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Use of organochlorine contaminants to measure sedimentation rates in estuaries: a case study from the Manukau Harbour

Terry M. Hume*, Michael E. Fox and Robert J. Wilcock***

Organochlorine contaminants are widely distributed in sediments of the Manukau Harbour. The first appearance of DDT in cores is a potential stratigraphic marker because it can have appeared only since extensive applications of DDT on New Zealand pastures for grass grub control began in *c.* 1950. The technique permits calculation of average annual sedimentation rates, but precision is limited by bioturbation. A nett sedimentation rate of about 5 mm yr^{-1} was determined from measurements of DDT for muddy tidal flats in Drury Creek. This compared well with a rate of 5 mm yr^{-1} based upon a pollen dating technique. The past widespread use of DDT may enable comparisons to be made of very recent sedimentation rates in other New Zealand estuaries. Other contaminants identified in the Manukau Harbour sediments include dieldrin, lindane, PCB's and chlordane.

Keywords: Historical sediments, stratigraphic marker, estuary, DDT, technique

INTRODUCTION

Determining the historical accumulation rates of sediments in estuaries can be difficult. There are no universally applicable techniques, because the availability of data, the characteristics of the site and facilities for laboratory analysis vary from place to place. The accepted approach is to choose techniques appropriate to the situation from the range of documented methods. Of particular use are those techniques that have wide geographic applicability and allow comparison between sites over similar periods of time. In New Zealand estuaries, techniques for determining historical accumulation rates have been limited to comparisons of bathymetric data (*e.g.* Macpherson, 1978; Dahm, 1983; Burton and Healy, 1985), direct measurement of changes in surface elevation of tidal flats (*e.g.* Pickrill, 1979), radiocarbon dating of shell material (*e.g.* Hume and McGlone, 1986), establishing time horizons from pollen stratigraphy (Hume and McGlone, 1986), and measuring sediment thickness above a layer of wood debris of known age (Hume and Gibb, 1987). Overseas, natural and man-made radionuclides are commonly used to date sediment stratigraphy.

Organochlorine wastes originating from rural, urban and industrial sources are transported to estuaries by sediment and water runoff and by airborne drift from neighbouring catchments. Some residues become immobilised in the sediment because they are strongly partitioned to the particulate phase and sorbed to living organisms, organic detritus and inorganic particles. The organochlorine insecticide DDT was used extensively in pastoral and horticultural catchments throughout New Zealand, principally for the control of grass grub (*Costelytra* spp), from about 1950 until its phasing out by legislative ban in 1970 (Thompson, 1970).

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DDT breaks down to produce DDE and DDD, and each of these substances exists in two isomeric forms (o, p' and p, p'-). Thus, up to six forms of DDT residues may be detected in sediment samples. All forms of DDT are chemically very stable and readily bond to sediments. The total concentration of all forms is referred to in this paper as t-DDT. The presence of t-DDT residue in New Zealand pasture and soils is well reported but we are aware of only one description of t-DDT in New Zealand estuarine sediments (van Roon, 1982). DDT's widespread use, persistance in the environment and diffuse source runoff origin could make it a potentially useful stratigraphic marker in estuarine sediments. Ideally t-DDT could provide two marker horizons in the sediment column: a lower first appearance datum coinciding with its first use, and an upper level coinciding with its ban.

This paper examines how residues of persistent, man-made contaminants may be used to measure very recent sedimentation rates in estuaries. DDT is particularly suitable in New Zealand because the dates of its introduction and withdrawal from use in agriculture are known. It also reports the wider distribution of t-DDT and other persistant organochlorine contaminants in Manukau Harbour sediments.

METHODS AND MATERIALS

Choice of location

Contaminant accumulation in sediments can be modified at a deposition site by physical factors, such as sediment composition and particle size, sedimentation and resuspension, as well as by bioturbation. To make between site comparisons more valid all sites sampled (Fig. 1) were low energy, mid-tide, mud flat environments where fine grained sediments settle and contaminants are likely to accumulate. All of them were broadly similar in composition. They were sandy muds and muds with low organic carbon content, about 50-60% water content and low bulk densities (Table 1).

Sample collection

In July 1987 two short cores (50 mm diameter and about 500 mm in length) were collected from Drury Creek, a tidal arm of the Pahurehure Inlet in the Manukau Harbour (Fig. 1).

