Marine Sediment Contaminant Monitoring: Organic Contaminant Data Review 2003-2010

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Marine Sediment Contaminant Monitoring: Organic Contaminant Data Review 2003-2010

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Executive Summary

This document provides a review of organic contaminant data in marine sediments sampled in Auckland Council (AC), and the former Auckland Regional Council (ARC), monitoring programmes.

The aims of the review are to:

- Summarise the organic contaminant "status" of Auckland's marine sediments, as indicated by comparison of contaminant concentrations with sediment quality guidelines for the protection of benthic ecological health (ARC 2004);
- Assess the quality of the organic contaminant monitoring data and its suitability for measuring concentrations in Auckland's marine sediments; and
- Make recommendations for future organic contaminant monitoring.

The review focuses on the "organochlorines" (OCs) – organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). These are legacy "persistent organic pollutants" (POPs), which are no longer legally used in New Zealand, but remain in the environment as a result of their slow rates of degradation. OCPs were historically used in horticulture and agriculture, and PCBs in a wide range of industrial applications and domestic products, including electrical insulators, flame retardants, and some plasticisers.

A description of the sediment contaminant monitoring programme's purpose and design, and review of other key chemical contaminants (metals and polycyclic aromatic hydrocarbons; PAH), have been provided in a previous Auckland Council report (Mills et al. 2012).

Organochlorine Status

Contaminant "status" was assessed by comparison with Environmental Response Criteria (ERC; ARC 2004). The ERC for organic contaminants are expressed in "total organic carbon (TOC) normalised" concentration units. This method provides compensation for decreased bioavailability (and hence potential toxicity) of organic contaminants in sediments with higher levels of organic carbon. There is some uncertainty about the appropriateness of this approach (see section 3.1), so status was also assessed by comparison with non-normalised concentrations. Because both approaches have been used, and allowance has been made for the moderate level of uncertainty associated with much of the analytical data, the status classifications were not always clear cut. However, it is considered that this provides a more realistic assessment than would have been obtained by a rigid comparison with ERC thresholds.

The status of organochlorine pesticides and PCBs was assessed from data collected from surveys carried out in 2003 and 2007 at former State of the Environment (SoE) monitoring programme sites, and from rural/low density urban estuary sites sampled in 2009 and 2010.

Nine (possibly 10) of the 27 SoE sites had OCP concentrations in the ERC-Red range in samples taken in 2003. Six of these 10 ERC-Red SoE sites were reassessed in 2007 and were found to have lower concentrations than were reported in 2003. Only two of the six sites reassessed in 2007 had OCP concentrations approaching ERC-Red levels, and none were above ERC-Red thresholds when concentrations were expressed in organic carbon-normalised units (as defined by

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ERC). DDTs and dieldrin were the only OCPs that reached ERC-Red levels in either the 2003 or 2007 surveys.

The usefulness of the PCB data for SoE sites was limited by a high analytical detection limit (DL) in the 2003 survey, which resulted in most data being below DL. This prevented reliable comparisons with ERC. However, based on the very limited results it is conceivable that there may be sites in the more heavily contaminated estuary zones around Auckland (e.g. muddy industrial Tamaki Estuary sites, muddy Waitemata Harbour sites in older developed catchments) that might approach, or exceed, the ERC-Red threshold for PCBs.

Pesticide and PCB levels at the rural/low density urban estuary sites sampled in 2009 and 2010 were assessed using more sensitive analytical methods with low DLs. Concentrations were found to be very low, well below ERC-Red levels, and at many sites little higher than analytical laboratory blank levels (i.e. the concentrations due to the reagents and sample handling within the lab, rather than present in the samples). These results indicate no significant contamination by these OCs at these locations.

Status assessment at the SoE sites showed that sites with elevated (ERC-Red) concentrations of OCPs (DDTs and/or dieldrin) also had high metals' concentrations, in particular zinc (Zn). The addition of the OCP data therefore did not change the ERC status of any sites (except possibly at Mangere Cemetery, where the status may have changed from ERC amber to red, but this was marginal).

Data quality

The analytical data reviewed was highly variable in its "quality" – i.e. its suitability for assessing the (generally) low OC concentrations found in Auckland's marine sediments. Data was grouped into "screening", "semi-quantitative", and "quantitative" categories based on detection limits (DLs), quality assurance (QA) information, and quantitation protocol (e.g. recovery correction).

Much of the data from surveys conducted in 2003 and 2007 at SoE sites was classed as "semi-quantitative" or "screening" data, which limited its usefulness in quantitatively defining contaminant concentrations.

More recent data, the 2009 and 2010 surveys of rural/low density urban estuaries (Kaipara, Mahurangi, "7 estuaries", Whangateau), was analysed using sensitive quantitative methods. This provided high quality baseline data for these locations, and showed that only very low OC concentrations were present (well below ERC-Red thresholds at all sites).

Any future OC analyses must use these high sensitivity (and currently high cost) analytical methods in order to obtain reliable quantitative data that is suitable for comparison with guidelines and for analysis of trends.

Emerging contaminants

"Emerging contaminants" or "chemicals of potential environmental concern" (CPEC) are a very broad class of chemicals found in many products of day-to-day use, which are often manufactured or consumed in high-volume. They include, among others, plasticisers, flame retardants, pharmaceuticals and personal care products, detergents and other cleaning agents, various petroleum products, pesticides and biocides (e.g. weed killers, fumigants, wood preservatives,

antifouling agents), and compounds derived from wastewater and drinking water treatment, landfill or incineration.

CPECs of potential relevance for the Auckland region were reviewed by Ahrens (2008). Based on this review, a scoping study of sediments from 13 estuarine locations around Auckland was undertaken in 2008, with samples analysed for 34 of the key CPEC that could be analysed by commercial laboratories at the time (Stewart et al. 2009). These samples were later also analysed for pharmaceutical residues (Stewart 2013).

The CPEC data indicated that residues of some emerging contaminants are present, at widely varying concentrations, in Auckland's estuarine sediments. The significance of CPECs with respect to urban runoff impacts is yet to be determined, but elevated concentrations (i.e. above DLs) of polybrominated diphenyl ethers (PBDE flame retardants), phthalates (plasticiser), glyphosate (herbicide) and possibly dithiocarbamates (fungicides) have been reported at urban monitoring sites. The initial data suggest that sewage discharges (as indicated by Puketutu Island data) – perhaps historically, rather than current – may be significant sources of some key contaminants (e.g. PBDEs).

