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Identification of a Point Source of Chlordane Contamination from a Timber Treatment Facility

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Technical Chlordane is a multi-component chlorinated hydrocarbon pesticide formulation containing in excess of 140 different compounds (Dearth and Hites 1991). Chlordane has been used extensively as a timber preservative in both the LOSP pressure treatment method or as an antibiotic component of the adhesives in plywood manufacture (Shaw 1990). The widespread use of chlordane, combined with its broad spectrum toxicity, propensity to bioaccumulate, and persistance in the environment make chlordane a significant environmental pollutant (Shigenaka 1990).

Manukau Harbor is a large (344 km^2) shallow inlet adjacent to Auckland city, New Zealand (Figure 1). Earlier studies (Fox *et al.* 1988; Holland *et al.* 1993) showed levels of chlordane in Manukau Harbor comparable with heavily industrialised countries such as Japan and the USA. The initial study showed that the levels of contamination increased approaching the Mangere Inlet - Onehunga region of the harbor . A survey of industry in this area indicated that a timber treatment facility was the most likely source. Chlordane can be released into the timber yard by spillage, and by drip from recently treated timber. Since chlordane is virtually insoluble in water (Callahan *et al.* 1989; Verschueren 1983), this poses little threat if contained. However, the surface material in the yard is susceptible to erosion by wind and rain, and can easily be carried off the site as dust or sediment in runoff (Norstrom and Muir 1988). Runoff can remove large amounts of sediment which can run directly into culverted stormwater drains and so travel unimpeded into the harbor, or flow into small streams where vegetation and the stream topography may hinder its travel to the sea.

A shallow, open drain collects runnoff from the timber yard and channels it into a marshland bordering the site. Water flows into the marsh through a partially culverted stream. Another partially culverted stream drains from the oppposite end of the marsh, emptying into the Mangere Inlet. The location of this timber treatment facility relative to the Manukau Harbor is illustrated in Figure 1.

MATERIALS AND METHODS

Samples of the gravel surface from the timber yard, the drain leading from the yard to the swamp, the marsh, and the stream leading to Mangere Inlet were taken in October 1988 and July 1989. A final sample from the drain exiting the timber yard was taken in February 1990. A description of the samples is given in Table 1. Further sampling could not be undertaken as the topsoil from the whole area was excavated and removed by city authorities in an attempt to decontaminate the site. The samples were frozen at -20°C until analysis.

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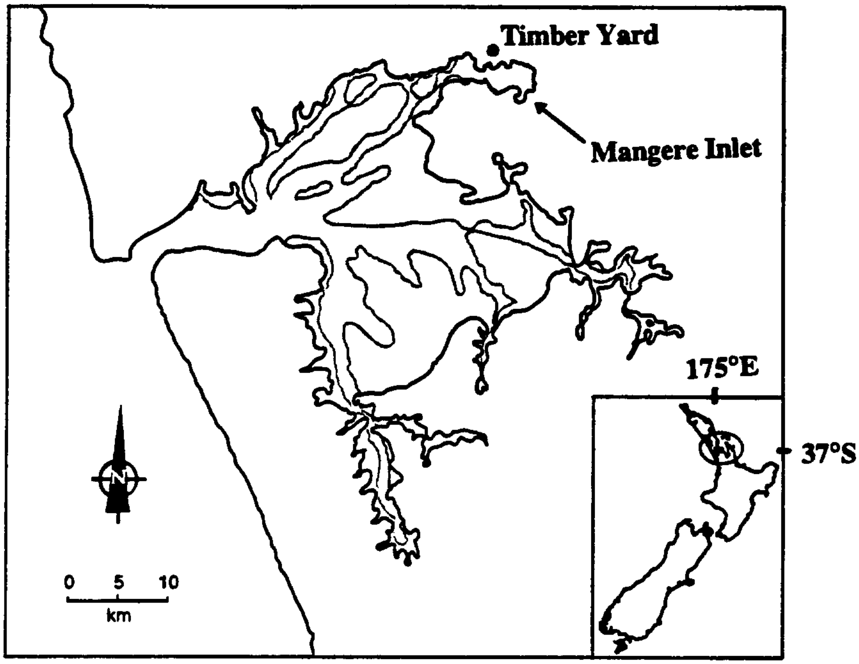

Figure 1. Manukau Harbour and environs.