Table 1 – Compositional characteristics of surficial sediment cores (0-2 cm) from the Manukau Harbour

Sample location	Bulk density gm cm^{-3}	Water content %	Readily oxidizable carbon %	– Texture – sand %	mud %	Residue (ng g-1) p,p'-DDE	p,p'-DDD	p,p'-DDT	t-DDT
Muddy Creek	1.40	54.3	1.39	29.6	70.4	0.34	0.14	NQ	0.48
Mangere Inlet	1.40	53.9	1.20	15.7	84.3	0.78	0.63	0.13	1.54
Waiuku Inlet	1.36	56.0	1.03	21.7	78.3	0.50	0.28	0.12	0.90
Pukaki Creek	1.34	58.0	1.32	14.1	85.9	0.62	0.50	0.08	1.20
Drury Creek	1.37	55.8	1.41	5.0	95.0	0.58	0.26	0.08	0.92

NQ = not quantified

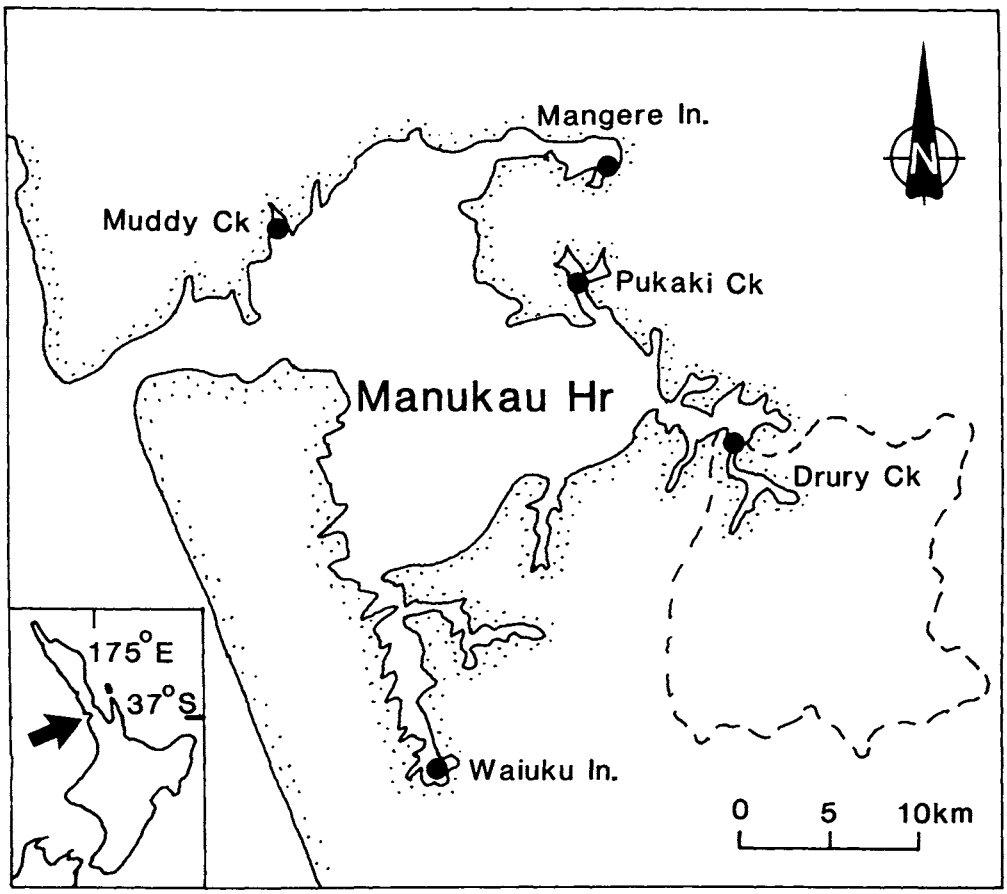

Fig. 1 – Sample sites in the Manukau Harbour. Both long cores and surficial sediments were sampled at Drury Creek. The dashed line shows the Drury Creek catchment boundary.

Plastic tubes were pressed into the soft muddy tidal flats from a boat driven aground at the waters edge at mid tide. Driving a steel rod into the sediment showed the mud to be at least 3 m deep. Comparison of sediment surface levels measured inside and outside the core tubes demonstrated that core compaction was *c.* 20%. The cores were extracted, then sealed and transported to the laboratory in an upright position. On the day of collection the cores were split, cut into 1 cm sections, bulked and frozen in polyethylene containers.

Surficial sediment samples from the Drury Creek site and 4 other locations in the Manukau Harbour (Fig. 1) were collected as part of other studies in November 1986 (Roper *et al.*, in press). At each of these locations 5 replicates were collected, by coring the top 2 cm of sediment, and then frozen on the day of collection. We analysed a sample from each location, prepared by bulking splits of the 5 replicates, for organochlorine contaminants, including DDT.

