

Mapping the Distribution of DDT Residues as DDE in the Soils of the Irrigated Regions of Northern New South Wales, Australia Using ELISA and GIS

H. M. SHIVARAMAIAH,[†] I. O. A. ODEH, IVAN R. KENNEDY,* AND JOHN H. SKERRITT[‡]

Australian Cotton Cooperative Research Centre, Department of Agricultural Chemistry and Soil Science, The University of Sydney, NSW 2006, Australia

An enzyme-linked immunosorbent assay (ELISA) specific for DDE [1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene] has been used to map DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane] residues in the top 10 cm of soil in three river valleys of northern New South Wales, Australia. Despite being almost 20 years since DDT was last applied for cotton growing in these areas, the relationship between sites of greatest application and current residue levels was strong. DDE concentrations in the range 0–2 ppm were found, although most the 389 soil samples examined contained less than 0.2 ppm of DDE. Although some relationship between mode of land use and current residue levels was apparent, this varied from valley to valley and may have reflected different farming practices and times of application. The study demonstrates that the combination of ELISA and geographical information system (GIS) analysis provides an effective means of displaying levels of soil contamination by a pesticide and the possible need for remediation.

KEYWORDS: ELISA; DDT; DDE; pesticide residues; GIS; cotton; soils

INTRODUCTION

The insecticide DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane] and several of its breakdown products are persistent organochlorine molecules. DDT has been applied in large quantities to control pests for many decades (1) and proved economical and versatile for use in both agricultural and public health applications. Indiscriminate use and its long persistence in soil has resulted in extensive soil contamination with DDT and its metabolites. Although it is recognized as one of the more persistent organochlorines, there are comparatively few data on levels of soil contamination at long periods after application (2, 3). Detection of DDT and its metabolites in milk and meat, together with insect resistance, led to many countries restricting and eventually banning the use of DDT in the 1980s and 1990s, although some developing countries such as India and Mexico have continued to use DDT, especially for public health applications such as malaria control (4). Despite not being used by many countries for some years, the long-term persistence of DDT and its metabolites in soil (5–7) as DDD [1,1-dichloro-2,2-bis(4-chlorophenyl)ethane] and DDE [1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene] has been reported. DDT was used very extensively in cotton-growing areas of Australia such as the Namoi and Gwydir valleys until being banned in 1982. The

main residue observed after several years in these soils is DDE, although at the more heavily contaminated cattle-dip sites DDT itself is the major residue (8, 9) and DDD is also found (10). The conversion of DDT to DDD is favored by anaerobic conditions such as those encountered with soils that are periodically or permanently flooded (11). Usually DDT and other organochlorine pesticides are quantified by gas chromatography methods involving solvent extraction cleanup and electron capture detection. Although these methods are efficient, they require cleanup of the samples and also utilize large volumes of solvents. Alternative methods are therefore necessary to overcome these problems.

In this regard, an enzyme-linked immunosorbent assay (ELISA) method has been developed (12, 13). This method is used in this study to monitor DDT/DDE residues in soil samples collected from the Macintyre, Namoi, and Gwydir valleys of northern New South Wales, Australia. A field survey of three valleys for DDE residues in a range of soil types and land uses was carried out to determine the current extent of contamination with DDE and to examine whether there is a need for remediation.

MATERIALS AND METHODS

Soil Sample Collection. Soil samples for this study were collected from the Macintyre, Gwydir, and Namoi valleys in New South Wales, Australia (Figure 1). Development of the Australian cotton industry commenced in the 1960s in the Namoi Valley near Wee Waa, and spread to the Gwydir and Macintyre Valleys in subsequent decades.

* Corresponding author. Tel: 612 9351 3546. Fax: 612 9351 5108. E-mail: i.kennedy@acss.usyd.edu.au.

[†] Present address: Central Food Technology Research Institute, Mysore, Karnataka, 570013 India.

[‡] Present address: Australian Centre for International Agricultural Research, Canberra ACT 2601, Australia.