The concentrations of pharmaceuticals were in the parts per billion (ppb or ng/g) range. A preliminary examination of the spatial distribution of these chemicals suggests that sites potentially influenced by treated wastewater discharge or wastewater overflows, and possibly historical landfills, may have higher concentrations of most of the surveyed pharmaceuticals. Stewart (2013) recommended further investigation of pharmaceuticals in raw and treated wastewaters, development of analytical capability for testing residues of pharmaceuticals most relevant to New Zealand (NZ), and toxicological studies to determine the effects of key chemicals on NZ biota.

Recommendations for future monitoring

There are currently few robust quantitative data for OCPs and PCBs at urban monitoring sites in Auckland. Therefore, there is a limited baseline from which to assess contaminant distributions (status) or trends. Conducting baseline analysis at a broad range of sites, in particular "high risk" urban sites (as indicated by metals' concentrations) might therefore seem worth considering.

However, because of the high analytical cost associated with reliable OC analysis, the apparent correlation between metals concentrations and OCP levels, and the likelihood of generally declining OC levels in the environment, the value of undertaking these analyses at a wide range of sites is uncertain.

Shellfish bioaccumulate OCs, and therefore contain higher concentrations than their surrounding environment (water or sediment). These higher concentrations provide a more sensitive indicator of ambient concentrations. Continued use of shellfish monitoring may therefore be a better alternative to sediment analysis for tracking broad-scale trends over time in OCP and PCB levels.

Overall, while the existing data are fairly limited, some general conclusions about the probable relevance of OCPs in Auckland's marine sediments were reached. The data suggest that the OCP concentrations are likely to follow similar spatial patterns to metals (particularly Zn), with elevated levels generally associated with sites influenced by heavily urbanised/industrialised catchments, and possibly point sources of contamination (e.g. landfills).

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Because there appears to be a relationship between OCP levels and metals' concentrations, further analysis of OCPs would probably provide little extra beneficial information for contaminant status assessment. From this point of view, it seems there is no great value in conducting further OCP analyses. However, targeted sampling of sites where benthic ecology is worse than would be expected from the concentrations of key metal contaminants may still be of some benefit.

PCB data are very limited. Analysis of key "high risk" sites (e.g. urban sites with elevated metals' concentrations) would be worthwhile to provide a better perspective on the probable importance of this group of contaminants. As recommended for OCPs, high sensitivity analytical methods, with good quality assurance, are required to obtain reliable PCB data.

Continued investigation of emerging contaminants is warranted. Development of analytical capability for testing residues of compounds most relevant to NZ, and toxicological studies to determine the effects of key chemicals on NZ biota, should be undertaken. Initial focus should probably be given to understanding the composition and concentrations of emerging contaminants in key contaminant sources (e.g. raw and treated wastewaters, landfill leachates), and at receiving environment sites directly affected by these sources. As analytical capabilities are developed and demonstrated to be capable of producing reliable results at lower concentrations, monitoring a broader range of sites could be undertaken.

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1.0   Introduction

1.1   Purpose

This document provides a review of organic contaminant data in marine sediments sampled in Auckland Council, and the former Auckland Regional Council, monitoring programmes.

The aims of the review are to:

- Summarise the organic contaminant "status" of Auckland's marine sediments, as indicated by comparison of contaminant concentrations with sediment quality guidelines for the protection of benthic ecological health (ARC 2004);
- Assess the quality of the organic contaminant monitoring data and its suitability for measuring concentrations in Auckland's marine sediments; and
- Make recommendations for future organic contaminant monitoring – sites, methods, and contaminants which, based on the information reviewed, should be the focus for any future efforts.

1.2   Contaminants covered in this review

The review focuses on the "organochlorines" (OCs) – organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). These are legacy "persistent organic pollutants" (POPs), which are no longer legally used in New Zealand (Scobie et al. 1999), but remain in the environment as a result of their slow rates of degradation. OCPs were historically used in horticulture and agriculture, and PCBs in a wide range of industrial applications and domestic products, including electrical insulators, flame retardants, and some plasticisers.

These contaminants enter Auckland's marine receiving waters largely as a result of runoff from horticultural (or ex-horticultural) land and from urban stormwater runoff. High localised concentrations are also found in port and wharf areas (e.g. Devonport Naval Base, and Ports of Auckland) due to historical activities associated with operations in these areas.

The OCs are considered to be contaminants of "secondary" importance for potential effects of Auckland's urban stormwater discharges on marine receiving environments (ARC 2004). This is because their use in NZ has been discontinued, and therefore inputs into the marine environment should be decreasing over time.

Another key group of organic contaminants sourced from urban activities are the polycyclic aromatic hydrocarbons (PAHs). Sources of PAHs include combustion of fossil fuels (e.g. vehicular exhaust), oil spills/leaks, and historical use of coal tar in roading. Because they continue to be produced and discharged into the environment, PAHs (along with metals such as zinc (Zn), copper (Cu), and lead (Pb)) are considered to be primary contaminants of concern for stormwater impacts (ARC 2004). An assessment of status and trends in PAHs has been reported elsewhere (Mills et al. 2012), and therefore PAHs have not been included in this review.

A brief summary of results for "emerging contaminants" – a very broad class of chemicals found in many products of day-to-day use, which are often manufactured or consumed in high-volume –

has also been included, based on data collected in a scoping study undertaken in 2008 (Stewart et al. 2009) and subsequent analyses of pharmaceuticals from the same samples (Stewart 2013)..

Scobie et al. (1999), and the Ministry for the Environment website – http://www.mfe.govt.nz/publications/hazardous/stockholm-convention-pops-dec06/html/page5.html – provide details of organochlorine use and regulation in NZ. Drawing on these information sources, the following sub-sections provide a brief overview of the OCPs, PCBs, and "emerging contaminants".

1.3   Organochlorine pesticides

Persistent organochlorine pesticides, including DDT, dieldrin and lindane, were used heavily in New Zealand from the mid-1940s until the 1970s. Although few records were kept of the volumes imported into the country, the most substantial quantities are likely to have been imported during the 1950s and 1960s. The main areas of use were agriculture, horticulture, timber treatment and public health. Smaller amounts were also used for amenity purposes (e.g. turf care) and in households.