Analysis

All samples were thawed at room temperature before analysis. Readily oxidizable carbon (ROC) was determined by acid dichromate oxidation, followed by titration with ammonium ferrous sulphate (Gaudette *et al.*, 1974). Samples were split into sand, silt and clay fractions by wet sieving, and divided into size classes as defined by Folk (1974). Percent water and

bulk density were determined on the core sample sections prior to analysis by standard volumetric methods.

Pollen analysis

Samples 2-3 cm^3 in size were warmed in 10% potassium hydroxide to remove humic compounds, boiled in an acetic anhydride-sulphuric acid mixture for four minutes to destroy cellulosic compounds, and heated in hydrofluoric acid (40%) for 1-2 hours to remove silica. A strong chlorine bleach was used to remove abundant lignin in the preparations. Preparations were mounted in glycerine jelly, and pollen was identified and counted. An average of 220 pollen grains and spores of terrestrial plants were counted for each level. Biological corrosion had affected most pollen grains and spores in the core, so the results were to some degree inaccurate.

DDT analysis

About 10-20 g of sample was air dried at 20°C, ground to a fine powder, then weighed. The sample was next placed in a coarse fritted glass extraction thimble containing a 1 cm bed of prepurified anhydrous sodium sulphate, and extracted with redistilled dichloromethane in a soxhlet extraction apparatus. The dichloromethane was removed on a rotary evaporator at 20°C with n-heptane as a keeper solvent. Polar coextractives were removed on a pasteur pipette minicolumn containing 6% deactivated Florisil PR (Alltech Associates) and anhydrous sodium sulphate. The DDT and its degradation products (t-DDT) were eluted with n-heptane. A second fraction was eluted with 6% diethyl ether in n-heptane to check for complete recovery of t-DDT. Sulphur was removed from the purified extract by the addition of small pieces of freshly cleaned copper wire until bright pieces remained. The extract was evaporated to 1.0 ml under a stream of dry N_2 at 20°C and stored in a refrigerator until analysed by electron capture gas chromatography. Quantitative gas chromatography was performed on a Varian Model 3700 gas chromatograph equipped with a 20 m x 0.53 mm ID RSL200 column (Alltech Associates) and a Varian ^{63}Ni electron capture detector. Standard solutions of p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDT, o,p'-DDE and o,p'-DDD, supplied by Supelco Limited and Alltech Associates at concentrations of 2 and 10 pg μl^{-1} in n-heptane, were used for quantification. Confirmation of identity was performed on a medium polarity DB624 column 20 m x 0.53 mm ID (J and W Limited).

The precision of analysis (90% confidence intervals) of p,p'-DDE at 0.20 ng g^{-1} was $\pm$0.01ng g^{-1} (1 ng g^{-1} = 1 part per billion).

RESULTS AND DISCUSSION

DDT identification

Analysis of the Drury Creek core (Table 2) identified the parent compound DDT and its metabolites DDE and DDD (p,p'- and o,p'-isomers). Although all six DDT, DDE and DDD compounds were detected at the top of the core, the o,p'-isomers were present in much smaller amounts than the p,p' isomers. p,p'-DDD was detected throughout the core but could not easily be distinguished from o, p'-DDT. p,p'-DDT could not be resolved from an interfering chromatogram peak at depths below 5 cm. For these reasons, and in the interest of obtaining a simple stratigraphic marker, pp'-DDE (the predominant end product of weathered DDT) was chosen as the analytical variable.

DDT profile in core

p,p'-DDE was most abundant in the top 19 cm of the core, with traces at greater depths (Fig. 2). The concentration profile varied from about 0.01 to 0.5 ng g^{-1}, with maxima at about

Table 2 – Compositional characteristics of the Drury Creek core

Depth cm	Bulk density gm cm^{-1}	Water content %	Readily oxidisable carbon %	Texture sand %	silt %	clay %	Residue (ng g^{-1}) p,p'-DDE	p,p'-DDD	p,p'-DDT	t-DDT
0-1	1.27	66.2	1.66	8	92	<1	0.52	0.25	0.06	0.83
0-1 unfiltered							0.52			
0-1 filtered							0.48			
2-3	1.34	59.0					0.31	0.12	0.03	0.46
4-5	1.34	58.8	1.13	15	84	1	0.22	0.12	ND	0.34
6-7	1.34	57.7					0.25	0.10	ND	0.35
8-9	1.36	56.0					0.24	0.07	ND	0.31
9-10	1.38	54.7					0.28	0.08	ND	0.36
10-11	1.38	53.5	1.15	19	80	1	0.30	0.16	ND	0.46
11-12	1.39	53.8					0.30	0.90	ND	0.39
13-14	1.39	54.3					0.21	0.04	ND	0.25
16-17	1.39	54.2					0.12	0.06	ND	0.18
18-19	1.39	53.0					0.11	0.05	ND	0.16
21-22	1.41	52.8	1.46	30	69	1	0.01	0.04	ND	0.05
45-46	1.40	54.8	1.58	29	70	1	0.03	0.05	ND	0.08