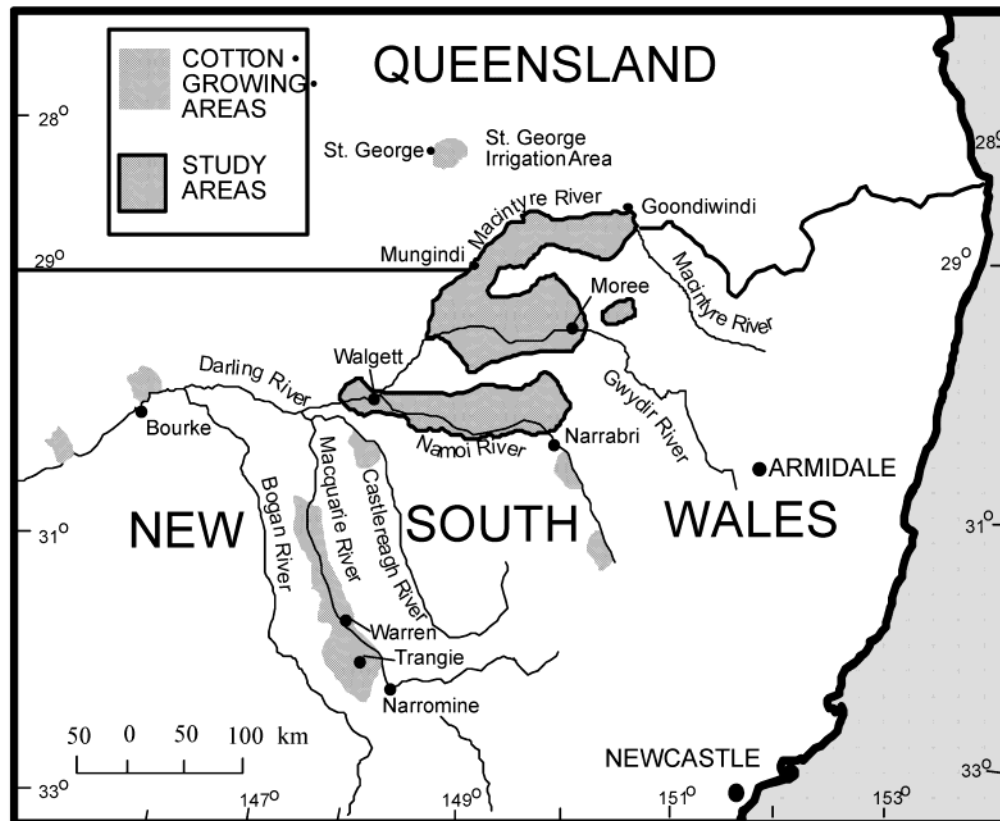


Figure 1. Study locations in NSW, Australia, showing the sample sites in the three valleys.

The dominant soil types are Vertisols (14) characterized by a large proportion of cracking clay. The Vertisols vary from gray to black and brown clays, interspersed with red and yellow brown earths (Alfisols). Sample collection sites were randomly located based on a stratified simple random scheme (15) with 120 sites in the Macintyre valley, 151 in the Gwydir valley, and 118 in the Namoi valley (Figure 1). The scheme allowed for preferential sampling in such a way that the sites covered a variety of land-use types, ranging from cultivated to stock routes, native pastures, and woodland. Soil samples from each valley were taken from four depths (0–10, 10–20, 20–30, and 60–70 cm). Each sample was sealed in a polythene bag and transported to the laboratory for further analysis. The soil samples were air-dried and passed through 2-mm sieve and stored in a cool room until solvent extraction. Only samples from 0–10 and 10–20 cm depths were used for this study.

Extraction of Pesticide Residue from Soil. For extraction of DDT and DDE residues for ELISA, 10 g of soil was weighed into a 100-mL glass jar and 25 mL of 90% methanol in water was added. The jars were shaken for 1 h and allowed to stand overnight as the particles settled. The supernatant was then collected and diluted to 1:20 in 0.1% of fish gelatin in PBS (FG-PBS) for analysis by immunoassay. The efficiency of this extraction method had previously been validated through an international collaborative trial (13). For instrumental analysis, 50 g of soil was weighed into a stoppered conical flask and 150 mL of 90% methanol diluted with water was added. The flasks were shaken overnight and the extract was filtered through paper (Whatman, Maidstone, Kent, UK) containing 2 g of anhydrous sodium sulfate. The methanol solvent in the filtrate was exchanged with hexane (20 mL) and concentrated to 5 mL using a Kuderna–Danish apparatus and then chromatographed on a Florisil column. The column was eluted with 150 mL of hexane/diethyl ether (3:1). The first 10 mL of eluate was discarded, and the remainder was concentrated to 5 mL. Gas–liquid chromatographic (GLC) analysis was performed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a ^{63}Ni electron capture detector.

ELISA. Bovine serum albumin (BSA) and horseradish peroxidase (HRP) were purchased from Boehringer-Mannheim, Germany. Fish skin

gelatin (FG) and Tween 20 were obtained from Sigma Chemicals, St. Louis, MO. Methanol (analytical reagent grade) was obtained from Ajax Chemicals, Clyde, NSW, Australia. Maxicorp polystyrene 96-microwell plates were purchased from Nunc, Roskilde, Denmark. Standard curves were prepared using DDE (100 ppm) stock solution in methanol. From this stock, a 1000 ppb standard was prepared by dilution in 0.1% FG-PBS and then serially diluted using borosilicate glass tubes to obtain 200, 40, 20, 4, 2, and 0 $\mu\text{g/L}$ (ppb) for the standard curve. Standard curves for soil analysis were prepared using an extract of soil diluted 1/20 in 0.1% FG-PBS. The Vertisol soil sample used for spiking was established as free from organochlorine pesticide residue by solvent extraction followed by gas–liquid chromatographic (GLC) analysis as described below. Subsamples (10 g) of this soil were distributed into glass jars (with aluminum-foil-lined caps) and spiked with 0, 0.5, 1, 2, 5, and 10 mg/kg (ppm) concentrations of DDT.

After initial optimization of assay conditions, a simple treatment with alkali was used to dehydrochlorinate DDT. KOH (100 μL , 10% (w/v)) was added to 2 mL of pesticide standard or sample, mixed briefly, and left at room temperature for 60 min. To achieve optimal conversion conditions, the effects of solvents, sample matrix, temperature, and time of incubation were studied. Sensitivity of the assay (with and without alkali treatment) was determined as the concentration of pesticide causing 50% inhibition of color development (IC₅₀) relative to a pesticide free control.

