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VARIABILITY DISTRIBUTION OF RESIDUAL PESTICIDE CONCENTRATIONS IN SOIL

BY

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ABSTRACT

The concentrations of 13 different pesticides (c) were measured in Torrifluvents soil samples (0-15 cm depth) covering an intensively cultivated 83,000 ha in the Nile delta, Egypt. Fractile diagrams indicated that the values of c were more accurately described as lognormally than normally distributed for all the 13 pesticides. The number of observations required to yield an estimate of the mean concentration within a prescribed accuracy was shown to depend upon the nature of the pesticide and extent of the spatial variability of the field soil. The wide range of sample sizes was such that 341 soil samples would be sufficient to estimate phenthoate while sample size of 12,681 would be needed to estimate DDE within ± 10% of the true mean at the 0.05 significance level.

INTRODUCTION

The total quantity of pesticides which were used in Egypt from 1952 to 1984 was 6.2×10^{8} Kg of which 8.8,2.2,1.8 and 1.2% were toxaphene,DDT, lindane and endrin, respectively (Abdel-Gawad, 1985a and El-Sebae & Soliman,1982). Thus,a field study of residual concentrations made several years after the banning of DDT and the restriction of other persistent pesticides such as toxaphene would help to evaluate the ability of agricultural soil to degrade these contaminants over time (Shaaban & Elprince,1989). However,one important methodological problem for the evaluation of residual pesticide concentrations in soils is: How large must a sample be to be considered a valid representative of population under investigation?. This same problem has been,during the last 20 years, examined for many soil properties (Ameyan, 1986).

The number of observations necessary to obtain a given accuracy of the estimate of the mean can be calculated by using statistical methods once the mathematical form of the distribution and a measure of the variance are known (Hald, 1952). Many actual frequency distributions,if they are continuous,can be graphed as the familiar bell-shaped-, the Gaussian-, or the normal-curve. Many parameters are log-normally distributed , others may be described by other distributions (Harbaugh & Carter,1970). Recently, it has been found that values of soil properties such as silt content and available P are normally distributed (Ameyan, 1986), while the hydraulic conductivity (k), soil water flux (v), and apparent diffusion coefficient (D) are log-normally distributed(Biggar & Nielsen,1976). Marked contrasts have been observed in the variability levels of soil properties (Ameyan, 1986 and Khan & Norcliff, 1982),and hence,in the number of samples required to estimate each property. For a 150 ha field, 100 observations would allow the mean value of v to be estimated within ± 50% of its value , 200 observations estimate within ± 50% of the true mean value of D , and 1300 observations estimate within ± 10% of the true mean value of k at the 0.05 significance level (Biggar & Nielsen, 1976 and Warrick & Nielsen, 1980).

The objectives of this study are to determine the frequency distributions of residual pesticide concentrations for 13 different pesticides in soil and to estimate the optimum number of soil samples necessary to obtain a given accuracy of the estimate of the mean.

MATERIALS AND METHODS

The experimental data used in this study are those reported by Abdel-Gawad (1985 b) who measured residual pesticide concentrations in soil samples (0-15 cm depth) covering the intensively cultivated 83,000 ha at Alkalubia Governorate located in the Nile delta of Egypt. Soils of the Nile delta are Torrifluvents composed primarily of recent alluvial flood deposits transported from the volcanic Ethiopian highlands. Montmorillonite, kaolinite, feldspars, quarts and illite are the dominent minerals of these soils (Sheta,1981). The pesticide residues were extracted by propylene carbonate and analysed by gas chromatography (Abdel-Gawad,1985b).

Pesticide Formula:

Malathion: $C_{10}H_{19}O_6PS_2$ succinic acid,mercapto -diethyl ester, S-ester with 0,0-dimethyl phosphorodithiate ; Endosulfan: mixed$C_9H_6Cl_6O_3S$ 6-9-methano-2,4,3-benzodioxathiepin , 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-3 oxide, (3α, 5a β, 6α, 9α, 9a β) and (3α, 5aα, 6 β, 9 β, 9aα) ; Phenthoate: Dimethyl S-(α-ethoxycarbonyl) benzyl phosphorothiolothionate ; DDE-p,p: $C_{14}H_8Cl_4$ Benzene,1,1'-(dichloroethenylidene)bis(4-chloro-