*ND – none detected (<0.1 ng g^{-1})

11 cm, and at the surface. The profile can be interpreted as follows:

(1) Traces of DDE detected below the 19 cm level could be due to bioturbation or perhaps contamination during corer penetration.

(2) The profile between 19 cm and the surface may result either from changing inputs of DDT from the catchment (relating to application rates and storm events/runoff), or from a change in sedimentation rate at the site. The 0-19 cm profile has a fairly uniform sediment texture and organic carbon content, so these factors probably have little influence on t-DDT levels.

(3) The increase in the DDE concentration from 19-11 cm probably coincides with its first use in the catchment in *c.* 1950. It is likely that any sharp horizon has been blurred by bioturbation.

(4) High levels in the upper profile are not due to modern inputs of DDT. Its widespread

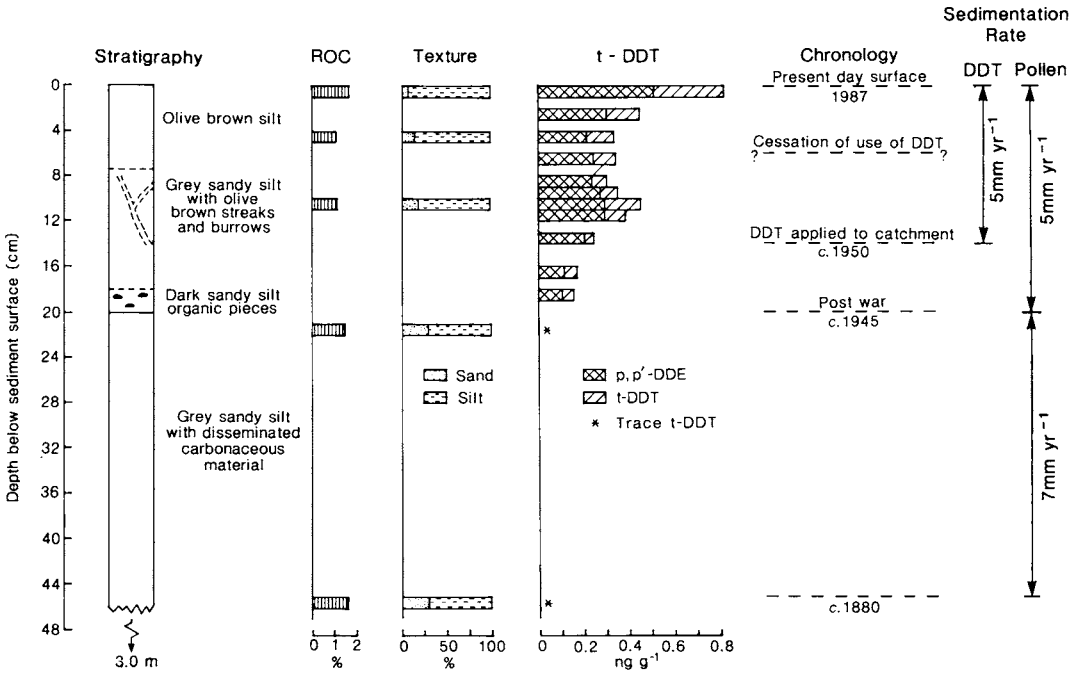

Fig. 2 – Drury Creek core log showing readily oxidizable carbon (ROC), texture, DDT concentration and sedimentation rates based on pollen and DDT measurements.

use ceased in about 1970. Furthermore, the t-DDT fraction consists largely of the weathered, products (o,p'- and pp'-DDD and DDE) rather than the parent o,p' and p,p'DDT. The relative amounts of p,p'-DDE and p,p'-DDD suggest prolonged weathering first in aerobic soils, to produce DDE, then in anaerobic sediments, to produce mainly DDD (Albone *et al.*, 1972). Hence DDE in the upper levels of the core probably reflects continuing supply from the catchment via soil erosion, even though 17 years have passed since DDT applications ceased. DDT is still being found in New Zealand soils at concentrations ranging from 0.1-1.0 $\mu g\ g^{-1}$ in the upper 10 cm of the soil profile (P. Holland, pers. comm. 1988). The t-DDE peak at the surface (0-1 cm) is perhaps partly explained by the more fine-grained and organic-rich nature of the upper layer (Fig. 2), factors which are associated with greater sorption of contaminants (Oloffs *et al.*, 1973). Analyses of Drury Creek sediment from which the biota had been removed suggest there is some DDT accumulation in fauna that concentrate in the top layers of sediment.