The DDE assay method (12) used an immunogen which included all elements of the DDE structure except that one of the *p*-chloro groups was replaced by β -alanine carboxamide for coupling to carrier proteins. Antibodies were diluted in 50 mM carbonate buffer (10 $\mu\text{g/mL}$) and were coated at 100 μL per well overnight at 20 °C. The microwells were washed twice with PBS (50 mM sodium phosphate/0.9% NaCl, pH 7.2) containing 0.05% (v/v) Tween 20 (PBS/T) and then blocked with 150 μL of BSA/PBS (1% bovine serum albumin) in PBS (16). A 100- μL aliquot of DDE standard or sample, followed by 100 μL of peroxidase conjugate diluted in PBS containing 0.5% (w/v) fish skin gelatin (Sigma), was incubated for 1 h at 20 °C. The plates were washed with water five times, tapped dry on a paper towel, and 150 μL of a substrate solution of 97 parts hydrogen peroxide substrate/3 parts

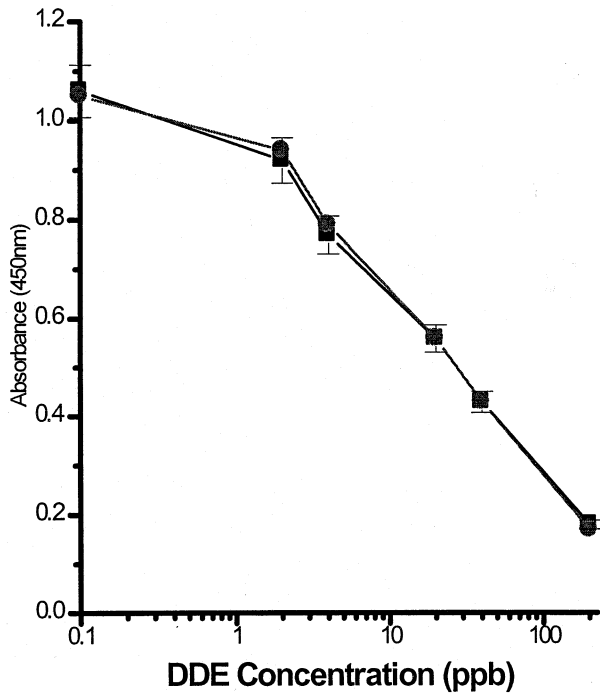


Figure 2. Standard curve for ELISA of DDE in methanol and organochlorine-free soil extracts diluted 1:20 in FG-PBS.

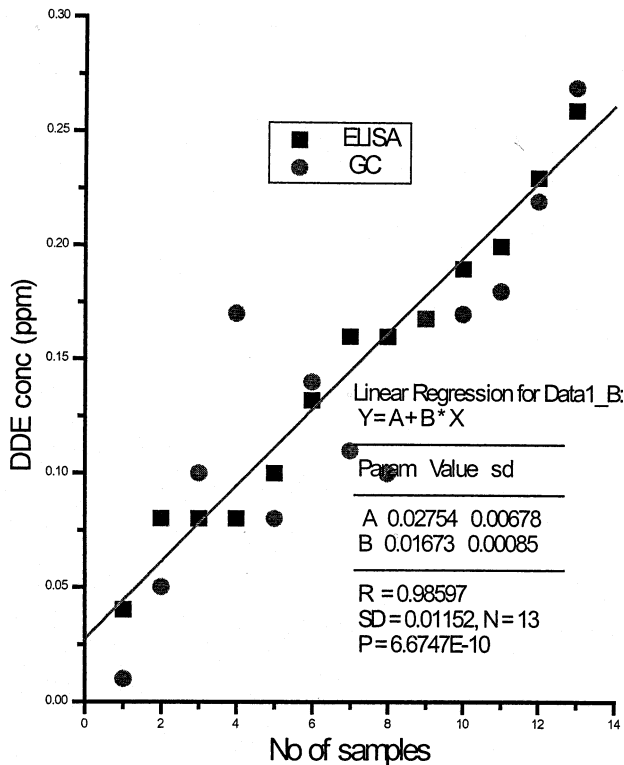


Figure 3. Effect of alkali treatment on detection of DDT and DDE by ELISA measured as DDE. Inhibition curves of DDT and DDE after incubation with KOH for 60 min.

chromogen (3,3',5,5'-tetramethylbenzidine/hydrogen peroxide in acetate buffer, pH 5.5) was added, and the plates were incubated 30 min at 20 °C. Color development was stopped by adding 50 μ L of 1.25 M sulfuric acid, and the color intensity was read at 450 nm. For control and blanks, distilled water and solvent were used. The IC₅₀, minimum detectable limit and percent recovery of DDE were calculated from the standard graph.

Analysis of Soil Samples by ELISA. Standard curves in 90% methanol in water were compared using standard curves prepared in

Table 1. Recovery of DDE Spiked in Soil Using ELISA and GC Analysis

sample	DDE spike concentration (ppb)	concentration of DDE (ppb) recovered by ELISA method	concentration of DDE (ppb) recovered by GC method
1	500	280	275
2	1000	980	960
3	2000	1850	1800
4	5000	4780	4750
5	10000	9820	9780

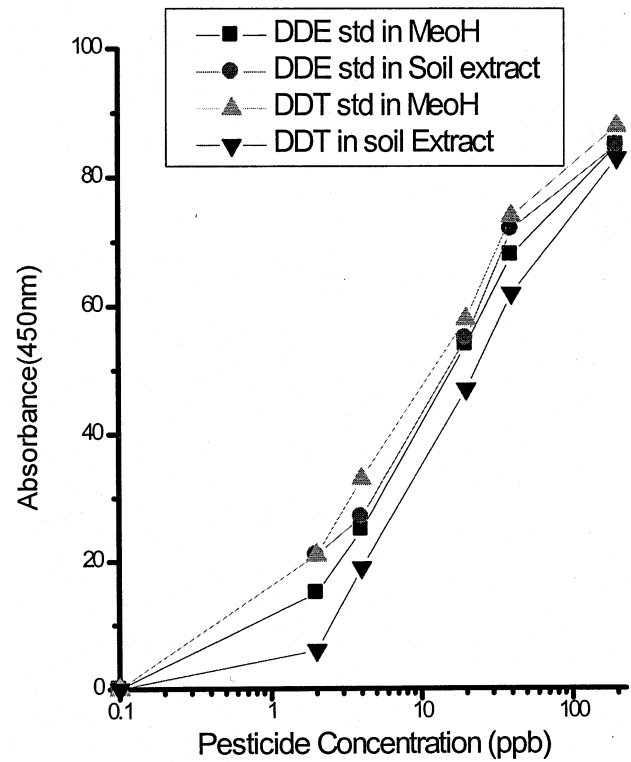


Figure 4. Correlation of the results of GC and ELISA analysis for DDE in soil samples from the Namoi Valley.

soil extract diluted to 1/20 in 0.1% FG-PBS. Comparisons were made between 90% methanol and soil extract. Soil extracts were spiked with DDT and equilibrated for 1–2 h before analysis. Both samples and the standards were treated with alkali for 60 min. Soils were extracted and analyzed with respect to standard curves prepared in methanol.