The use of pesticides in New Zealand was not subject to compulsory regulatory control until the Agricultural Chemicals Act 1959 established the Agricultural Chemicals Board. The use of persistent organochlorine pesticides was then progressively restricted by a succession of legislation, so that, by the mid 1970s their use had effectively ceased in agriculture and horticulture. All persistent organochlorine pesticides except pentachlorophenol (PCP) were formally deregistered by the Pesticides Board in 1989, and PCP was deregistered in 1991.

Key OCPs used in NZ, and included in the analyses reviewed in this report, are as follows.

DDT: A pasture insecticide used to control grass grub and porina caterpillars. Frequently mixed with fertiliser or lime and applied to agriculture pastures, as well as lawns, market gardens and parks. There are six compounds making up "Total DDT" – the o,p'- (or 2,4'-) and p,p'- (or 4,4'-) isomers of DDE, DDD, and DDT. The relative abundances of these compounds can provide information on the weathering of the original parent material (predominantly p,p-DDT).

Lindane: Gamma hexachlorocyclohexane (γ-HCH). Used as an insecticide in agriculture for the control of lice on cattle, ectoparasites in sheep and grass grub in pasture. Also used for insect control on vegetables and in orchards. Household uses included fly spray, flea control, and carpet moth. Commercial hexachlorocyclohexane (HCH) was not officially used in New Zealand, although many dip sites show evidence of the use of crude HCH.

Aldrin and **Dieldrin**: Introduced in 1954 for use as stock remedies in sheep sprays or dips for controlling sheep ectoparasites. Aldrin was used to control horticultural pests such as wireworm, soldier fly and blackvine weevil, and in limited quantities to control household spiders. Dieldrin was used for controlling carrot rust fly, crickets and armyworm and was also used for timber preservation (mostly in plywood glues) and to mothproof carpets.

Chlordane: Technical chlordane is a complex mixture of over 50 different chlorinated cyclodiene compounds, including chlordene, cis- (or alpha) chlordane, trans- (or gamma) chlordane, heptachlor, and nonachlors. Broad spectrum agricultural insecticide, also used in the timber

industry as a treatment against termites and borer, and as an insecticide in glues used for the manufacture of plywood, finger jointed and laminated timber.

Hexachlorobenzene (HCB): Used experimentally between 1970 and 1972 as a seed dressing fungicide for cereal grain.

Heptachlor and **Endrin:** Only small amounts of these pesticides were ever used in New Zealand.

Endosulfan: This is an OCP insecticide that has been used in New Zealand to control various insect pests on a range of vegetable crops, berries, and ornamentals. It was also used for earthworm control in turf at parks, sports grounds etc. The technical formulation comprises two structurally similar compounds with the same molecular formula (stereoisomers), endosulfan I and II, in an approximately 70:30 ratio. It is moderately persistent in receiving environments and is bioaccumulative. A major degradation product is endosulfan sulphate, which is generally more persistent than the parent compounds and is of similar toxicity. Use of endosulfan was prohibited in NZ from January 2009.

Of these OCPs, the most prevalent compounds found in marine receiving water sediments and biota in Auckland are DDTs (usually dominated by DDE and DDD rather than the parent DDT), dieldrin, and (in biota) chlordane (Kelly 2007).

1.4   Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a complex group of chemicals based on the biphenyl molecule with 2 to 10 chlorine atoms attached. There are 209 possible compounds ("congeners") formed in this way. Technical PCB mixtures contain a large number of congeners, the distribution depending on the amount of chlorine used in the manufacture. Each congener is given a code (e.g. PCB 138 is 2,2',3,4,4',5'-Hexachlorobiphenyl), with congener codes generally increasing with a greater level of chlorination.

In the environment, the PCB mixture is typically dominated by mid-to-higher chlorinated congeners (penta- to heptachloro), which were dominant in some of the commonly used technical products, have a greater number of possible congeners, and are more environmentally persistent because of low water solubility and low volatility (compared with lower chlorinated congeners).

PCBs have a range of highly desirable properties – they are not flammable, have high electrical resistance, good insulating properties and are very stable even when exposed to heat and pressure. This made them ideal for insulators in transformers and capacitors, and for a myriad of other applications including hydraulic fluids, heat transfer systems, plasticisers, pigments, adhesives, liquid cooled electric motors, and fluorescent light ballasts.

Unfortunately, they are also toxic (ecotoxic, and also toxic to animals and humans, including probable carcinogenicity), persistent, and bioaccumulative. Note that PCB toxicity is related to their spatial structure. The most toxic PCBs (at least to humans) are the "coplanar" species (PCBs 77, 126, and 169), which have dioxin-like toxicity. These compounds made up <1% of commercial PCB mixtures, and are therefore present at only very low concentrations in the environment.

PCBs were never manufactured in New Zealand, but were imported and used extensively in the electricity industry as insulating fluids or resins in transformers and capacitors. PCBs were also

used in smaller quantities as heat transfer fluids, plasticisers, printing inks, flame retardants, paint additives, sealing liquids and immersion oils.

An active programme to remove PCBs from NZ began in the mid-1980s, and peaked in the mid-1990s. PCBs and associated wastes were shipped to Europe for destruction by high temperature incineration. Approximately 1470 tonnes of PCBs (including PCB contaminated material) were exported from New Zealand from 1987 to 2004. Over 90% of the significant PCB holdings (comprising high volumes and/or high-risk locations such as schools, hospitals and export industries) in New Zealand have now been withdrawn and disposed of. However, small amounts of PCBs, possibly more than 100 tonnes, could still be present across the country, in older fluorescent tube ballasts (ca. 75%) and in other capacitors (25%).

1.5   Emerging contaminants

"Emerging contaminants" or "chemicals of potential environmental concern" (CPEC) are a very broad class of chemicals found in many products of day-to-day use, which are often manufactured or consumed in high-volumes. They include, among others, plastics, resins and plastic additives (plasticisers, flame retardants), pharmaceuticals and personal care products (e.g. disinfectants, antibiotics, fragrances, sunscreens, drugs, natural and synthetic hormones), detergents and other cleaning agents, various petroleum products, pesticides and biocides (e.g. weed killers, fumigants, wood preservatives, antifouling agents), and compounds derived from wastewater and drinking water treatment, landfill or incineration.

