used were pesticide grade or equivalent.

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Analytical standards of organochlorine pesticides were obtained from the Environmental Protection Agency (U.S.). Standard stock solutions (100 µg/mL) were prepared in n-hexane and kept refrigerated.

Grain storage areas on properties throughout the State of New South Wales were sampled by regional inspectors in the period of September 1987 to January 1988. At each site, a sampling area of 15 cm by 15 cm was swabbed in 3 replicates with hexane soaked cotton wool swabs. After collection the swab specimens were placed in screw-top glass jars (with an aluminium foil lid insert) and transported to the laboratory where they were analysed by gas liquid chromatography.

For residue analysis, the samples (each consisting of 3-6 swabs) were transferred from each respective sample container using hexane-washed forceps to a glass stoppered 250 mL conical flask. Hexane (100 mL) was added, using a 10-15 mL portion to rinse out the sample container. The glass stoppered flasks were then mechanically shaken on a Denley reciprocal shaker for 60 minutes. The extracts were subsequently filtered through Whatman #41 filter papers, and the filtrates diluted 1:10 prior to injection onto a GLC column for screening by electron capture (EC) detection.

Due to the mixture of pesticides used in some grain storage areas, especially fenitrothion and other EC sensitive organophosphorus compounds e.g. dichlorvos, a "micro" clean-up step (based on the modified method of Cole *et al* 1967, and Ahmad and Marolt 1986) was introduced.

The "micro" clean-up procedure was performed by column chromatography on partially deactivated alumina. Alumina (BDH Chemicals, Activity II) was prepared by heating it up to 550°C for 4 hours, followed by the addition of 5% by weight of distilled water. The deactivated alumina was added to a disposable Pasteur glass pipette (containing a small piece of cotton wool to hold the packing in place) to a depth of 1.5 cm and overlaid with 0.5 cm anhydrous sodium sulphate. An appropriate aliquot of the OCP extract (1.0 mL of filtrate) was quantitatively transferred to the top of the prepacked Pasteur pipette column. The extracts were eluted with 10 mL hexane (containing 4% acetone) into a 10 mL volumetric flask. After diluting to volume, the eluate was subsequently used for screening for OCPs.

The OCP gas chromatographic analyses were performed on a Varian Aerograph Model 3700 gas chromatograph, equipped with a Ni-63 electron capture detector and a 1.5 m by 2.0 mm i.d. glass column packed with 7% OV-210 and 3.5% OV-101 on Chromsorb Q (100-120 mesh). A second chromatographic column, 2 m by 2.0 mm i.d. glass column packed with 5% SE-30 on Chromsorb W HP (100-120 mesh) was utilised to confirm the peak identities. Injector, column and detector temperatures were set at 200, 170 and 300°C respectively. Nitrogen was used as carrier gas at a flow rate of 35 mL/min. Quantitations were performed with a 3390 A Hewlett-Packard integrator.

RESULTS AND DISCUSSION

Figure 1 shows the location of regions throughout the State of New South Wales involved in the screening for OCP residues in grain storages.

In all, grain storages on 378 properties (representing over 1200 grain storages) were tested for OCPs throughout New South Wales. The main cereal producers are the regions (2) (New England, Hunter and Metropolitan), (5) (Murray and Riverina) which produce both summer and winter crops; and the regions (3) (Orana and Far Western), (4) (Central West, South East and Illawarra) where mainly winter crops are produced. Region (1) (North Coast area) was not included in this particular survey as it is not a cereal producing region and farm storage is limited.

Table 1 shows the regional breakdown of testing, whilst the number of occurrences (percentage for the region) is given in Table (2).

For comparative purposes, the OCP results were calculated in terms of microgrammes of OCP per square metre (µg/sq.m). A base level of 20 µg/sq metre was determined as the maximum acceptable OCP level in which grain could be stored for extended periods of time and still remain under the MRL (maximum residue limit) for a given organochlorine pesticide.

The ubiquitous nature of the more persistent OCPs is evident from Table 1, with 34% of the samples indicating positive contamination, of which 20.4% were over the acceptable limit necessitating clean-up operations prior to grain storage.