Spatial Analysis. The spatial analysis carried out here is based on the geostatistical theory of regionalized variable (17). The theory proposes that data values are a realization of a random function, which can be modeled by a variogram or a covariance function. A data set can be processed for semivariance through the computation of the spatial correlation or covariance between sample pairs at a certain distance apart. The plot of the semivariance and the corresponding distance or lag at which the pairs are separated produces the variogram. The variogram describes the magnitude, spatial scale, and general form of variation of a given variable (18). In the case of an intrinsic random function, the variogram provides the parameters for spatial interpolation or ordinary kriging of the random variable, which could be displayed in a geographical information system (GIS) map. This procedure was adopted for the DDE residue values for the three valleys. First, the semivariance of DDE residue in each of the valleys was computed by

$$\gamma(h) = \frac{1}{2m(h)} \sum_{i=1}^{m(h)} [z(x_i) - z(x_i - h)]^2$$

where $z(x_i)$ is the value of pesticide residue at location x , and $z(x_i - h)$

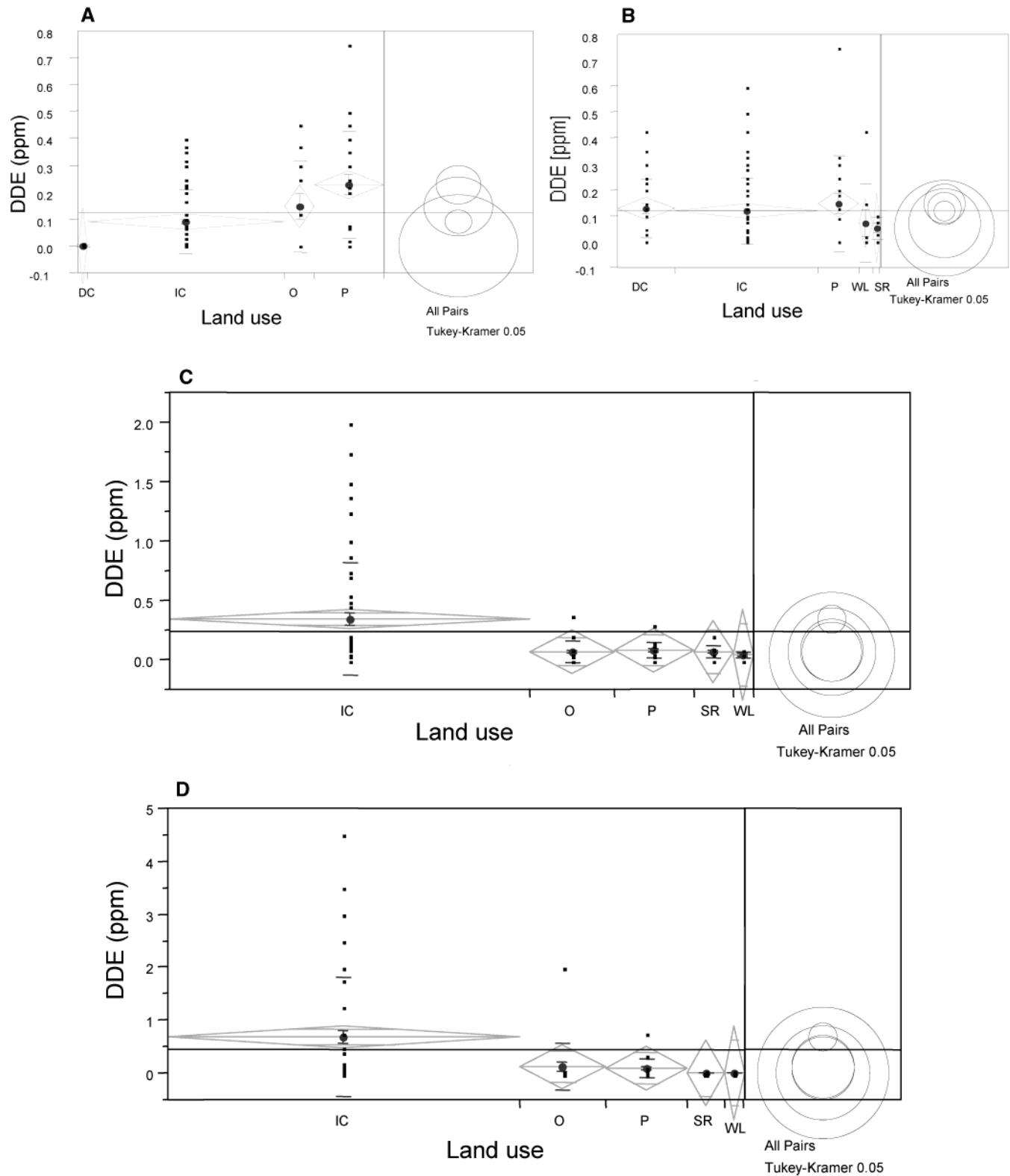


Figure 5. (A) One-way analysis of variance on topsoil (0–10 cm depth) DDE residues in relation to land use in the Macintyre Valley. Land uses: DC, dryland cotton; IC, irrigated cotton; O, other crops; P, pastures. (B) One-way analysis of variance on topsoil (0–10 cm depth) DDE residues in the Gwydir Valley. Land use key: DC, dryland cotton; IC, irrigated cotton; P, pastures; SR, stock routes; WL, woodland. (C) One-way analysis of variance on topsoil (0–10 cm depth) DDE concentration in the Namoi valley. (D) One-way analysis of variance on subsoil (10–20 cm depth) DDE concentration in the Namoi valley.

