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Persistence of Chlordane Applied to an Intertidal Sandflat

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Recent findings by Fox et al. (1988) and Hume et al. (1989) have established the presence of organochlorine residues in Manukau Harbour, New Zealand. Components of technical chlordane were found to be present in concentrations of 0.9 - 5.3 ng/g (dry weight), which were similar to sediment concentrations reported for Tokyo Bay and San Francisco estuary (Fox et al. 1988). Technical chlordane is a multicomponent mixture of C_{10} hydrocarbons, obtained by Diels-Alder condensation of hexachlorocyclopentadiene with cyclopentadiene, followed by chlorine addition. The principal use of technical chlordane in New Zealand has been for plywood preservation (Shaw 1990), and residues found in Manukau Harbour are thought to have emanated from nearby timber treatment yards.

Chlordane compounds are persistent in the environment and bioaccumulate in marine organisms (Kawano et al. 1988, Norstrom et al. 1988). Principal metabolites are heptachlor epoxide, formed from the quantitative oxidation of heptachlor, and oxychlordane, formed from *cis* and *trans* chlordane and from *trans* nonachlor (via dechlorination to *trans* chlordane). Oxychlordane is persistent and toxic and is a major metabolite produced in mammals and birds (CCREM 1987, Kawano et al. 1988). Information about the fate of chlordane compounds, summarised by Callahan et al. (1979), is generally sparce and does not refer to the time scales of the processes. Little is known about the behaviour and sublethal effects of chlordane compounds in coastal ecosystems.

This paper reports the persistence and mobility of chlordane residues in an intertidal sandflat in Manukau Harbour following the controlled addition of technical chlordane. The field trial was conducted as part of a study evaluating the ecological implications of chlordane residues on marine macrobenthic communities.

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MATERIALS AND METHODS

A paraffin based solution of technical grade chlordane was provided by Forest Research Institute, Rotorua, New Zealand. The formulation was approximately one third the strength of manufactured technical grade chlordane and contained 6.70% *cis* chlordane and 8.09% *trans* chlordane, compared to the respective proportions of 19% and 24% cited for technical chlordane (Sovocool et al. 1977). Crystalline standards were used to quantify the following components: compound C, heptachlor, *alpha* chlordene, *gamma* chlordene, *trans* chlordane, *cis* chlordane and *trans* nonachlor. Where crystalline standards were not available, the response factors of closely related compounds with the same number of chlorine atoms were used: *trans* chlordane for compound K and *trans* nonachlor for *cis* nonachlor (Norstrom et al. 1988). Descriptions of these compounds are given by Dearth and Hites (1991), and Smith et al. (1990). These nine compounds constitute about 90% of the mass of chlorinated material in technical chlordane, the remainder being a mixture of by-products and starting materials from its manufacture (Callahan et al. 1979, Sovocool et al. 1977). Oxychlordane and heptachlor epoxide standards were prepared by oxidation of 1,2 dichlorochlordene and heptachlor, respectively, using chromium trioxide in acetic acid.

Technical chlordane was applied to an intertidal sandflat in Manukau Harbour near Wiroa Island (37°01'S, 174°49'E). Preliminary analyses established that the study area was free from contamination by organic substances, including chlordane compounds. The experiment was conducted on two sites, each 12 m x 25 m, established at mid-tide level. The sites were separated by 20 m and were chosen for their similarity in physical appearance and near-surface sediment composition (Table 1), and wave exposure. Both sites were treated similarly, except that the experimental site was contaminated with technical chlordane whereas the reference site was not. The experimental site was divided into 10 equal subareas (6 m x 5 m). Sample locations within each subarea were obtained from randomly derived cartesian coordinates. Coordinates were redrawn if the selected location fell within a 0.5 m radius of a previously sampled area to preclude any localised modification of sediment chemistry. Samples were taken before the application of technical chlordane and 1, 3, 5, 13, 19, 44, 71, 112 and 199 (semi-diurnal) tides later. The reference site was divided in two: the half nearest the experimental site, and the half furthest away, to determine if there was movement of contaminated sediment from the experimental site.