Table 1. Sample description.*

Sample	**Description**
A1	Small drain exiting timber site (stagnant, green)
A2	Point where drain from timber yard entered the marsh (~10m from A1)
A3	Small drain exiting bowling green
A4	Point at which small stream leaves marsh
A5	Muddy sample from where stream draining swamp enters Mangere Inlet
A5 (S)	Sand sample from same area as A5
B1	Same area as A1
B4	Same area as A4
B5	Mud from same area as A5
B6	Stream sediment - upstream of the marsh
B7	Soil sample from marsh at point where stream from bowling green entered
B8	Surface soil from timber yard
C1	Same area as A1 and B1
C5	Mud from same area as A5 and B5

A October 1988; B July 1989; C February 1990

* All samples were sediment taken from top 2cm layer

Each sample was thawed and mixed thoroughly. Then approximately 100g was removed and air dried at 40°C for 16 hours or until sufficiently dry that it could be ground to a free flowing powder. The dry sample was then ground and sieved through a 1mm sieve to remove the larger rocks and shells which were discarded. The samples (40g) were Soxhlet extracted with methylene chloride (210mL) and the extracts cleaned up on a florisil column using the procedure described by Smith (1991) and Pridmore *et al.* (1991).

Routine analysis was performed on a Hewlett Packard 5890 gas chromatograph (GC) equipped with an autoinjector and an electron capture detector (ECD). The ECD detector was chosen for its superior sensitivity and selectivity towards polyhalogenated compounds which have high ECD response factors. Individual compounds were identified by comparing retention times with a standard mixture containing 13 of the major chlordane components. For samples with sufficiently high levels of chlordane contamination the GC was interfaced to a Hewlett Packard 5970 mass selective detector (MSD). The ion chromatograms that are produced by the MSD are essentially compound specific, which allowed individual compounds to be identified with a higher degree of certainty. A 12m, 0.2mm id, FSOT capilliary column with an 0.25μm HP-1 stationary phase was used for all analyses. He was used as carrier gas, at a flow rate of 30cm/sec. A 2μL aliquot of sample was introduced into the GC injector which was held at 250°C. The purge delay was set at 30sec. The GC oven was programmed as follows: initial temperatue 110°C for 2min; heated to 130°C at 25°C/min, then to 210°C at 2°C/min, finally to 280°C at 25°C/min and held for 20 min. Compounds were identified by matching the retention times of peaks in the sample with retention times for authentic standards. Quantitation was achieved by comparison with an internal standard (γ-hexachlorocyclohexane) which was added to the sample while in the extraction thimble. Response factors for individual chlordane components were determined before each batch of samples was analysed, using a response factor mix containing known amounts of 13 of the major chlordane components and the internal standard in heptane. Blank determinations showed a total interference equivalent to a total chlordane concentration of ~0.5 ng/g. The method reproducibility was established by dividing a single sample, similar in composition to sample B8, Table 1, into 5 subsamples and analysing each of these separately. The results of these analyses are presented in Table 2. Further details concerning the development of this methodology are outlined elsewhere (Smith 1991).

Table 2. Concentrations of the chlordane components in soil extracts (ng.g^{-1}).

	cpd C	hept	α-chl	γ-chl	t-chl	c-chl	t-nona	c-nona	cpd K	Total chl
mean conc.	28	14	34.6	81	183	206	141	62	16.5	767
std. deviation	2	1.3	3	6	20	22	12	5	2	77
RSD(%)	7	9	8	8	11	11	8	8	11	10

Abbreviations: cpd C, compound C; hept, heptachlor; α-chl, α-chlordene; γ-chl, γ-chlordene; t-chl, *trans*-chlordane; c-chl, *cis*-chlordane; t-nona, *trans*-nonachlor; c-nona, *cis*-nonachlor; cpd K, compound K; Total chl = sum of 9 compounds analysed.

RESULTS AND DISCUSSION

Chlordane was found in all samples collected. The amounts of 9 major components are given in Table 3. In addition, β-chlordene, and the compounds commonly referred to as unknown 1 (heptachlor isomer) and unknown 2 (octachlordane isomer) were detected. With the exception of sample B7, all samples taken from within the marsh, or from its outlet had concentrations of chlordane at least 2 orders of magnitude less than the samples from the timber yard (B8), or the small drain leading from there to the marsh (Site 1). These two high level samples were sufficiently contaminated that GCMS studies could be performed.

The total ion chromatograms of the timber yard extract (B8) and of technical chlordane are very similar, which demonstrates that chlordane is the major non-polar extractable found on the site. This was in contrast to other off-site extracts where polycyclic aromatic hydrocarbons (PAHs) and/or DDT and its metabolites were the dominant contaminants.