is the value of at location $x_i - h$. The lag h is the separating distance between the locations in a pair. Now there is m number of pairs for each lag h . As stated earlier, the semivariogram is the plot of $\gamma(h)$ versus the lag h . As h increases, the $\gamma(h)$ also increases until a certain value called the sill. The h at which the sill is reached is termed as the

range. The intercept of the plot at zero lag is termed the nugget. The latter is related to the error term in the spatial variance. The sill, the range, and the nugget as derived for DDE values for a given layer were used to interpolate the DDE residue values into a fine grid for display in a GIS map.

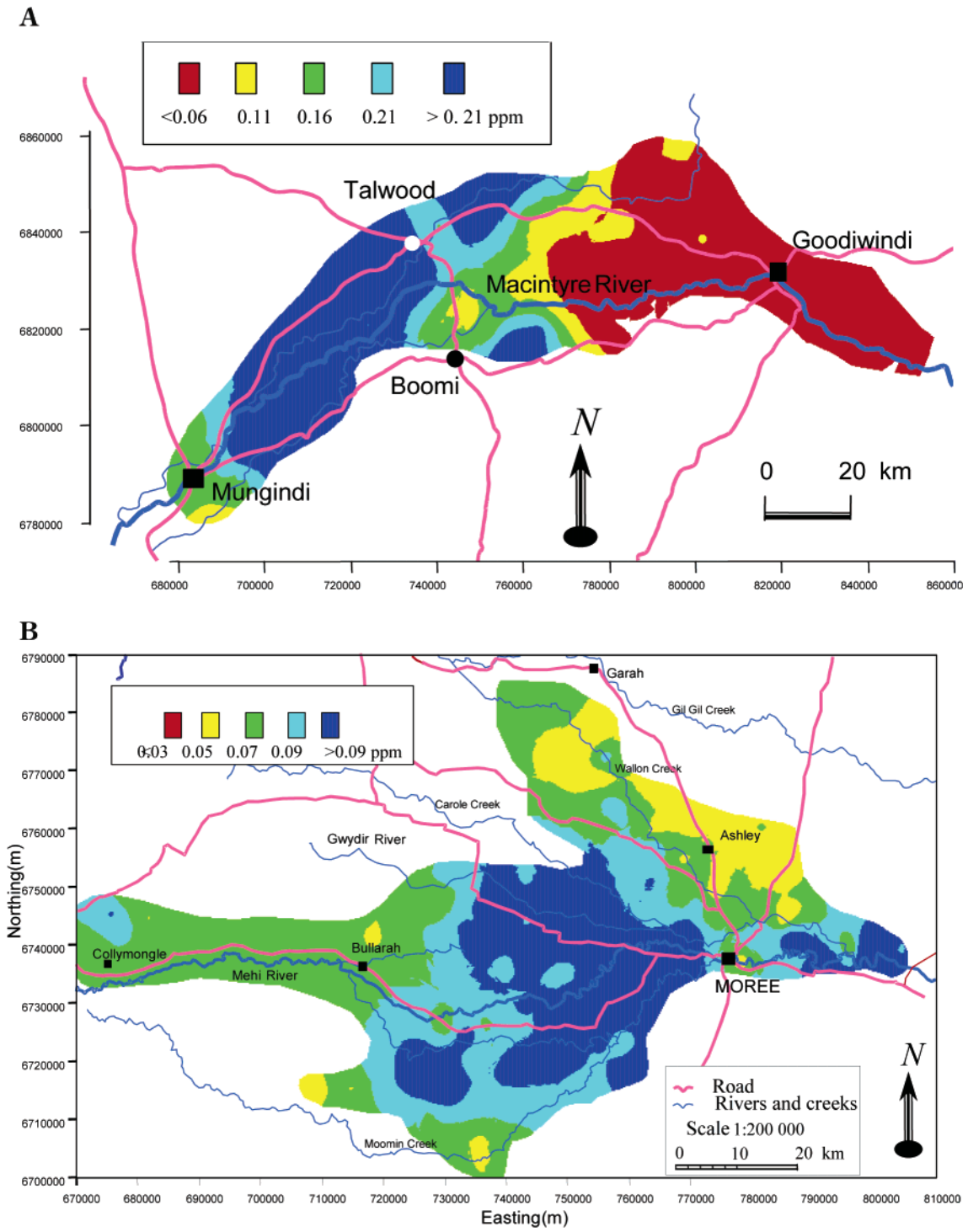


Figure 6. Distribution of topsoil (1–10 cm) DDE residues in (A) the Macintyre Valley, and (B) the Gwydir Valley.