Pollen stratigraphy

We had no absolute method of dating to check the 1950 time horizon indicated by the DDT profile. However analyses of pollen grains confirm that core sediment below the DDT predates 1950.

Changes in catchment vegetation associated with agricultural activities are recorded as changes in pollen abundance in the core (Fig. 3). Because these agricultural activities are datable by independent historical evidence, the date of the changing pollen assemblage and the corresponding sediment can be determined. The 45 to 26 cm zone falls within the early European farming period; the high ratio of bracken to grass indicates rough pasture. Traces of kauri pollen at the base of the core indicate only remnants of the once extensive forest which was cleared by Europeans within a few decades of their arrival in Auckland in *c.* 1840.

We tentatively date the base of the core at *c.* 1880. The 20 cm to surface zone is distinguished by a decrease of bracken and wetland plants and ferns, and an increase of grass. It indicates the establishment of improved pasture, clearance of swamps, and generally more intensive usage of the landscape. The pine curve also rises sharply, and relates to the extensive plantings in pines for timber production in New Zealand since the late 1930's. Ten to 20 years must be allowed for full pollen production of the pine trees, so it would be reasonable to put a post-war date for the 20 cm level. Privet, which appears at 13 cm, may indicate urbanization of the catchment and the establishment of urban hedges.

Sedimentation rates

Very recent sediment accumulation rates were estimated for the Drury Creek site from the DDE and pollen depth profiles using the general expression

$$s = \frac{(d-m)c}{t}$$

where s = sediment accumulation rate, d = maximum depth of marker, m = mixing depth or depth of bioturbation zone, c = compression factor, t = length of time since marker entered the environment in significant concentrations.

A mixing depth of 5 cm was used for the calculations based on observations of bioturbation in surface sediments (Roper and Thrush, pers comm. 1988), the depth to which the sediments were strongly sulphurous, and values inferred for muddy intertidal flats reported in the literature (Thayer, 1983). Sediment compaction during coring, measured as 12 cm, was considered to result largely from the expulsion of interstitial pore water and animal burrow collapse. This large amount of core compaction emphasises the need to report sedimentation rates as mass/time compared to thickness/time if comparisons are to be made with other sites where sediments have a different bulk density. We report the former in this study (Fig. 2) but are nevertheless forced to report rates also as thickness/time to make comparisons with other New Zealand studies. For our calculations it is assumed that compaction was uniform over the 46 cm core, making c = 1.26.

From the DDE profile

$$s_{1950\text{-}1987} = \frac{(d_{DDE(1950)}-m)c}{t_{1950\text{-}1987}}$$

Using d = 19 cm, m = 5 cm, c = 1.26 and t = 37 yrs gives an average annual sediment accumulation rate of 5 mm yr^{-1} (or 0.60 gm cm^{-3} yr^{-1}). Similarly, using the pollen marker horizon at 1945, $S_{1945\text{-}1987}$ was computed as 5 mm yr^{-1} (or 0.60 gm cm^{-3} yr^{-1}) using d = 20 cm, m = 5 cm, c = 1.26 and t = 42 years. The pollen markers allow us to calculate the nett sedimentation rate between 1880 and 1945 as 7 mm yr^{-1} (or 0.64 gm cm^{-3} yr^{-1}).

Thus, accumulation of muddy sediments on the Drury has averaged 5 mm y^{-1} since *c.*1950 (Fig. 2).

These rates represent maximum rates for the estuary because the core site is considered to be a highly favourable area for deposition. Compared with other New Zealand estuaries the 5 mm yr^{-1} is higher than the 3 mm yr^{-1} (1840-1945) calculated for muddy tidal flats in the neighbouring Upper Waitemata Harbour (Hume and McGlone, 1986), and the 3 mm yr^{-1} (present day) on sandy tidal flats in Pauatahanui Inlet (Pickrill, 1979), but similar to the 6 mm yr^{-1} (1933-1984) for sandy tidal flats in the lower Tairua estuary (Hume and Gibb, 1987).