In contrast to the classic "priority organic pollutants" (e.g. OCPs, PCBs, PAHs), which have high environmental persistence, high bioaccumulation and high acute toxicity, many CPECs have a somewhat lower environmental hazard profile. Nevertheless, some CPECs have the potential to exert chronic adverse effects by being neuroactive, acting as hormone mimics (endocrine disrupting chemicals), or having significant carcinogenicity.

The on-going consumption of high production volume chemicals, including some CPECs, increases the potential for accumulation of these substances in receiving environments, and therefore for causing adverse effects on ecological health.

CPECs of potential relevance for the Auckland region were reviewed by Ahrens (2008). This review identified 42 CPECs, including flame retardants, plasticisers, estrogens, antifoulants and pesticides, and ranked them along with priority organic pollutants (POPs) according to their potential significance and relative environmental hazard. Highest environmental hazard ratings were assigned to POPs (such as OCPs and PCBs), and landfill and incinerator wastes, due to the large number of compounds present; some of which have high persistence, bioaccumulation and toxicity. Lowest environmental hazard was assigned to organic peroxides (due to their short life-time) and food additives. Among specific chemicals of potential environmental concern, halogenated flame retardants, surfactants (and metabolites), and certain pharmaceuticals and personal care products (notably oestrogens) ranked highly; mostly as a result of high persistence and bioaccumulation as well as their elevated potential to cause endocrine disruption.

Based on this review, a scoping study of sediments from 13 estuarine locations around Auckland was undertaken in 2008, with samples analysed for 34 of the key CPECs that could be analysed

by commercial laboratories at the time (Stewart et al. 2009). Subsequently, a range of common pharmaceuticals was also analysed on these samples (Stewart 2013). The findings are summarised later in this review (section 5.0).

2.0 Data used in this review

The contaminants monitored, sample sites and sample numbers, and analytical providers, methods and detection limits (DLs) are summarised in Table 2-1 and Table 2-2. An overall assessment of the quality of the data is also provided, based on the analytical methods used, the DLs, and quality assurance (QA) information provided. Raw data for SoE site monitoring from 2003 and 2007 can be found in Reed and Webster (2004), and Reed and Gadd (2009), respectively.

2.1 Data categorisation

Based on the assessment of the analytical data, the available data have been categorised as follows:

- **"screening" data** – these are unlikely to be quantitatively accurate, due to a combination of high DLs, simple analytical methods that are more prone to interferences and potential misidentifications, and lack of comprehensive laboratory QA data (e.g. surrogate/spike recovery data, blank results, Certified Reference Material (CRM) results). While their quantitative reliability may be limited, screening data are still useful for "range finding" (i.e. establishing the general order of magnitude of contaminant concentrations) and possibly for identifying locations with markedly higher contaminant levels;

- **"semi-quantitative" data** – these are quantitatively more robust than the screening data, as a result of employing better analytical methods (e.g. with lower DLs and/or higher resolution) and/or more comprehensive QA data. These analyses are conducted using robust extraction, clean up and instrumental identification/quantitation methods, which reduce interference and improve the reliability of unambiguous compound identification. However, the results may only be "semi-quantitative" (or quantitative in a broad sense) because of a wide range of acceptable compound recoveries (e.g. 40–120%), which are not "recovery corrected" (e.g. from surrogate internal standards). The "semi quantitative" data are suitable for comparing sites and for tracking general trends over time, but the limitations in their accuracy/precision needs to be taken into account when doing so, to ensure conclusions drawn from the data are consistent with the data quality; and

- **"quantitative" data** – these data have been acquired using robust analytical methods, with low DLs appropriate for the types of samples being analysed, and have comprehensive QA data (including blanks, surrogate recoveries, and/or CRM results). Correction for analyte losses during analysis using surrogate spikes within each sample is a feature of these data. These data can confidently be used for trend detection and comparison with guidelines.

As summarised in Table 2-2, much of the OCP and PCB data acquired in the monitoring programmes reviewed here would be classed as screening or semi-quantitative, due to a combination of high DLs (relative to the concentrations present in Auckland sediments) and/or a lack of comprehensive QA information (which prevented confirming the quantitative accuracy of the results). In contrast, the PAH data used in the "Status and Trends" assessment (Mills et al. 2012) is considered quantitative, having the analytical method and QA attributes listed above.

2.2 Data reviewed

The data included in this review, categorised as outlined above, were as follows.

Screening results were obtained for OCPs from 27 sites in the former ARC SoE programme, sampled in 2007 (Reed and Gadd, 2009). Detection limits were 10 ng/g per compound, which is approximately 50–100 times too high to be useful for trend detection or comparison with guidelines at most sites. Samples from 9 of these sites were subsequently reanalysed using quantitative methods with much lower DLs.

Semi-quantitative results were obtained for OCPs and PCBs sampled in 2003 from 27 SoE programme sites. Detection limits were 0.5 ng/g for individual OCPs, and 1 ng/g for individual PCB congeners. These DLs are too high for robust trend detection or comparison with guidelines by a factor of about 5–10 times, especially for PCBs, as evidenced by < DL values being recorded for most compounds at many sites. Because the ambient concentrations of OCPs and PCBs were mostly close to (or below) analytical DLs, the accuracy and precision of the data are likely to be relatively low. Blind duplicate analysis results showed substantial differences between results for some samples, and also high variability between replicates from the same site (Reed and Webster 2004). No laboratory blank or surrogate/spike recovery data were provided for these analyses.

Quantitative results have been obtained from:

- sampling undertaken in the Whangateau Harbour (7 sites, collected in 2009), Kaipara Harbour (6 sites collected in 2009), Mahurangi Harbour (2 sites collected in 2009), and the "7 estuaries" programme (one site in each of Puhoi, Orewa, Okura, Waikopua, Waiwera, Mangemangeroa, and Turanga estuaries, collected in 2010). These sites were sampled to increase regional data coverage and assess background levels. The sampling locations covered by these surveys are generally rural or low density urban/rural, and hence are likely to have low contaminant levels. However, estuaries in rural catchments may also be subject to inputs of legacy OCPs as a result of soil disturbance during development. Sites for OC analysis were selected to target locations with highest probable contaminant levels (based on metals' data and sediment texture). Sampling was undertaken by NIWA, as part of benthic ecology assessments (e.g. Hailes et al. 2010; Halliday and Cummings 2012; Townsend et al. 2010). Samples were analysed for OCPs and PCBs.
- nine sites from the SoE programme, sampled in 2007. Eight of the nine sites were urban, and one (Paremoremo) is largely rural (but with some urban influence). These samples were analysed for OCPs (Reed and Gadd, 2009).