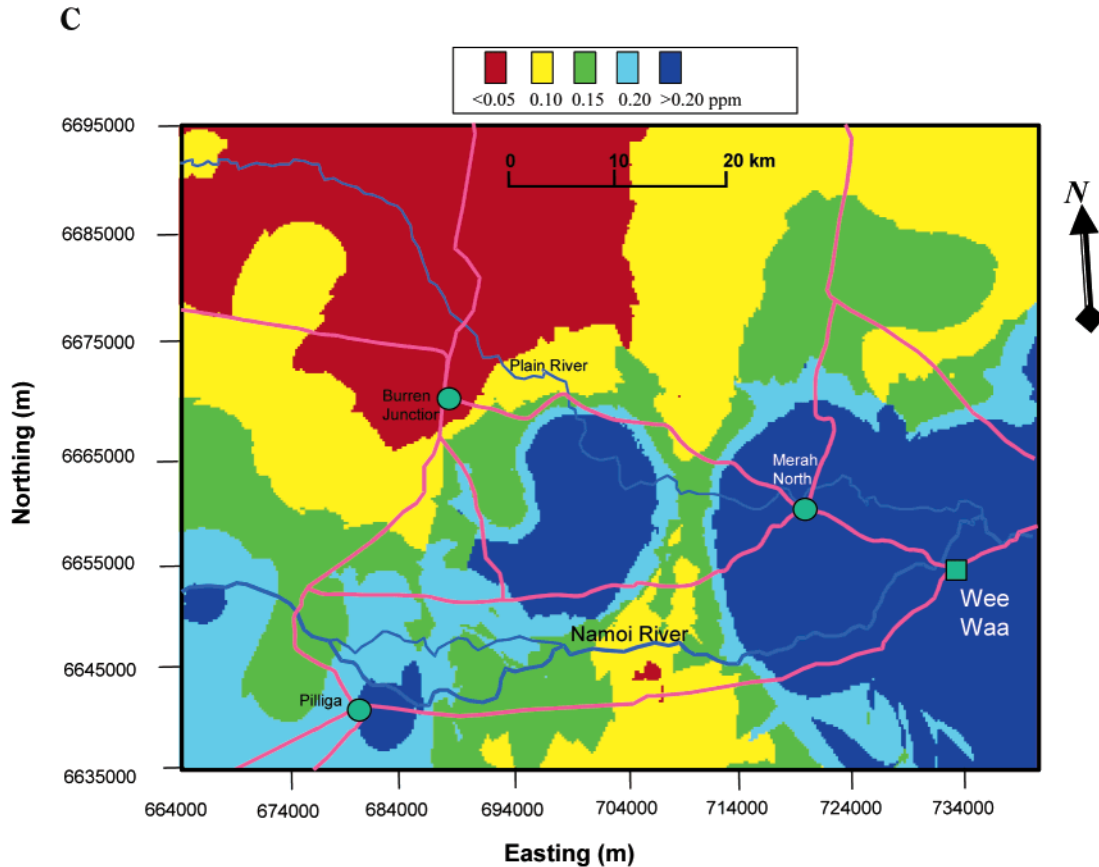


Figure 6. Continued. Distribution of topsoil (1–10 cm) DDE residues in (C) the Namoi Valley.

RESULTS AND DISCUSSION

The standard curve for DDE analysis by immunoassay is shown in **Figure 2**. Using standards of DDE dissolved in methanol, an IC_{50} of 20 ppb was obtained. Because the DDE was to be detected in soil extract, a standard curve was also prepared using pesticide-free soil extract. Initial experiments indicated that sample interference occurred at a 1:10 dilution of soil extracts, as indicated by elevated IC_{50} values for DDE. This could be overcome by diluting 1:20 in 0.1% FG-PBS, as the standard curve so-prepared was superimposable with the standard curve in soil extract.

GLC analysis revealed that DDE was the only detectable product of the alkali treatment, so residues were detected utilizing a DDE ELISA assay. The time course of conversion of DDT to DDE was followed by ELISA both in the methanol and in the soil extract (not shown). The conversion of DDT to DDE is almost complete after 1 h, as evident by the overlapping of the standard curves prepared in both solvent and soil extract (**Figure 3**). This result indicates that analysis for DDE and DDT plus DDE would have been possible if soil extracts were analyzed before and after alkali treatment. **Table 1** indicates that the recovery values calculated by the ELISA method were comparable to that of GLC values. For both methods, a recovery of more than 95% was achieved compared with the amount spiked. In the range from 0 to 10 ppm, DDE recoveries of greater than 95% were achieved. Immunoassay and gas chromatographic analyses of individual soil samples were conducted on different dates without the knowledge of the result obtained using the other method. Unlike immunoassay, where all samples can be analyzed within a few days of the time of field collection, gas chromatographic analysis can take weeks or even months to complete. Some initial discrepancies found for apparent DDE

content in larger samples between the two methods were later found to be due to variation in individual soil sub-samples. Therefore, for the data reported in this paper, both the GLC and immunoassay analyses were performed on the same 90% methanol extracts of soil samples.

A comparison of gas chromatography and immunoassay data for 15 soil samples collected from Namoi Valley at a 0–10-cm depth showed a good correlation with a regression coefficient of 0.95 (**Figure 4**). The recoveries of DDT residues in soil (analyzed as DDE by immunoassay) correlated well with the spiked concentrations (**Table 1**). The extraction method used for soil samples thus provided recoveries greater than 85%.