Catchment yield of DDT

It is interesting to consider the fate of the large quantities of DDT used for grass grub

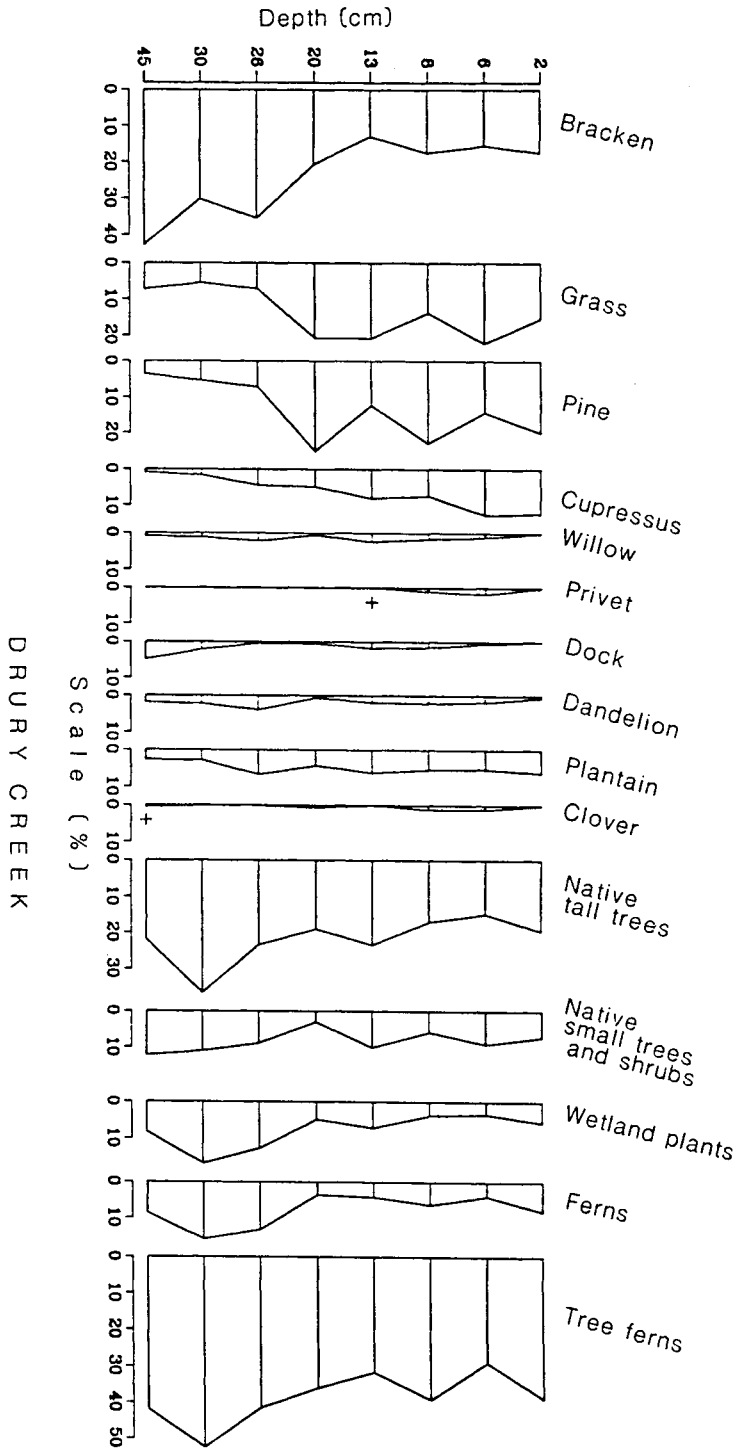

Fig. 3 – Pollen diagram for the core taken from Drury Creek. Values given as percentages of the pollen sum which includes all trees, shrubs, herbs and bracken, but excludes other ferns and wetland plants. Analysis and figure provided by Dr M.S. McGlone, Botany Division, DSIR.

control in the Drury Creek catchment. Discussions with residents who have farmed in the area for 30 or more years, and with agricultural contractors, manufacturers and researchers familiar with the region, have enabled us to make some rough estimates of DDT use. Between 1950 and 1970, DDT was applied to about 5000 ha of dairy farms at a rate of about 2 kg ha^{-1} every 3 years (Gallaher and Evans, 1961). Thus, up to 70,000 kg of DDT may have been applied to the catchment. Annual DDT losses to runoff were estimated for the catchment from the product of sediment yield (using a typical value of 170 kg ha^{-1} yr^{-1} for creeks in the region: Tonkin and Taylor, 1986), total area of treated dairy farms, and typical DDT soil concentrations for dairy pasture between 1950 and 1970 at (1 μg g^{-1}: Harrison, 1962, 1970). This gives a conservative estimate of 17 kg total runoff of DDT since 1950. The calculations do not take into account degradation and other processes which might remove DDT. If for Drury Creek (surface area 426 ha) we assume the average concentration of t-DDT in the top 15 cm is 0.42 ng g^{-1}, and the dry bulk sediment density is 0.6 g cm^{-3}, then the mass of t-DDT in the sediments is about 0.2 kg. Either substantial amounts of DDT are retained in the catchment soil, or, if they enter Drury Creek, they are flushed to the outer harbour.