Quantitative addition of chlordane to the experimental site was carried out by treating sand collected adjacent to the study site with a solution of technical chlordane dissolved in dichloromethane (DCM), and applying the dried, treated sand using a mechanical seed spreader. The applied dosage was intended to be 80 ng/cm^2 of technical chlordane, roughly equivalent to an average concentration (to a depth of 10 cm) of 10 ng/g (dry weight).

Table 1. Surficial sediment composition at the two study sites.

	experimental site	reference site
% mud	6.2	5.2
% sand	84.2	91.5
%gravel (predominantly shell)	9.6	3.3
median grain size (ø)	1.84	2.16
Inclusive graphic standard deviation	1.45	0.91
% R.O.C.	0.35	0.33

Sediment grain size was determined by the methods described in Folk (1968) on a composite of 10 evenly spaced samples (about 5 m apart) taken to a depth of 3 cm. Percentage reactive organic carbon (%R.O.C.) was determined by the method of Gaudette and Flight (1974). All % values are for sediment dry weights.

Sediment cores to a depth of 10 cm were taken for chemical analysis from the study site using a stainless steel corer, coincident with biological sampling (*Pridmore et al. in prep*). On each sampling occasion cores from each of the 10 subareas in the experimental site, and from the two halves of the reference site, were collected and stored in polyethylene bags at -20°C until analysed. Thus, a total of 90 sub-area cores from the experimental site and 18 cores from the reference site were collected and analysed during the trial. In addition, sediments were bulked from each sampling occasion and analysed to determine any changes in chlordane chemistry. Depth profiles of sediment chlordane residues were determined by sectioning cores from selected sites, at the 0-2 cm, 2-5 cm and 5-10 cm depth intervals. The trial was conducted from 3 July 1989 to 17 October 1989.

Prior to analysis, each sediment sample was thawed, mixed well, and an aliquot (c. 150 g) removed and airdried at 40°C. The dried sample was ground and sieved (500µm mesh) to remove stones and shells, and a subsample (40 g) extracted by Soxhlet apparatus for 6 hours with DCM. (Some CHL compounds were detected in the rejected coarse material, but were insignificant in comparison to that in the dry fines). The evaporated extract was cleaned by dry florisil chromatography, and the sulphur removed with bright copper wire. Keeper solvent (heptane) was added and the extract evaporated under nitrogen to 1 ml, prior to analysis by gas chromatography with electron capture detection (GC-ECD).

Analysis was performed with a Hewlett Packard 5890 GC equipped with an HP 7636A automatic injector, and a fused silica capillary column (J & W Scientific DB1, film thickness 0.25 µm, 20 m x 0.32 mm i.d.), operating at 70-280°C. The injector was operated at a temperature of 250°C, and the detector at 320°C. Carrier gas (H_2) flow was 40 cm/sec. Quantitation was by comparison with an internal standard (lindane), added just prior to Soxhlet extraction. Field sample analyses were expressed as "total chlordane" (CHL), defined here as the sum of: *cis* and *trans* chlordane, *cis* and *trans* nonachlor, heptachlor and compounds C and K (Dearth and Hites 1991; Smith et al. 1990). *Alpha* and *gamma* chlordene were not quantified because of interfering peaks in their chromatograms. Compound C and heptachlor were occasionally subject to interfering chromatogram peaks that occurred when sample extracts were stored for more than 1 month at -20°C. Missing values (46 out of 180) for those sample extracts were estimated from the average ratios of concentrations of heptachlor and compound C to those of *cis* and *trans* chlordane for uncontaminated extracts, from samples collected at the same time. The seven CHL components constitute about 75% of technical chlordane (Sovocool et al. 1977). Concentration data are expressed as ppb (parts per billion = ng CHL/g dry fines). The sediment detection limit for individual CHL components was 0.06 ppb.