Dieldrin, lindane (gamma-BHC) and DDT were the main OCPs present in swab samples, followed by chlordane, heptachlor and aldrin. The slight differences in the four regions examined in the grain storage survey seem to be related to the differing cropping techniques of the southern regions to those used in the northern regions and to the previous application of organochlorine insecticides. Regions 3 and 4 appeared to have had the greatest usage of lindane and dieldrin respectively (as indicated by the number of occurrences (% for region) which were significantly higher in comparison to regions 2 and 5 (Table 2).

Lindane and dieldrin have been used as effective seed dressings against the attack of soil insects such as the wheat bulb larvae (Way 1959; Lord *et al* 1967; Griffiths 1976; Snelson, 1987) and would account for their presence in these areas. The other OCPs aldrin and heptachlor have been similarly used during the 1960s and 1970s but were withdrawn during the early 1980s. The widespread usage of DDT and its prolonged persistence in the environment however (Moriarty 1975) makes it difficult to be sure of the origin of these residues.

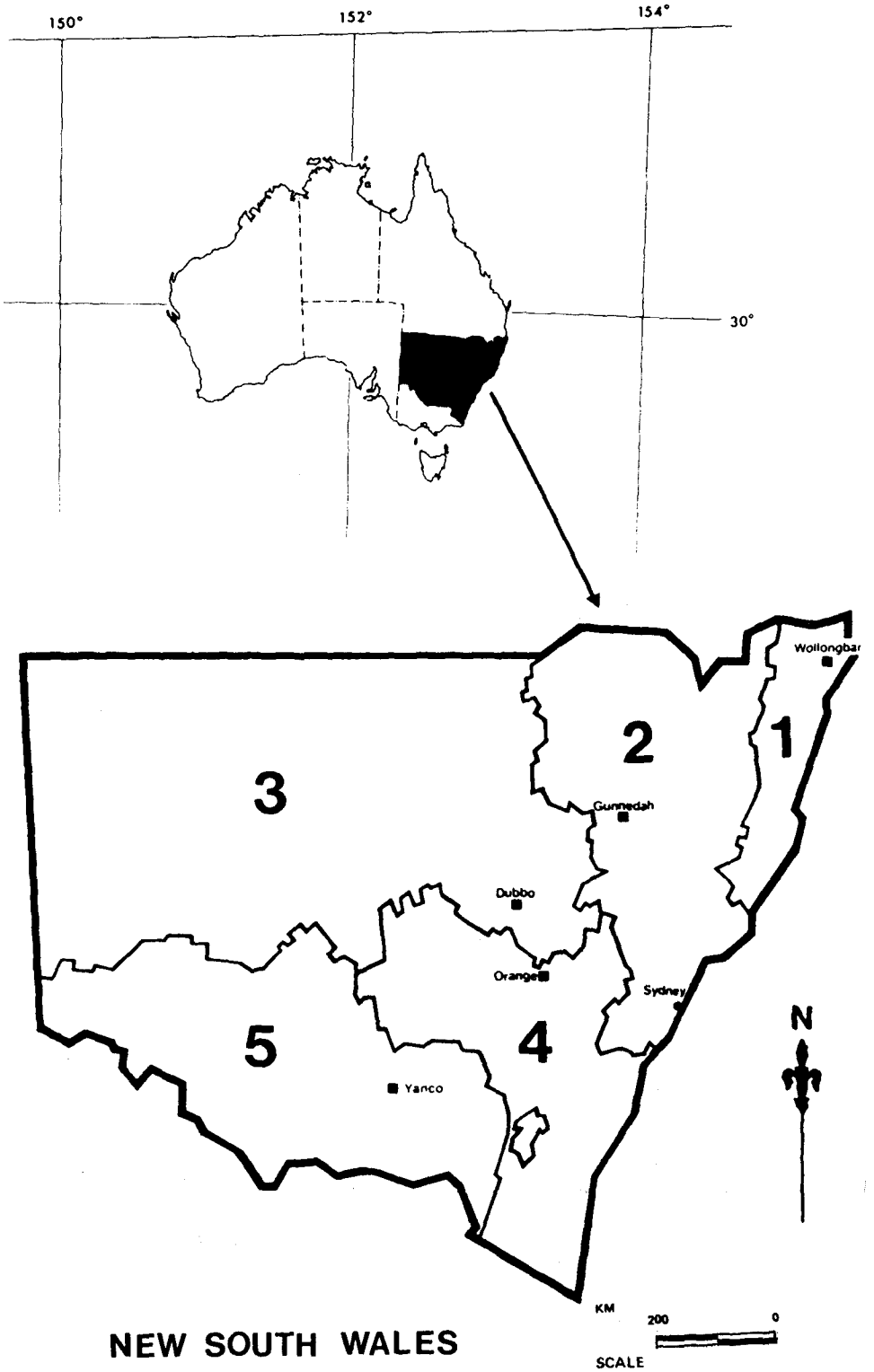

Figure 1. Location of the regions sampled in New South Wales.

Table 1. Regional Breakdown of Testing.

	Samples taken	Samples containing organochlorines	Samples above limit (> 20 µg/sq m.)
Region 2	844	259 (30.7%)	170 (20.1%)
Region 3	156	58 (37.2%)	15 (9.6%)
Region 4	291	106 (36.4%)	59 (20.3%)
Region 5	179	78 (43.5%)	56 (31.3%)
	1470	501 (34.1%)	300 (20.4%)

Table 2. Number of Occurrences (% for Region)

Organochlorine* Pesticide	Region 2 (North East)	Region 3 (South East)	Region 4 (North West)	Region 5 (South West)
Aldrin	317 (14.98%)	28 (13.66%)	76 (12.56%)	26 (12.26%)
Chlordane	315 (14.89%)	37 (18.05%)	108 (17.85%)	26 (12.26%)
DDT	346 (16.35%)	36 (17.56%)	92 (15.21%)	39 (18.40%)
Dieldrin	421 (19.90%)	37 (18.05%)	109 (18.02%)	65 (30.66%)
Lindane	348 (16.45%)	36 (17.56%)	136 (22.48%)	27 (12.74%)
Heptachlor	369 (17.44%)	31 (15.12%)	84 (13.88%)	29 (13.68%)
Totals	2116	205	605	212