DDT elsewhere in the Manukau Harbour

Comparison of the organochlorine insecticide residues in surficial sediments from 5 sites in the Manukau Harbour (Fig. 1) demonstrated the wide distribution of DDT and its metabolites (Table 1). This suggests t-DDT could be used as a stratigraphic marker in very recent sediment of the Manukau Harbour, or at least in those areas with fine-grained sorptive sediments, and where sedimentation rates are high. t-DDT concentration ranged from 0.9-1.5 ng g^{-1}, but bore no obvious relationship to catchment size or use. This is not surprising in view of its widespread use and the variety of physical and biological mechanisms that serve to redistribute t-DDT in the environment.

The use of t-DDT to date historical rates of sedimentation is limited by biogenic and physical process which cause sediment mixing, although limiting comparisons to similar depositional environments is recommended. However, sediment mixing is also a problem with other dating methods that utilize pollen or radionuclide markers.

Use of DDT to date cores in New Zealand

The technique has potentially widespread use in New Zealand despite some drawbacks. Because of New Zealand's pastoral farming heritage, DDT is probably as widely distributed in other estuarine sediments from *c.* 1950 as it is in the Manukau Harbour. The most valuable sampling locations are likely to be protected environments such as embayments in tidal creeks where there are high nett accumulation rates of fine grained sediments. The chemical analysis procedures described here can be undertaken at many laboratories. Although the analyses are time consuming, the chromatograms provide much valuable additional information on a wide variety of man-made organic contaminants in sediments. Importantly, quantitative analysis is possible at very low concentrations, so that only very small samples are required; this is useful when analysing core material. Because DDE is stable in anoxic subsurface sediment, it will be a stratigraphic marker for decades. The lower boundary of DDE, although blurred by bioturbation, defines a common time horizon in the sediments, enabling direct comparison of sedimentation rates from place to place. There is no upper cutoff coinciding with the DDT ban in 1970 because of the combined effects of bioturbation and continued delivery to the estuary of DDE by soil erosion. t-DDT has little potential use as a provenance indicator since its use was widespread.

Table 3. – Concentrations of DDT, DDE and DDD in surficial sediment of various estuaries and coastal embayments. t-DDT is the sum of DDT and its metabolites DDE and DDD.

Location year		Residue (ng g^{-1} dry wt) Mean	Range	No.of samples	Sampling method	Reference
Upper estuary of St Lawrence River, 1973	DDT	11.8	tr-34.4	25	Shipek sediment sampler	Canonne and Mamarbachi, 1975
Los Angeles Harbour **	t-DDT	768	115-3212	7	Reineche and Campbell grab	Choi and Chen, 1976
Mississippi Delta Gulf of Mexico**	t-DDT	4.2	0.2-9.3	22	Core (0-10 cm)	Giam *et al.*, 1978
Eastern Mediterranean coast of Turkey c. 1978	t-DDE t-DDT	4 11	2-8 3-21	8 8	Grab sampler	Basturk *et al.*, 1980
Upper Gulf of Thailand 1979	t-DDT (+ DDE) (0-10 cm)	?	22-56	12	Ekman-Berge dredge	Menasveta and Cheevaparanapiwat, 1981
Galveston Bay Texas 1979	t-DDT	0.21	0.01-1.4	8	Ekman grab	Murray *et al.*, 1981
New York Harbour**	p,p'-DDD	92	65-123	2	Core (0-10 cm)	Bopp *et al.*, 1982
Puget Sound, Washington 1980	DDT DDE DDD	– – –	0.41-186 0.21-10.6 0.24-20.3	6	nr	Konasewich *et al.*, 1982
Seattle Harbour 1980	DDT DDE DDT	3164 775 321	– – –	1	nr	Konasewich *et al.*, 1982
Delaware River, New Jersey, 1980	DDE DDD DDT t-DDT	28.1 20.0 8.0 56.1	0.8-210 2.1-94.0 <0.1-45.0 3.0-349	10	nr	Hochreiter, J.J., 1982
Upper Waitemata Harbour, New Zealand	DDE DDD DDT	<1 3 3	<1* <1-5 <1-6*	4 4 4	nr	van Roon, 1982
Yavaros Lagoon Caimanero-Huizache Lagoon NW Mexico**	t-DDT t-DDT	- 12	0-7.6 0-16.4	14	Grab sampler	Rosales *et al.*, 1985
San Francisco Bay California**	t-DDT (0-2 cm)	1.56	0.31-3.6	9	van Veen Grab	Chapman *et al.*, 1987
Manukau Harbour, New Zealand 1987	p,p'-DDE p,p'-DDD p,p'-DDT t- DDT	– – – –	0.34-0.78 0.14-0.63 tr-0.13 0.48-1.54	5 5 5 5	Core (0-2 cm)	Hume *et al.* (this study)