RESULTS AND DISCUSSION

No CHL components were detected in sediments of the reference site during the experiment. Total CHL residues for each of the ten sub-areas were combined to give mean loads (mass per unit area) for the experimental site during the study (Fig.1). Individual sediment loads varied markedly for tides 1 and 3 (three values were greater than 100 ng/cm^2), but were much more uniform thereafter. No significant correlation was observed between CHL concentrations and sediment organic carbon contents for the experimental core samples ($r = 0.01$, $n = 69$) and it is probable that the high values resulted from uneven application of treated sand, rather than from preferential binding of CHL components to organically enriched sediments (Karickhoff 1984).

The applied load of technical chlordane (80 ng/cm^2) corresponded to an initial CHL load of 58 ng/cm^2. During the first tidal cycle, 36% of the pesticide disappeared from the site, leaving 37 ng/cm^2. The sediment load (to a depth of 10 cm) stayed close to this level for a further 43 tides, and then declined to a value of 22 ng/cm^2 by tide 71. No other reduction in CHL was detected throughout the remainder of the experiment. Thus, the overall change in mass was about 62% over a period of 106 days, with more than half of this occurring over the first tide cycle. Some redistribution of CHL from the applied sand, having a low organic carbon content, to more organically enriched silts in the trial site, may have occurred during the first high tide over the sandflats. The only significant loss of CHL from the sediments after the first tide ocurred between tides 44 and 71 (Fig.1) when a storm passed through the study area.

Other data on chlordane persistence in marine sediments is not available for comparison. Oloffs (1978) has found detectable residues of chlordane in lake sediments after 421 days, following addition to the water column, with very little alteration in composition apart from the quantitative epoxidation of heptachlor. It might be expected that chlordane compounds in intertidal sediments would be broken down or removed by photolysis, hydrolysis, volatilization and bioaccumulation

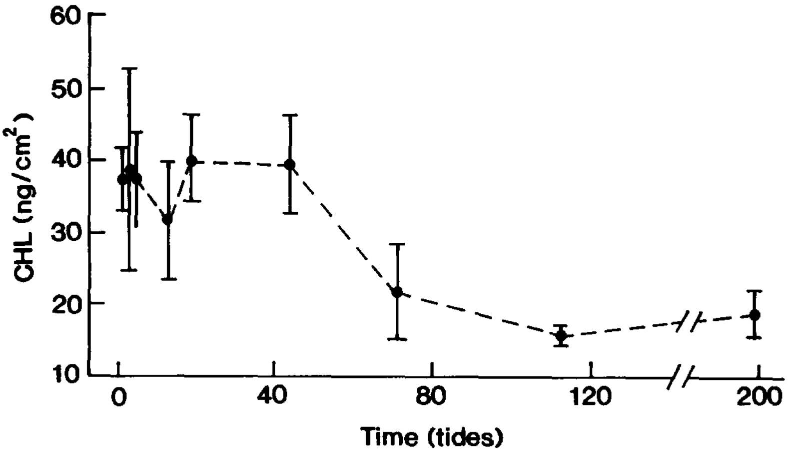

Figure 1: Change (mean ± standard error) in the amount of CHL in the sediment of the experimental site over time

(Callahan et al. 1979). Chlordane compounds are sparingly soluble in water and thus have a high affinity for sediment organic carbon. The sorbent-sorbate interaction may indirectly mediate solution phase processes by controlling the pollutant (CHL) release into the aqueous phase (Karrickhoff 1984), thereby stabilising the sediment residues to some extent. Sediment erosion, and replacement with uncontaminated sediment, probably contributed to the loss of CHL from the experimental site.

The relative proportions of the seven CHL components in the bulked sediment samples changed little throughout the trial and were similar to those in technical chlordane. Of the major compounds, *cis* chlordane increased by 5% while *trans* chlordane and *trans* nonachlor declined during the course of the study by 6% and 2%, respectively. Studies on changes in the composition of technical chlordane in aqueous and non-aqueous environments (Bevenue et al. 1969) and weathering studies (Thruston 1965) have shown the components eluting before *trans* chlordane to be volatile, such that after 100 days the chlordanes and nonachlors comprised 95% of the remaining technical chlordane. In this study, compound C, a hexachlorinated component of CHL (Smith et al. 1990) which elutes before *trans* chlordane, did not decline at a faster rate than the heavier components and was consistently about 9±2% of CHL; the same proportion as in the applied technical chlordane.