The emerging contaminant data obtained in the NIWA scoping study (Stewart et al. 2009, Stewart 2013) were a mix of screening data (e.g. dithiocarbamates, biocides, plasticisers), semi-quantitative (steroid hormones) and quantitative (polybrominated diphenyl ethers – PBDEs). This reflects a lack of quantitative analytical methods available for many of these compounds at the relatively low concentrations they are found in receiving water sediments. The emerging contaminant data have not been assessed in detail here, since the survey was a scoping/research study and is not part of the routine regional sediment contaminant monitoring undertaken by Auckland Council. A brief review of the initial survey data was given by Mills (2008).

In summary, using the criteria outlined above, there are good quality quantitative OCP data for very few (8) urban sites. Most of the urban site data are semi-quantitative or screening level quality. There are good quality OCP and PCB data for the largely rural sites covered in the Whangateau, Kaipara, Mahurangi, and "7 estuaries" surveys.

Site locations are shown in Figure 2-1.

Figure 2-1 Locations of sites where organochlorine pesticides, PCBs and emerging contaminants have been analysed.

Table 2-1 A summary of samples taken for analysis of organochlorines in Auckland's marine sediment monitoring programmes.

Contaminant Group		Sampling					
Class	No. of Compounds	Year	Programme	Sites	Reps per site	Sampler	Data Reports
OCP	23	2003	SoE	27	3	ARC	Reed & Webster (2004)
	23	2007	SoE	27	3	ARC	Reed & Gadd (2009)
	24	2007	SoE	9	1 composite	ARC	Reed & Gadd (2009)
	26	2009	Whangateau Hbr	7	1 composite	NIWA	DSL data report to ARC & NIWA (2011)
	26	2009	Kaipara Hbr	6	1 composite	NIWA	DSL data report to ARC & NIWA (2011)
	26	2010	Mahurangi Hbr	2	1 composite	NIWA	DSL data report to ARC & NIWA (2011)
	26	2010	"7 estuaries"	7	1 composite	NIWA	DSL data report to ARC & NIWA (2011)
PCB	33	2003	SoE	27	3	ARC	Reed & Webster (2004)
	52	2009	Whangateau Hbr	7	1 composite	NIWA	DSL data report to ARC & NIWA (2011)
	52	2009	Kaipara Hbr	6	1 composite	NIWA	DSL data report to ARC & NIWA (2011)
	52	2010	Mahurangi Hbr	2	1 composite	NIWA	DSL data report to ARC & NIWA (2011)
	52	2010	"7 estuaries"	7	1 composite	NIWA	DSL data report to ARC & NIWA (2011)

Table 2-2 A summary of analytical methods used for organochlorine analyses

Group	Year	Programme	Analysis		D.L. (ng/g)	Quality Assurance Reported			Recovery Corrected?	Classification
			Lab	Method		Blanks	CRM	Duplicates		
OCP	2003	SoE	R.J. Hill	Extraction, GPC/SPE cleanup, GC-ECD	0.5	NR	NR	Yes (5)	No	Semi-quantitative
	2007	SoE	R.J. Hill	Extraction, GPC/SPE cleanup, GC-ECD	10	NR	NR	NR	No	Screen
	2007	SoE	AsureQuality	USEPA 1699, HRGC/MS Isotope Diln	0.01 - 4.5	Yes	NR	No	Yes	Quantitative
	2009	Whangateau Hbr	AsureQuality	USEPA 1699, HRGC/MS Isotope Diln	0.006 - 0.55	Yes	NR	No	Yes	Quantitative
	2009	Kaipara Hbr	AsureQuality	USEPA 1699, HRGC/MS Isotope Diln	0.004 - 0.18	Yes	NR	No	Yes	Quantitative
	2010	Mahurangi Hbr	AsureQuality	USEPA 1699, HRGC/MS Isotope Diln	0.003 - 0.09	Yes	NR	Yes (1)	Yes	Quantitative
	2010	"7 estuaries"	AsureQuality	USEPA 1699, HRGC/MS Isotope Diln	0.004 - 0.21	Yes	NR	Yes (1)	Yes	Quantitative
PCB	2003	SoE	R.J. Hill	Extraction, SPE cleanup, GC/MS	1	NR	NR	Yes (5)	No	Semi-quantitative
	2009	Whangateau Hbr	AsureQuality	USEPA 1668A, HRGC/MS Isotope Diln	0.0001 - 0.02	Yes	NR	No	Yes	Quantitative
	2009	Kaipara Hbr	AsureQuality	USEPA 1668A, HRGC/MS Isotope Diln	0.0001 - 0.01	Yes	NR	No	Yes	Quantitative
	2010	Mahurangi Hbr	AsureQuality	USEPA 1668A, HRGC/MS Isotope Diln	0.0002 - 0.01	Yes	NR	Yes (1)	Yes	Quantitative
	2010	"7 estuaries"	AsureQuality	USEPA 1668A, HRGC/MS Isotope Diln	0.0002 - 0.02	Yes	NR	Yes (1)	Yes	Quantitative

Notes:

RJ Hill Labs' methods are based on USEPA methods 3540 and 3611, with solvent extraction, solid phase extraction (SPE) and gel permeation chromatography (GPC) clean up, and gas chromatography/mass spectrometry in selective ion monitoring mode (GCMS-SIM) for PCB and dual column electron capture detection (GC-ECD) for OCP. Trace method DLs are usually 1 ng/g (ppb) and include GPC and SPE clean up. Screening level methods have DLs of 10 ppb and have SPE cleanup only.

AsureQuality analyses are based on high resolution gas chromatography/mass spectrometry (HRGC/MS) using isotope dilution for quantitation (including recovery correction). DLs vary between compounds and samples. Endosulfans had higher DLs than other compounds.

"NR" - not reported. "CRM" - Certified Reference Material. Duplicates - number of duplicates analysed in the analytical batch given in brackets.

2.3 Data treatment and graphical presentation

2.3.1 Concentration units

The concentration units used in this review are parts per billion (ppb). The abbreviations used for ppb include μg/kg (micrograms per kilogram) and ng/g (nanograms per gram).