*wet weight determination, **sampling date not reported, t = total of o,p' and p,p' isomers, tr = trace, nr = not reported

Table 4 – Contaminant concentrations and catchment use for the Manukau Harbour surficial sediments (Fig. 1).

Site	Catchment use	Contaminant group (ng g^{-1} dry wt)				
		t-DDT	PCB	Lindane	Dieldrin	Chlordane
Muddy Creek	Bush	1.2	2.1	1.5	0.3	1.4
Mangere Inlet	Urban/industrial	2.3	14.2	2.0	0.5	5.3
Pukaki Creek	Urban/rural/airport	1.6	5.0	0.1	0.5	2.4
Drury Creek	Rural/urban	1.4	0.9	0.3	0.3	0.9
Waiuku Inlet	Rural/industrial*	1.2	0.5	0.1	0.3	0.9

*minor land use

Comparison with DDT levels elsewhere in New Zealand and overseas

A comparison of the levels of t-DDT residues in Manukau Harbour sediments with those from overseas estuaries and coastal embayments shows that the Manukau sediments contain generally less t-DDT (Table 3). The t-DDT levels in sediments from San Francisco Bay, California (Chapman *et al.*, 1987) and Galveston Bay, Texas (Murray *et al.*, 1981) are of the same order as those reported here. This is contrary to the commonly held belief that New Zealand estuarine sediments are relatively unpolluted compared with those in more populous and industrialised countries overseas (Fox *et al.*, 1988). Levels in the adjacent Upper Waitemata Harbour (van Roon, 1982) are broadly similar to those in the Manukau, given that the Waitemata analyses were undertaken on wet samples (probably about 50% water content)

The Manukau Harbour surficial sediments and cores contained a wide variety of organic contaminants in addition to DDT. There are more than 40 compounds including PCB's, lindanes, dieldrin and chlordanes (Table 4). Their distribution and origin are described by Fox *et al.* (1988). Dieldrin has a widespread and fairly uniform (0.3-0.5 ng g^{-1}) distribution similar to that of DDT, suggesting a non-recent diffuse source input which fits well with its recorded widespread use as a pesticide on pastures, discontinued in 1966 (Harrison, 1973). Therefore, like DDT, it may also be useful as a stratigraphic marker. On the other hand PCB's (0.5-14.2 ng g^{-1}) and chlordane (0.9-5.3 ng g^{-1}) are in greatest concentrations at sites receiving runoff from industrial/urban catchments, because they are used in New Zealand as industrial chemicals. These contaminants are strongly sorbed to fine-grained particulate matter and are stable in anoxic sediments. More detailed investigations may determine specific compounds in these groups that can be used as tracers of suspended sediment dispersion about point source inputs.

CONCLUSIONS

The environmental persistence of DDT compounds and their known period of use in New Zealand makes them potentially useful stratigraphic markers. The lower horizon of p,p'-DDE in shallow subsurface sediments of the Manukau Harbour can be used as a stratigraphic marker of *c.* 1950. Its widespread distribution in the harbour makes it useful for determining

very recent sedimentation rates in places where physical and biological conditions have been favourable for its preservation. In this study, a sedimentation rate of 5 mm yr^{-1}, for intertidal flats of Drury Creek, was determined from p, p'-DDE stratigraphy, for the period 1950-1987. This compared well with 5 mm yr^{-1} determined from a pollen dating technique for the period 1945-1987. The DDT method may be used in other estuarine locations where there are records of DDT use in the catchments.

The DDT concentrations reported in this study were comparable with those in the Waitemata Harbour, and with some overseas harbours.

Other persistent, organochlorine contaminants having a widespread use in agriculture, such as dieldrin, may be used a stratigraphic marker, for the same reasons as DDT. PCB's and chlordane, being industrial chemicals used in the Manukau Harbour catchment, have more localised inputs than DDT and could be tracers of fine particulate transport. Dieldrin may be useful in the same way.

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