* Values include break-down products (e.g. DDE is reported with DDT values).

All six persistent OCPs were found throughout the regions examined, indicating widespread previous usage of these pesticides. As a result of this survey and the subsequent clean-up operations of contaminated grain storage areas, positive steps have been made to ensure that the quality of export produce is maintained.

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REFERENCES

Agricultural Memo for the Farmer, September 1987 Western Australian Department of Agriculture

Ahmad N and Marolt RS (1986) One-Step Extraction and Cleanup Procedure for Determination of *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE in Fish. J Assoc Off Anal Chem 69(4):581-586

Cole I, Barry D, Frear DEH, Bradford A (1967) DDT Levels in Fish, Streams, Stream Sediments, and Soil Before and After DDT Aerial Spray Application for Fall Cankerworm in Northern Pennsylvania. Bull Environ Contam Toxicol 2:127-146

Edwards CA (1973) Environmental Pollution by Pesticides. Plenum Press, London

Fukuto TR, Sims JJ (1971) Metabolism of insecticides and fungicides. In: White-Stevens R (ed) Pesticides in the Environment, vol. 1 Part 1, Dekker, New York, p 145

Griffiths DC, Jeffs KA, Scott GC, Maskell FE, Roberts PF (1976) Relationships between control of wheat bulb fly (*Leptohylemyia coarctata* (Fall.) and amounts of dieldrin, carbophenthion and chlorfenvinphos on treated seed. Plant Pathol 25:1-12.

Lord KA, Scott GC, Jeffs KA, Griffiths DC, Maskell FE (1967) Persistence and distribution of insecticidal seed-dressings for control of the wheat bulb fly, *Leptohylemyia coartctata*. Ann Appl Biol 60:173-180

Moriarty F (1975) Organochlorine Insecticides : Persistent Organic Pollutants. Academic Press, New York

Snelson JT (1987) Grain Protectants. ACIAR Monograph Series, Canberra

Way MJ (1959) Experiments on the mode of action of insecticidal seed-dressings, especially against *Leptohylemyia coarctata* Fall; Muscidae, the Wheat Bulb fly. Ann Appl Biol 47:783-801

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