The abbreviation ng/g has been chosen as the preferred notation because of its simplicity, and because it is not susceptible to being changed to mg/kg (parts per million) due to font changes during report editing affecting the symbol used for micrograms.

Concentrations have also been expressed in "TOC-normalised" units, where the concentration is given as ng/g at 1% Total Organic Carbon (TOC). These units are obtained by dividing the dry weight concentration (in ng/g) by the TOC content (in per cent) of the sediment. Comparison with sediment quality guidelines (SQG), for example the ARC "Environmental Response Criteria" (ERC; section 3.0) may require use of TOC normalised units.

All samples analysed for OCPs and PCBs reviewed here were analysed on freeze dried, < 500 μm (< 0.5 mm) sieved sediment. The concentrations therefore apply to this fraction of the sediment, which in reality represents essentially all the sediment at the sites surveyed (i.e. there is generally very little material > 500 μm present).

2.3.2 Less than detection limit values

The relatively low concentrations of OCs requires sensitive analytical methods to obtain data above DLs. Many of the data collected to date for the Auckland sediments were below DLs (< DL), partly because the concentrations at many sites are low, and partly because the analytical methods used in the 2003 and 2007 surveys had DLs that were high relative to ambient concentrations.

In addition to DLs differing between surveys, for the data from AsureQuality, DLs also differed between samples and analytes (which is entirely realistic because of the differing sensitivity, and varying levels of matrix interference, for different compounds).

The high and variable DLs create problems for comparing data obtained between surveys, between sites, and for calculating contaminant group totals (e.g. Total DDTs, Total PCBs).

In an attempt to summarise the data in the most transparent way, < DL values have been treated in two ways when calculating (and plotting) group totals (total DDTs, chlordane, PCBs):

- treating the < DL values as equal to zero. This provides an indication of the lower bound of the actual group total concentration. This method was used when comparing data from the 2003 survey (high DLs) with the 2007 data (low DLs); and
- including the < DL values as being equal to the DL. This provides an upper limit to the group total concentration. This method was used when plotting the data, to show the contribution that the < DL values made to the totals (explained further below).

The "real" concentration is likely to lie somewhere between these two bounds. For this reason, < DL values are often treated as 0.5 times the DL. Because of the variable and often high DLs in the data reviewed here, it was considered more appropriate to show the actual range of values, including presenting the < DL values at the DL.

Summary plots of the OCPs (Total DDT and dieldrin) and PCBs (sum of seven major congeners) distinguish the contributions from both the < DL and > DL values to the group totals. The sum of the < DL values (treated as equal to DL) have been shown in blue and those above DL in orange. The combined height of both bars therefore represents the maximum possible total concentration, where < DL values have been treated as equal to the DL.

Where laboratory blank data were available, these have also been shown – for the rural estuary sites the contaminant concentrations were often comparable with the blanks, so including the blank data in the plots provides a useful "reality check" for assessing whether these very low levels are real (present in the environment) or largely due to the influence of the laboratory analysis process.

2.3.3 Medians used for data averaging

The 2003 survey of SoE sites analysed three replicates per site. As outlined above, many values were below DL, or had a mix of above DL and below DL values. Some had anomalously elevated concentrations for one replicate. This was possibly an artefact of using a semi-quantitative analytical method with relatively high DLs. It is also possible that a high degree of variability occurs between replicates. However, this seems unlikely given the degree of homogenisation and across-site averaging achieved by the sampling protocol (ARC 2004).

To provide a robust indicator of site "average" concentrations with these data, the median value of the three replicates was used. This reduced the influence of the occasional high values.

The exception to this approach was for DDTs at Meola Inner in the 2003 survey. The initial set of results gave Total DDTs (< DL values treated as = 0) of 8.8, 244, and 70 ng/g for each of the three replicates. The concentrations in replicates 2 and 3 were very high, and were mostly p,p'-DDT, indicating the presence of unweathered parent DDT. This was considered unusual, so analysis of archived replicates 4 and 5 was undertaken. These further analyses gave much lower concentrations, more consistent with replicate 1. The "average" DDT concentrations for Meola Inner used in the status assessment was therefore the median of *all* the analyses undertaken (n = 7). For Total DDT (< DL = 0), this gave a median of 13 ng/g, compared with the original data (n = 3) of 70 ng/g.

The high level screening data from the 2007 survey (DLs of 10 ng/g) did not detect DDT at the high levels found in the initial results from the 2003 survey. This provided additional support for the use of the reanalysis data, and the lower median concentration used for the 2003 data set.

Note that the reanalysis results were not reported in Reed and Webster (2004) as they were undertaken after the publication of that report.

2.3.4   Comparisons with Environmental Response Criteria (ERC) thresholds

As discussed further in section 3.0, the concentrations of organochlorines have been compared with the Environmental Response Criteria (ERC) to assess potential adverse ecological effects.

Because the analytical data acquired in 2003 are considered to be only semi-quantitative, and are likely to have considerable margins of uncertainty, it was considered prudent to include values within 10% of the ERC-Red value as possibly exceeding the threshold. Values in this category have been identified in the relevant status assessment tables shown in section 3.0.

2.3.5   PCB data from the 2003 survey

The DL for the PCB analyses conducted in 2003 was 1 ng/g per congener. A total of 33 congeners were analysed. Two of these, PCBs 28 and 31, were co-eluted, giving a total of 32 quantified compounds, and a DL for Total PCBs of 32 ng/g. This is well above the ERC-Red threshold of 22 ng/g. Therefore assessing the ERC status of PCBs was not possible.

However, the definition of "Total PCBs" for comparison with sediment quality guidelines is unclear. Generally about 30 or so individual PCB congeners are measured to provide a Total PCB value. However, a substantial proportion of the total PCBs is made up from a smaller number of dominant PCB congeners, the exact makeup varying depending on the PCB source(s). For sites impacted by diffuse pollution , tetra-, penta-, hexa-, and hepta-chlorinated congeners generally make up most of the total PCB concentrations (with penta- and hexa-chlorinated congeners dominating).

For example, the highest Total PCB concentration that the author has measured in Auckland estuary sediments (apart from specific contaminated sites) was 34 ng/g (from a contaminated Tamaki Estuary site sampled in 1995; Nipper et al. 1998). The total PCB was the sum of 28 congeners, with DLs of 0.05–0.1 ng/g. Of this total, approximately 88% was made up from 13 dominant tetra- to hepta-chlorinated congeners (PCBs 52, 101, 151, 118, 153, 105, 141, 138, 187, 128, 156, 180, and 170).