Toxaphene: $C_{10}H_{10}Cl_8$ (mixture of chlorinated camphenes(chlorine 67-69%) of uncertain identity ; op DDT: DDT-o,p' $C_{14}H_9Cl_5$ Benzene, 1-chloro-2-(2,2,2-trichloro-1-(4-chlorophenyl) ethyl) DDT-p,p': $C_{14}H_9Cl_5$ Benzene,1-1'-(2,2,2-trichloro-ethylidene) bis(4-chloro- ; Endrin: $C_{12}H_8Cl_6O$ 2,7:3,6-Dimethano napth(2,3-b)oxirene,3,4,5,6,9,9-hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-(1aα, 2 β, 2a β, 3α, 6α, 6a β, 7 β, 7aα) ; Chlordane: $C_{10}H_6Cl_8$ 4,7-Methano-1 H-indene,1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-isomers Aldrin: $C_{12}H_8Cl_6$ 1,4:5,8-Dimethanonaphthalene,1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a -hexahydro-(1α, 4α, 4a β, 5α, 8α, 8a β) ; Parathion: $C_{10}H_{14}NO_5PS$ Phosphorothioic acid, O,O-diethyl O-(4-nitrophenyl)ester; Chlorpyrifos: $C_9H_{11}Cl_3NO_4P$ Phosphoric acid , diethyl 3,5,6-trichloro-2-pyridinyl ester ; Lindane: $C_6H_6Cl_6$ cyclohexane, 1,2,3,4,5,6-hexachloro,(1α, 2α, 3 β, 4α, 5α, 6 β isomer).

RESULTS AND DISCUSSION

The Frequency Distributions:

The fractile diagram in Fig.(1) shows the probability units $[(x - \xi)\,\sigma^{-1}]$ versus the 139 values of lindane concentration in soil, c. The basis for making the graph in Fig.(1) is the cumulative distribution function P(x) for normal

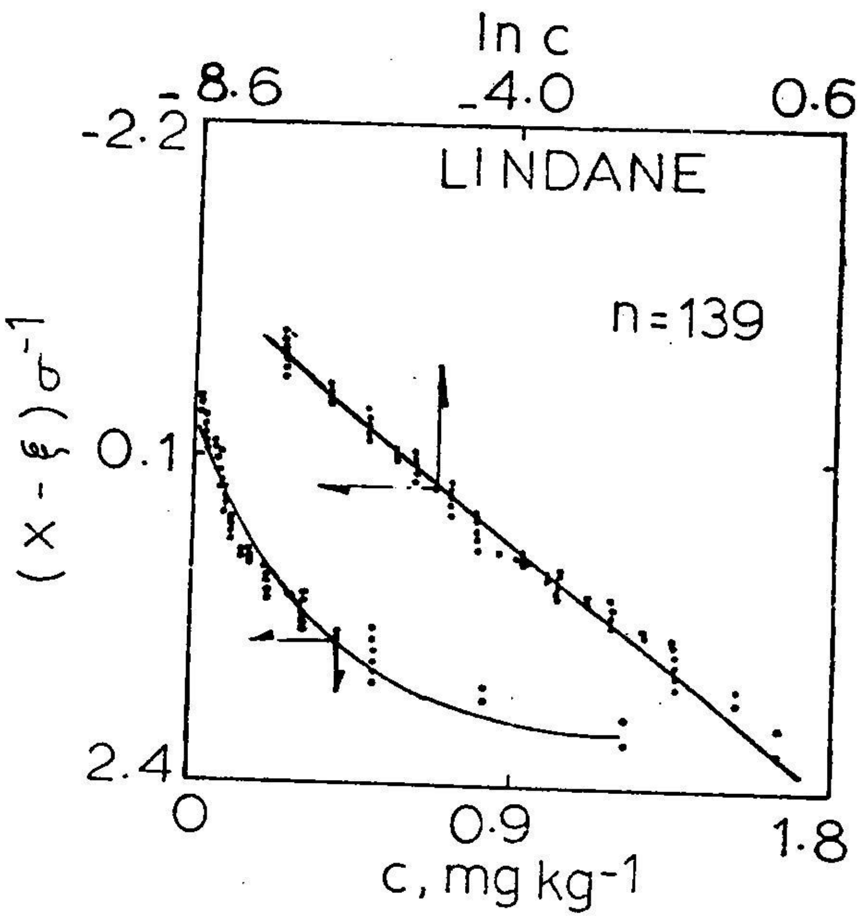

Fig.(1): Fractile diagram for lindane residue in soil, stemming from Eq.(1). Probability units [$(x - \xi)\ \sigma^{-1}$] are plotted versus c, and ln c for x=c and x=ln c, respectively.