When the top layer (0–10 cm) of the soil was analyzed, DDE was detected in 65 samples out of 120 sites in the Macintyre Valley, 97 samples out of 151 sites from the Gwydir valley, and 94 samples out of 118 sites in the Namoi Valley. Detected concentrations ranged from 0.01 to 0.45 ppm in the Macintyre (**Figure 5A**), 0.01–0.75 ppm in the Gwydir (**Figure 5B**), and 0.025–2.00 ppm in the Namoi (**Figure 5C**) Valley soil samples. The soil samples analyzed were classified as dryland (rainfed) cotton (DC), irrigated cotton (IC), other crops (O), native pastures (P), stock routes (SR), and woodland (WL). The relative concentrations in the dryland cotton soil samples, on which DDT may never have been directly sprayed, was very low when compared to those in irrigated cotton soil samples, as shown by the results of one-way analysis of variance (**Figure 5A, B**) using the JMP program. The Tukey–Kramer test showing significant differences ($P < 0.05$) as nonoverlapping circles allows a comparison between soils sampled from different classes of sites to be compared, and only pasture and irrigated cotton showed a significant difference in these comparisons (**Figure 5A**). However, soils under pasture contained higher

levels of DDE residues (average 40 ppb) in the samples from Macintyre Valley. Higher concentrations were recorded in soil under crops other than cotton, such as legumes and cereals. Similarly, the relative concentration in irrigated-cotton soil samples was higher when compared to dryland cotton, but the highest concentration was recorded in native pastures in the vicinity of the cotton farms. Possibly, more extensive cultivation and consistent watering may result in a long-term remediation effect in cotton soils. This could result from accelerated biodegradation or by erosion in runoff.

These values for total DDT residues, mainly as DDE, are consistent with results obtained in independent studies on organochlorine residues in soils of the Namoi Valley using gas chromatographic procedures. DDT residue levels in the range of 0.4–3.6 ppm were observed in sediment samples taken from drains to the Namoi River from cotton farms before 1976 (9). A study conducted during the 1980s on behalf of the Australian Meat Research Corporation (19) found that the half-life for DDT in the Namoi Valley was about 3–4 years while that for DDE exceeded 15 years. Samples taken at a greater depth (10–20 cm) showed no DDE residues in the Macintyre Valley, but an increasing extent of contamination in the Namoi Valley (Figure 6D). These data are consistent with the relative periods of use of heavy applications of DDT in this valley. It is probable that the discovery of residues deeper in soils of the Namoi Valley reflects the cracking nature of Vertisols, allowing significant downward movement of residues carried on dry soil into the cracks.

Variograms indicating the distribution of DDE residues in the Macintyre, Gwydir, and Namoi Valleys are shown in Figure 7A–C, respectively. These suggest that a strong correlation exists between the original sites of application of DDT and the current levels of residues, because the areas with the highest levels of residues in each valley are also areas of intensive irrigation and cotton growing. The high levels observed near Wee Waa (Figure 6C) correspond to the earliest sites of Australian cotton-growing, where the greatest total amounts of DDT were deposited on soil as multiple seasonal applications for 20 years or more. This application likely ended in 1982 when other chemicals such as endosulfan were substituted for control of cotton insect pests (e.g., *Heliothis*) following the banning of DDT. In contrast to DDT, endosulfan is largely dissipated from soil from one season to the next, normally declining to less than 50 ppb in soils used for cotton growing, even as its more stable metabolite endosulfan sulfate (20). On the basis of this study, it is evident that DDE is plainly a much more persistent chemical than is DDT. It is consistent with other data in previous literature (21–22). The area around Pilliga (the Pilliga scrub) has low levels of residues consistent with little or no application, as it is an uncleared area, mainly consisting of native vegetation regrowth. The higher level in soil shown just east of Pilliga may well reflect applications for mosquito control to protect the local township. The variogram for the Macintyre suggests a strong contrast in past DDT usage when comparing the lower valley area (where residues were lower) with the upper. It would be of interest to determine whether there is evidence for such variation in actual practice. Given that the highest residue levels were observed where there was likely to have been the greatest use of DDT, this study provides an excellent example of validation of the ELISA technique as applied to DDE residues, and complements an earlier study by our group, of the dissipation of endosulfan residues in cotton farming in the same region of Australia (23). In both studies, the ability of immunoassay methods to analyze very large numbers of samples was

integral to obtaining detailed spatial and temporal data on the dissipation of residues.

ELISA has been shown to provide an effective technique for mapping DDT residues as DDE in the soils of three river valleys previously used for growing cotton. Although the persistence of DDE has been verified, indicating a half-life of more than 10 years in these soils, the levels observed do not represent a threat to human health, given the extremely tight binding of DDE to soil organic matter and its low volatility. Nevertheless, the DDE residues observed in soil do present a long-term environmental problem. It would be anticipated that biota, including birds that forage for food in this soil, will become contaminated at detectable levels as has been observed (24), particularly when bioconcentration factors are considered.

ABBREVIATIONS USED

DDT, 1,1,1-trichloro-2,2-bis(4-chlorophenyl ethane); ELISA, enzyme-linked immunosorbent assay; GIS, geographical information system; DDE, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene; DDD, 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane; BSA, bovine serum albumin; HRP, horseradish peroxidase; FG, fish skin gelatin; AR, analytical reagent; PBS, phosphate buffered saline; GLC, gas-liquid chromatography; IC₅₀, 50% inhibition of color development; DC, dryland cotton; IC, irrigated cotton; O, other crops; P, native pastures; SR, stock routes; WL, woodland.