Table 3. Concentrations of the chlordane components in soil extracts (ng.g^{-1}).

Date	Sites	cpd C	hept	α-chl	γ-chl	t-chl	c-chl	t-nona	c-nona	cpd K	Total chl
17/8/88	A1	601	233	1157	2037	3939	3165	3173	1318	777	16400
	A2	778	86	1260	2292	3445	3068	2840	1047	420	15200
	A3	1.2	0.4	0	1	1.1	1.1	1.2	0.6	0	6.5
	A4	0.9	0.4	0.7	1.7	2.3	2	2.1	0.8	1	12
	A5	0.8	0.4	0	1.3	8.3	0.7	1.5	1.4	1.6	16
	A5 (S)	0.9	0.4	0	1	0.7	0.8	1.1	0.8	0	5.7
4/7/89	B1	309	29	382	642	928	935	815	3.6	75	4400
	B4	2	0.8	2.7	5.2	1	1.1	1.2	3.6	1.2	19
	B5	1	1	1.6	2.6	3.4	2.8	3.6	1.8	0.5	18
	B6	0.4	0.7	1.4	0.2	0.1	1.5	1.6	1.1	1.6	8.6
	B7	3.9	0	9.4	14.3	3.6	6.1	29	5.5	87.2	159
	B8	27	9	71	146	310	283	280	164	108	1400
21/2/90	C1	228	100	255	732	1372	1194	1073	483	450	5900
	C5	0.1	0.1	0	0.2	1	0.8	1	0.7	0.6	4.5

The PAHs phenanthrene, anthracene, fluoranthrene and pyrene were common to all extracts analysed by GCMS, with the relative amounts being quite variable. Quantitative analysis could not be performed on these samples because no suitable internal standard had been added and PAH standards were not available. Chlordane and PAH concentrations were highest nearest the timber yard, and declined with increasing distance from the site. Mass spectral studies showed the major contaminants in Site 1 samples were PAHs. Because the PAHs were not significant contaminants in the timber yard extract (B8) they must originate from another source that feeds into the marsh. The only other industrial site bordering the marsh is a steel tube manufacturer, but the use of PAH containing substances here seems unlikely. A more likely possiblity is urban run off from roadways which is often highly contaminated with PAH from bitumen and vehicular emissions (Mix 1984; Neff 1985).

The presence of PAHs is of environmental concern in its own right, but a more detailed study of the PAH problem was considered beyond the scope of the present work. There was evidence from selected ion chromatograms that indicated the presence of more toxic PAHs, including benzo(a)pyrene, so further work to examine the distribution and levels of PAH in the Manukau Harbor is urgently required.

The results in Table 3 suggest chlordane levels at the most contaminated site (Site 1) may have been declining over the period studied. This could be due either to slight differences in the location the sample was collected from, or due to slow decontamination of the site since the closure of the facility.

Samples from Site 1 produced an extract with significantly different composition from the other marsh extracts. The B1 extract showed considerable chlordane and PAHs, but the extract from the heart of the marsh (B7) gave a quite different ECD trace, and this was shadowed by the total ion chromatogram. Chlordane and PAH residues were present, but DDT was also detected. DDT was the fourth largest contaminant by peak area, and was positively identified from its mass spectrum, and by matching retention times with an authentic standard. Since DDT residues were absent in the other samples they would not appear to be coming from the timber yard. The only other source was a small drain exiting from an adjacent bowling green. DDT was commonly used to control grass grub in pasture and could have been used for that purpose in this bowling green.

DDT and its metabolites have been ubiquitous environmental contaminants since their widespread use as pesticides, but it is usually the metabolites DDD and DDE that are detected because DDT itself is readily metabolised (Metcalf 1973). In this sample the DDT to DDD and DDE ratio indicated the predominant residue was DDT, which suggests the useage of DDT must have been recent. The dominance of the anaerobic metabolite DDD over the aerobic metabolite DDE suggests that the limited breakdown of DDT that had occurred probably took place under the predominantly anaerobic conditions prevailing in the swamp area (Pfaender and Alexander 1972).

The extracts from the site where the stream enters the Mangere Inlet (Site 5) showed no detectable chlordane residues and only low levels of PAHs, when analysed by GCMS. The major contaminants were hydrocarbons.