distribution (Biggar & Nielsen, 1976):

$$P(x) = (2\pi)^{-1/2} \int_{-\infty}^{(x-\xi)\sigma^{-1}} \exp(-U^2/2)\, dU \quad (1)$$

where; x is the value of c, is the mean of c, and σ is the standard deviation of the mean. Values of P (x) were obtained by ranking the 139 observations of c in increasing order or magnitude. For values of c less than the smallest observed value of c, P (x) was considered zero; for the largest observed value of c (i=139), P (x) was considered unity; and for the other observed values of c (i=1, 2, 3,.......,139), P (x) was considered equal to i/139. By using these values of P (x), corresponding values of U obtained from Eq.(2) were plotted versus c as shown in Fig.(1). Equation (2) reads as follows (Abramowitz & Segan, 1968):

$$U = t - \{(c_o + c_1 t + c_2 t^2)/(1 + d_1 t + d_2 t^2 + d_3 t^3)\}; 0.5 \leqslant P(x) < 1$$

$$U\Big|_{P(x)=\frac{(n/2)+i}{n}} = -U\Big|_{P(x)=\frac{(n/2)-i}{n}}; \quad 0 \leqslant P(x) < 0.5 \quad (2)$$

where $t = \ln\sqrt{(1/[1-P(x)]^2)}$; $c_o=2.515517$; $c_1=0.802853$; $c_2=0.010328$; $d_1=1.432788$; $d_2=0.189269$; $d_3=0.001308$

To test for a lognormal distribution , the values of P(x) obtained by the above procedure are plotted versus ln c as well (Fig: 1). For such a case, x is ln c, ξ is the mean of the 139 values of ln c, and σ is the standard deviation of ξ. From Fig.(1) it can be seen that the probability units are linearly related to in c, and hence the values of c are lognormally distributed. For a normal distribution the mode (the most frequently observed value), the median (the value in the middle of an equal number of smaller and larger values), and the mean are all identical. For a lognormal distribution the mode is equal to exp ($\xi - \sigma^2$), the median is exp (ξ), the mean is exp ($\xi + 0.5\ \sigma^2$), and the variance is exp $(\sigma^2 + 2\xi)[\exp(\sigma^2) - 1]$. The mode, the median, the mean, and the standard deviation (s) of c for lindane are 20,130,370 and 770 $\mu g\ Kg^{-1}$, respectively (Table 1).

Table (1) presents values of correlation coefficient squares, r^2 for fitting straight lines to (U, c) and (U, lnc) data. The high magnitude values of r^2 in the latter compared with the former indicate that the observed variations for all the pesticides are more accurately described as lognormal than normal.

Variability of Pesticide Residues:

The level of spatial (distance) variability of pesticide residues in soil has been assesed with the coefficient of variation (CV), that is, standard deviation divided by the mean expressed as a percentage. In this study, a pesticide is regarded as showing little variation where the CV is < 200%, moderate if CV is between 200 and 300%, high variability if CV is between 300 and 400%, and very high variability where the CV is above 400%.

Table (1) presents values of CV for the 13 pesticides under consideration. Thus, phenthoate and aldrin have little variability (class I); chlordane, lindane, parathion, endosulfan, and ppDDT have moderate variability (class II) ; chlorpyrifos , malathion , and toxaphene have high variability (class III); endrin, opDDT, and ppDDE have very high variability (class IV), with CV in exess of 400%.

Optimum Sample Sizes:

The optimum sample size required for each pesticide at given levels of precision has been calculated, using the equation for the computation of Student's t (Ameyan, 1986).

$$n = (s.t / (\bar{x} - \mu)^2 \qquad (3)$$

where $\bar{x}$ = sample mean, μ = population mean, s = standard deviation, n = number of soil samples and t = value of Student' t with (n-1) degrees of freedom at a given probability level. Thus, with the precision level for estimating endrin

Table (1): Pesticide residues in the soil (0-15 cm depth) of Alkalubia Governorate (83,000 ha), the Nile delta, Egypt.