LITERATURE CITED

- (1) Kausik, C. P. Persistence and metabolism of HCH and DDT in soil under subtropical conditions. *Soil Biol. Biochem.* **1991**, *23*, 131–134.
- (2) Samuel, T.; Agarwal, H. C.; Pillai, M. K. K. Persistence and binding of DDT and gamma HCH in a sandy loam soil under field conditions in Delhi, India. *Pestic. Sci.* **1988**, *22*, 1–15.
- (3) Martijn, A.; Bakker, H.; Schreuder, R. H. Soil persistence of DDT, dieldrin and lindane over a long period. *Bull. Environ. Contamin. Toxicol.* **1993**, *51*, 178–184.
- (4) Boul, H. L. DDT residues in the environment—a review with a New Zealand perspective. *N. Z. J. Agric. Res.* **1995**, *38*, 257–277.
- (5) Guenzi, D.; Beard, W. E. Anaerobic biodegradation of DDT to DDD in soil. *Science* **1967**, *156*, 1116–1117.
- (6) Agarwal, H. C.; Singh, D. K.; Sharma, D. B. Persistence and binding of *p,p'*-DDE in soil. *J. Environ. Sci. Health* **1994**, *29*, 87–96.
- (7) Agarwal, H. C.; Singh, D. K. Dissipation of organochlorines in northern Indian soils. In *Seeking Agricultural Produce Free of Pesticide Residues*, ACIAR No 85; Kennedy, I. R., Skerritt, J. H., Johnson, G. I., Highley, E. P., Eds.; ACIAR: Canberra, Australia, 1998; pp 156–170.
- (8) McDougall, K. W.; Singh, G.; Harris, C. R.; Higginson F. R. Organochlorine insecticide residues in some agricultural soils on the North Coast region of New South Wales. *Bull. Environ. Contam. Technol.* **1987**, *39*, 286–293.
- (9) Gilbert, W. S.; Singh, G. Pesticide residues studies in the Namoi Valley 1969–1975. *Technical Bulletin 38, NSW Agriculture and Fisheries*; Biological and Chemical Research Institute: Rydalmere, NSW, Australia, 1990.
- (10) Van Zwieten, L.; Ayres, M.; Andersen, L.; Morris, S. Bioremediation strategies for soils contaminated with agricultural chemicals. In *Pesticides in Soil, Water and Produce: Analysis, Environmental Monitoring and Remediation*, Symposium Proceedings; Kennedy, I. R., Baskaran, S., Sánchez-Bayo, F., Eds.; University of Sydney: Sydney, Australia, 1998; pp 57–62.
- (11) Xu, B.; Jianying, G.; Zhang, Y.; Haibo, L. Behaviour of DDT in Chinese tropical soils. *J. Environ. Sci. Health* **1994**, *B29*, 37–46.

- (12) Beasley, H. L.; Phongkham, T.; Daunt, M. H.; Guihot, S. L.; Skerritt, J. H. Development of a panel of immunoassays for monitoring DDT, its metabolites and analogues in food and environmental matrixes. *J. Agric. Food Chem.* **1998**, *46*, 3339–3352.
- (13) Maestroni, B. M.; Skerritt, J. H.; Ferris, I. G.; Ambrus, A. Analysis of DDT residues in soil by ELISA: an international interlaboratory study. *J. AOAC Int.* **2001**, *84*, 134–142.
- (14) Soil Survey Staff. *Keys to Soil Taxonomy*, 8th ed.; Soil Management Support Services Technical Monograph 19; Pocahontas Press: Blacksburg, VA, 1992.
- (15) Odeh, I. O. A.; McBratney, A. B. Sampling design for quantitative inventory of the irrigated cotton soil. In *Proceedings of the 7th Australian Cotton Conference*; Hotel Conard Jupitars, BroadBeach, Gold Coast, Queensland, Australia, 1994; pp 439–440.
- (16) Larkin, K. A.; Matt, J. J.; Ferguson, B. S.; Beasley, H. L.; Skerritt, J. H. Detection of DDT and its metabolites in soil by enzyme immunoassay. *Proceedings of the 10th Annual Waste Testing and Quality Assurance Symposium*, Arlington, VA; American Chemical Society Symposium Series; American Chemical Society: Washington, DC, 1994; pp 540–550.
- (17) Matheron, G. The intrinsic random functions and their applications. *Adv. Appl. Probabil.* **1973**, *5*, 439–486.
- (18) Goovaerts, P. *Geostatistics for Natural Resources Evaluation*; Oxford University Press: New York, 1997.
- (19) McDougall, K. W. *Management of Organochlorine Insecticide Contaminated Grazing Soils*, Final Report DAN34; Meat Research Corporation of Australia: Sydney, Australia, 1992.
- (20) Kennedy, I. R.; Sanchez-Bayo, F.; Kimber, S. W.; Hugo, L.; Ahmad, N. Off-site movement of endosulfan from irrigated cotton in New South Wales. *J. Environ. Qual.* **2001**, *30*, 683–696.
- (21) McDougall, K. W.; Harris, C. R.; Fenton, I. G.; Dowman, M. Persistence and effect of management practices on organochlorine residues in soils of subtropical New South Wales. *Bull. Environ. Contam. Toxicol.* **1995**, *54*, 172–184.
- (22) Wan, H.; Higginson, F. R.; Harris, C. R.; McDougall, K. W. Organochlorine insecticides residues in soils used for vegetables and tropical fruit production in the Cudgen-Duranbah area of New South Wales. *Bull. Environ. Contam. Toxicol.* **1989**, *42*, 77–180.
- (23) Lee, N.; Beasley, H. L.; Kimber, S. W. L.; Silburn, M.; Woods, N.; Skerritt, J. H.; Kennedy, I. R. Application of immunoassays to studies of the environmental fate of endosulfan. *J. Agric. Food Chem.* **1997**, *45*, 4147–4155.
- (24) Sánchez-Bayo, F.; Ward, R.; Beasley, H. A new technique to measure bird's dietary exposure to pesticides. *Anal. Chim. Acta* **1999**, *399*, 173–183.

Received for review November 20, 2001. Revised manuscript received May 27, 2002. Accepted May 29, 2002. H.R.S. is grateful to the Australian Centre for International Agricultural Research for the award of a John Allwright Fellowship for postgraduate study in Australia. Financial support from the Australian Cotton Cooperative Research Centre is also acknowledged.

JF011542I