To prove conclusively that chlordane was present on site, a surface scraping was taken from the site (B8). Extraction of 200g of this material followed by gel permeation and florisil cleanup yielded the cleanest of all chlordane containing extracts. The sample yielded total ion mass chromatograms of the following compounds: compound C, α-, β- and γ-chlordene, *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor and compound K. Heptachlor was not identified in the extract. The *m/z* 272 selected ion traces show a large peak at ~16 minutes in technical chlordane, however it is noticeably absent in the site extract. The absence of this ion, which is one of the strongest in the heptachlor mass spectrum, demonstrates heptachlor concentrations are below the level for detection by GCMS. Heptachlor undergoes epoxidation in water (Oloffs *et al.* 1978; Eichelberger and Lichtenberg 1971) to give the metabolites 1-hydroxychlordene and heptachlor epoxide, which is considerably more stable than heptachlor (Khasawinah 1989). The second fraction from the florisil column did show evidence of hepatchlor epoxide with the characterisic *m/z* 353 ion and the *m/z* 81 ion both evident when sample B8 was run using selected ion monitoring. There was no evidence for the *m/z* 317 ion characteristic of 1-hydroxychlordene.

We interpret the rapid reduction in chlordane levels over the short distance between the timber yard and the swamp, and the persistance of elevated chlordane levels over the 16 month study period, as evidence that the chlordane contamination was particle bound and did not exist in significant concentrations in free solution. This conclusion is consistent with the very low water solubility of chlordane (Callahan *et al.*, 1989; Verschueren K 1983).

When the concentration of each chlordane component in the samples is normalised to the sum of the 9 chlordane residues quantified, interesting differences between some samples become apparent. Normalised data for technical chlordane is included for comparison (Figure 2). In sample B8 the chlordane components of lower molecular weight than *trans*-chlordane all appear to be less abundant than in technical chlordane, whereas the higher molecular weight compounds are present in proportionately greater amounts than in the parent pesticide. Weathering studies on chlordane (Thurston 1985) showed that those components eluting before *trans*-chlordane suffered significant losses due to volatilisation. This could account for the loss of the lighter chlordanes from B8.

The composition of the chlordane is similar in all samples other than the extract from the timber yard itself. Unlike the other samples, B8 was taken from a non-aqueous environment and was also exposed to higher levels of sunlight. Studies of chlordane photoisomerisation (Benson *et al.* 1971) showed that sunlight was inefficient at converting chlordane to its photoisomers, which would suggest that sunlight is unlikely to have significantly altered the composition of B8. However since other studies have shown facile photo-transformations of a number of chlordane components take place in the presence of photosensitising agents (Mansour and Parlar 1978; Benson *et al.* 1971; Knox *et al.* 1979), the effect of sunlight cannot be entirely ruled out.

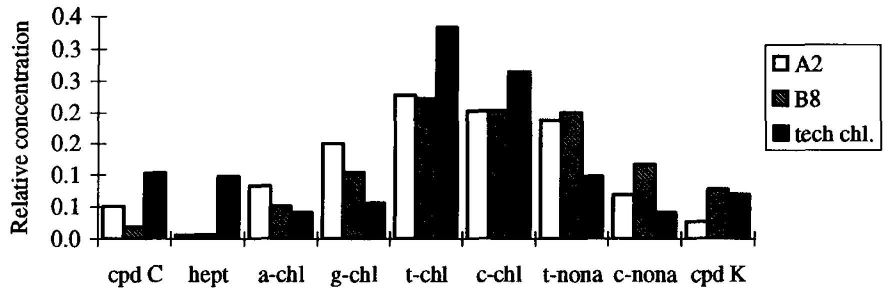

Figure 2. Concentrations of the chlordane components in soil extracts.

The increased volatility of the lighter chlordane components may provide a better explanation for why sample B8 contained lower relative amounts of compound C and Heptachlor. The heavier components, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and compound K constitiute 82% of the total chlordane residues found in B8 (site surface), which is significantly different to the average of 74% for all other samples and 68% in technical chlordane. However this explanation fails to account for the enhanced levels of γ-chlordene in the environmental extracts (see Figure 2). Therefore relative rates of volatilisation alone do not account for all the inter-sample differences. Other environmental processes must also result in important changes to the chlordane residue profile.

It has been established that inadvertant chlordane release from New Zealand timber treatment facilities can provide large point sources of chlordane. There are estimated to be 400 treatment sites in New Zealand (Shaw 1990) of which an unknown number use or have used chlordane. The data presented here indicate that there is a significant risk of chlordane residues on these sites contaminating the surrounding environment. Pollution control measures should be undertaken immediately to limit such contamination.

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