Pesticide	Contaminated samples	r^2 Normal	r^2 Lognormal	c, μg Kg^{-1} Mode	Median	Mean	s	CV
Phenthoate	100	0.3473	0.7587	10	20	30	30	94
Aldrin	144	0.2255	0.8570	20	90	220	360	162
Lindane	139	0.3820	0.9053	20	130	370	770	210
ppDDT	149	0.8245	0.8350	70	440	1160	2540	218
Endosulfan	121	0.2275	0.8356	10	50	100	220	223
Chlordane	152	0.6905	0.9424	20	150	380	1050	275
Parathion	130	0.1644	0.7984	10	70	160	460	283
Malathion	129	0.2821	0.7554	10	120	430	1380	320
Chlorpyrifos	121	0.2681	0.7869	10	120	420	1380	328
Toxaphene	134	0.8223	0.8764	30	440	1640	6230	379
Endrin	157	0.7995	0.9085	20	370	1660	6660	401
opDDT	107	0.6023	0.8932	10	180	670	3150	469
ppDDE	96	0.4576	0.7744	5	190	1240	7120	574

Table (2): Optimum sample size required for estimates within ± 5, ±10, and ±20% of the true mean at 95% confidence level for pesticide residues in the soil (0 - 15 cm depth) of Alkalubia Governorate (83,000 ha), the Nile delta, Egypt.

Pesticide	± 5%	± 10%	± 20%
Phenthoate	1,365	341	85
Aldrin	4,050	1,012	253
Lindane	6,781	1,695	423
ppDDT	7,345	1,836	459
Endosulfan	7,682	1,920	480
Chlordane	11,672	2,918	729
Parathion	12,353	3,088	772
Malathion	15,796	3,949	987
Chlorpyrifos	16,558	4,139	1 034
Toxaphene	22,170	5,542	1,385
Endrin	24,715	6,178	1,544
opDDT	33,930	8,484	2,121
ppDDT	50,724	12,681	3,170

where estimated sample mean = 1.66 and standard deviation = 6.66 mg Kg^{-1} set at ± 5% at the 0.05 confidence level. $(\bar{x} - \mu) = (0.05)(1.66)$, value of t = 1.96 and n= $[(1.96)(6.66)/(0.05)(1.66)]^2$; a sample size of 24,715 will give an estimate of the mean that will be within ± 5% of the true mean at the 95% confidence level.

The optimum sample sizes required for estimates within ±5,±10,and ±20% of the true mean for the 13 pesticides are given in Table (2). There are marked contrasts in the variability pattern of the pesticides (CV values) and, hence, the sample sizes required at given levels of precision. Sample sizes for the above stated four classes of pesticides are (85-253), (423-772),(987-1,385) and (1,554-3,170),respectively, to estimate the mean within ±20%. The wide range of sample sizes is such that sample sizes of 341 would be sufficient to estimate phenthoate,while sample sizes of 12,681 would be needed to estimate ppDDE within ±10% of the true mean.

CONCLUSION

The results of this study bring out two important features. The first is that the observed variations in pesticide residues are characterized by a small number of extremely large values of c, creating skew c distributions more accurately described as lognormal than normal. The second is the marked contrast in the variability patterns of pesticides, and, hence, the number of soil samples required to estimate the means of pesticide residues at different levels of precision.

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الاختلافات المسافية لبقايا تركيزات المبيدات في الاراضي

قدر عبد الجواد (١٩٨٥) تركيز ١٢ مبيد مختلف في عينات اراضي توريفلينفث (عمق:صفر-١٥سم) والتي تغطي محافظة القليوبية (٨٣ الف هكتار) بدلتا النيل بمصر. وباستعمال فراكتيل دياجرام اتضح ان قيم التركيز للتوكسافين و ب ب-ددت موزعة تقريبا توزيعا طبيعيا بينما قيم التركيز للاحدى عشر مبيد الاخرى فتوصف بدقة اكثر على انها موزعة توزيعا لوغاريتميا - طبيعيا وليس طبيعيا. ان عدد عينات الارض المطلوبة للحصول على تقدير لمتوسط التركيز وبدقة سبق تحديدها اعتمد على طبيعة المبيد ومدى الاختلافات المسافية للاراضي بالحقل. ان حجم العينة المطلوبة تراوح بين ١٧٧ عينة ارض للبراثيون و ٤٠٣١ لمبيد ب ب-ددش لتقدير المتوسط بخطأ قدره ± ٢٠٪ من قيمة المتوسط الحقيقي وذلك لمساحة الـ ٨٣ الف هكتار.