The metabolite oxychlordane was not detected in any of the sediments. Kawano et al. (1988) have detected oxychlordane in marine birds and mammals and related its presence to metabolic processes and monooxygenase activity, noting that the chemical is only slightly produced in lower trophic organisms. Traces of heptachlor epoxide, of unknown origin and age, were found in Manukau sediments by Fox et al. (1988), but were not found during the 3 months of this study.

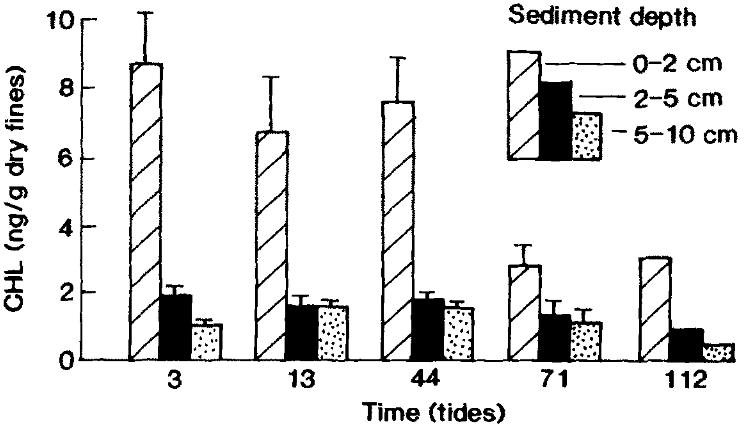

Figure 2: Concentrations (mean ± standard error) of CHL at different depths in the experimental site. Data for only one depth profile are shown for tide 112.

Depth profiles for tides 3, 13, 44, 77 and 112 are shown in Fig.2. Concentrations in the 0-2 cm range were similar from tides 3-44 but declined markedly from 7.6 to 2.8 ppb between tides 44 and 71. This equated to a change of 13 ng/cm^2 in (0-10 cm) CHL load between tides 44 and 71, compared with a measured difference of 18 ng/cm^2 (Fig.1). Concentrations for the 2-5 cm and 5-10 cm depth intervals showed little change between tides 3 and 71 and had ranges of 1.9 to 1.4 ppb and 1.6 to 1.0 ppb, respectively. The two deeper core concentrations declined further, after 112 tides. Thus, after some initial downward movement of CHL, there was little further vertical displacement. Bioturbation can influence solute transport in sediments (Aller and Yingst 1985). The lack of downward movement of CHL between tides 3 and 44 (Fig.2) suggests that any effects of bioturbation were within the error limits of our measurements. Nevertheless, bioturbation may have assisted in the initial downward movement of CHL by modifying the sediment into a more open fabric, with high near-surface porosity and low compaction and adhesion.

The main decrease in CHL concentration in the experimental site was from the top 2 cm, where sediment processes (viz. erosion, and dilution by uncontaminated sediment) and bioaccumulation would be most effective. Preliminary results from this study show that CHL concentrations for benthic infauna (i.e. worms, shellfish) averaged around 320 ng/g dry weight after 44 tidal cycles. Benthic biomass averaged 21 mg/cm^2 when these measurements were made. Hence, at tide 44, about 6.7 ng/cm^2 of CHL would have been held in the benthic biota. This is similar to the standard error of the mean load measurements (Fig. 1).

Our observations suggest that the most important processes regulating the fate of intertidal sandflat CHL residues was sediment transport, predominantly from the top 2 cm. The compositional stability of CHL during the trial suggests that physico-chemical processes, such as hydrolysis, dechlorination and volatilization were relatively less important pathways for CHL removal in this environment.

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