In the 2003 survey of SoE sites, seven congeners were found above DLs at one of the sites (Whau Wairau), with a maximum concentration of any one congener of 4 ng/g (which is not substantially above the DL of 1 ng/g). Only nine of the 27 sites had median Total PCB concentrations above DLs (see Figure 3-3).

These seven congeners (PCBs 101, 110, 118, 138, 149, 153, and 180) were summed at all sites to give a "Total PCB" concentration for data analysis and plotting. Five of these seven congeners were also analysed in the 1995 Tamaki sample described above – they made up approximately 60% of the Total PCBs in that sample.

In summary, the PCB analyses undertaken in 2003 had DLs that were too high for accurate quantitative assessment of the (generally) low PCB levels in Auckland sediments. The analyses were also insufficiently sensitive to provide robust comparisons with ERC. However, a partial sum using seven major congeners, has been used to provide a general indication of PCB concentrations. It is likely that this partial sum represents roughly 60% of a Total PCB concentration that would be obtained using lower DLs (0.05–0.1 ng/g). This proportion would vary depending on the range of PCB congeners analysed, site concentrations and PCB congener distribution, and on DLs.

3.0 Status Assessment

3.1 Environmental Response Criteria

The status of organic contaminants is assessed by comparing concentrations with sediment quality guidelines, the "Environmental Response Criteria" (ERC), published by ARC (2004). The ERC for OCPs and PCBs are listed in Table 3-1.

Table 3-1 Environmental Response Criteria (ERC) for secondary toxic organics (ARC 2004).

Values are concentrations, expressed in ng/g (μg/kg or parts per billion, ppb) at 1% total organic carbon (TOC) content.

Compound	ERC Green	ERC Red	Source
p,p'-DDE	< 2.1	>2.1	ISQG (CCME 1999)
p,p'-DDD	< 1.2	>1.2	ISQG (CCME 1999)
p,p-DDT	< 3.2	>3.2	ISQG (CCME 1999)
Total DDTs	< 3.9	>3.9	TEL (MacDonald et al. 1996)
chlordane	< 2.3	>2.3	ISQG (CCME 1999)
dieldrin	< 0.72	>0.72	ISQG (CCME 1999)
lindane	< 0.3	>0.3	ISQG (CCME 1999)
Total PCBs	< 22	>22	ISQG (CCME 1999)

ISQG = Interim Sediment Quality Guideline. TEL = Threshold Effects Level.

"Total DDTs" is the sum of o,p'- and p,p'- isomers of DDE, DDD, and DDT

"chlordane" is the sum of cis- and trans-chlordane

The ISQG and TEL are concentrations below which adverse effects on benthic ecological health are unlikely to occur. These guidelines are therefore fairly conservative, and act as an early warning of environmental degradation, which allows time for investigations into the causes of contamination to be carried out and options for limiting the extent of degradation to be developed.

ERC Green conditions reflect a low level of impact. Further investigations are not required unless significant changes in upstream catchment land use occur. The status is reassessed every 5 years.

ERC Red sites are higher impact sites where significant degradation has already occurred, and remedial opportunities are often more limited. Restoration of the site may not be feasible in the short term, but actions should be taken to slow the rate of contaminant accumulation and limit the spread of contaminants.

Unlike for metals and PAHs, there are no ERC-amber values for organochlorines. Exceedance of the ERC-Green concentrations triggers investigation of the sources and likely trends.

Note that the appropriateness of the 1% TOC normalisation adopted in the ERC (and by ANZECC guidelines) for organic contaminants is unclear. The guidelines upon which the ERC are based are expressed in ng/g (μg/kg or parts per billion; ppb) dry weight, not as TOC-normalised values. The

original "biological effects database for sediments" (BEDS; Long et al. 1995), which is the basis for the SQG derivation, uses chemical data in dry weight terms. It was noted that the TOC content of the sediments used in the BEDS usually ranged from 1–3% (average 1.2%), but chemical concentrations ranged over several orders of magnitude. The relatively small variation in TOC was considered relatively unimportant in influencing toxicity (Long et al. 1995).

ANZECC (2000) adopted TOC-normalisation, stating that *"normalising to 1% TOC was seen as acceptable to better define acceptable values for higher carbon percentages"* – i.e. accounting for the possible decrease in toxicity in organic-rich sediments due to reduced contaminant bioavailability due to contaminant–organic matter binding.

ANZECC (2000) also note that "*for sediments having >0.2% organic carbon (dry weight), sediment quality guidelines normalised to mg/kg organic carbon, have been shown to be valid for a range of sediment types. This cut-off in organic carbon content is judged to be necessary because at lower organic carbon contents, second-order effects such as particle size and adsorption to non-organic mineral fractions become more important*".

It is therefore ambiguous as to whether or not TOC-normalisation should be undertaken before comparing with ERC. The upper and lower limits of TOC content, beyond which normalisation is inappropriate (if any), are also unknown, although a lower limit of 0.2% TOC has been recommended (ANZECC 2000). More recently, the complexity around issues of detection and determining relevant biological toxicity, and further comparability between studies, continue to be discussed (Ciu et al, 2013 and Di Toro, 2013).

Because of these uncertainties, the approach of presenting data and ERC-Status both in dry weight terms (ng/g d.w.) and in TOC-normalised concentrations (ng/g at 1% TOC) has been adopted. A lower TOC threshold of about 0.2% has been used – below this TOC-normalisation was not conducted. SoE sites with TOC < 0.2% were sandy open coastal beach sites (Awaruku, Browns, Cheltenham and Vaughans) and Hobson Newmarket (a sandy textured site in Hobson Bay). For the rural harbour sites sampled in 2009/10, 9 of the 22 sites had TOC levels below 0.2%.

3.2   Status from 2003 sampling at SoE sites

The ERC status of the 27 SoE programme sites from the 2003 survey is presented in Table 3-2. Note that only results for OCPs have been presented in the table, because the ERC status of PCBs could not be reliably assessed (as explained in section 2.3.5).

Figure 3-1, Figure 3-2, and Figure 3-3 show the concentrations of Total and 1%TOC-normalised total DDTs, dieldrin, and PCBs at the SoE sites.

The results indicate that 9, possibly 10, of the 27 SoE sites approached or exceeded ERC-Red thresholds for OCPs. DDTs and dieldrin were the only compounds exceeding ERC-Red. The DLs for lindane were slightly too high to permit comparison with ERC (0.5 ng/g DL compared with the ERC-Red of 0.3 ng/g).

3.2.1 DDT

Similar patterns of contamination levels were shown for both Total DDT and 1%TOC-normalised Total DDT, with highest concentrations found at Henderson Upper (Figure 3-1). This is consistent with the long history of horticultural activity in the Henderson catchment, which is likely to be the major source of the DDT residues. There is also an historical landfill adjacent to the monitoring site, and this may be a contributing factor. However, elevated DDT residues are present in the upper estuary, and in stream sediments in the Henderson catchment (Diffuse Sources 2004).

Elevated DDT levels were also present at Meola Inner (although there is some uncertainty about the concentrations here – see section 2.3.3), in Mangere Inlet (Anns Creek and Mangere Cemetery sites), in the Whau River estuary (Whau Upper, Lower, and Wairau; although, see following note on exceptions), and at Oakley Creek. All these sites approached or exceeded ERC-Red for at least one DDT component, or for Total DDTs. These sites all receive runoff from intensively urbanised and/or industrialised catchments.

Lower, but detectable, concentrations were also found at Lucas Upper, Pahurehure Papakura, Hellyers Creek, and Paremoremo Creek (although, see following note on exceptions). These sites, which have more recently developed, or less intensively urbanised, catchments were below the ERC-Red threshold for DDTs.

The Whau River estuary and Paremoremo were exceptions with the 1% TOC-normalised data showing these sites to fall below the ERC-Red threshold; in contrast, Te Tokaroa and Te Matuku both received scores above the ERC-Red threshold. These results and the graphical presentation of the total and 1%TOC-normalised data across all areas and contaminants tested (Figure 3-1, Figure 3-2, and Figure 3-3) highlight the ambiguity around normalising results; particularly when DLs are close to the ERC-Red threshold. Care is required in the interpretation of the results and consideration given to the limitations presented earlier, these include: undetected contaminants that are assigned the DL value, particularly where the DL is close to the ERC-Red threshold; the 1%TOC-normalisation where low TOC content (Table 3-2) can inflate the normalised DLs, even when higher than the suggested 0.2% cutoff; or the second order effects to do with lower TOC levels.

In general, the 2003 survey data indicate that muddy estuaries receiving runoff from mature urban/industrial or historically horticultural catchments are likely to have appreciable DDT contamination, which may approach or exceed ERC-Red thresholds. The sites found to be ERC-Red for DDTs are also likely to be ERC-Red for dieldrin (section 3.2.2) and for metals (see section 3.5).

3.2.2 Dieldrin

Highest dieldrin concentrations were found at Whau Upper, followed closely by Mangere Inlet sites, Anns Creek and Cemetery (Figure 3-2). These sites exceeded the ERC-Red concentration.

Lower concentrations, but still approaching or exceeding ERC-Red, were present at Whau Lower and Wairau, Motions Inner, Middlemore, and Henderson Upper.

With the exception of Motions and Middlemore, the sites with elevated dieldrin concentrations also had high DDT concentrations.

As for DDT, it is likely that muddy estuaries receiving runoff from mature urban/industrial or historically horticultural catchments are likely to have appreciable dieldrin contamination, which may approach or exceed ERC-Red thresholds.

3.2.3 PCBs

Assessment of the PCB status was limited by the high DL for the 2003 analyses (1 ng/g per congener). The data plotted in Figure 3-3 show concentrations of the seven major congeners (Σ7 PCBs) found in the analytical results.

Highest PCB concentrations were found at Whau Wairau, followed by Whau Upper. The plots show these sites to be well below ERC-Red. However, as outlined in section 2.3.5, the Σ7 PCBs found above DLs may contribute only approximately 60% of a typical total PCB measured using more sensitive analytical methods. The Σ7 PCBs at Whau Wairau was 12 ng/g. Applying a 100/60 factor to this would give a more representative estimate of total PCBs of 20 ng/g, which is close to the ERC-Red threshold.

It is therefore conceivable that there may be sites in the more heavily contaminated estuary zones around Auckland (e.g. muddy industrial Tamaki Estuary sites, muddy Waitemata Harbour sites in older developed catchments) that would approach, or exceed, ERC-Red for PCBs. It would therefore seem appropriate to consider conducting a survey of these "high risk" sites, using high quality analytical methods to reliably assess PCB status.

3.2.4 Cautionary note regarding 2003 survey results

Reanalysis of samples from nine SoE sites taken in 2007 using more reliable and sensitive analytical methods found generally lower OCP levels than found in 2003 (see section 3.3). The OCP status reported here from the 2003 results may, therefore, be somewhat conservative. In reality, there may be fewer ERC-Red sites for OCPs than indicated by the 2003 survey data. Either reanalysis of archived samples, or analysis of fresh samples from the next round of monitoring (2013) is required to provide a more robust status assessment.

Median Total DDT at SoE sites in 2003

Meola Inner
Median of all results 13 ng/g

ERC = 3.9 ng/g

Reps 1-3 results 70 ng/g ➤

>D.L.
<D.L.

DL   Total DDT (ng/g d.w. in <500 μm fraction)

Median Total DDT at SoE sites in 2003

Sandy sites with very low TOC (<0.2%)
not plotted as TOC-normalisation not valid

Meola Inner
Median of all results 7.6 ng/g

ERC = 3.9 ng/g

Reps 1-3 results 42 ng/g ➤

>D.L. at 1% TOC
<D.L. at 1% TOC

Total DDT (ng/g d.w. at 1% TOC in <500μm fraction)

Figure 3-1 Total DDT and 1%TOC-normalised Total DDT concentrations at SoE sites sampled in 2003. Concentrations below detection limits (DL; 0.5 ng/g d.w. per compound) are shown at DL in blue. Concentrations above DL are shown in orange. The total bar heights therefore represent maximum possible total concentrations where < DL values have been treated as equal to the DL. Total DDT refers to the sum of the six "DDT" compounds: o,p- and p,p'- DDE, DDD, and DDT (n = 3 for each compound).

Median dieldrin at SoE sites in 2003

Chart: Dieldrin (ng/g d.w. in <500 μm fraction)

Legend:
- >D.L. (orange)
- <D.L. (blue)

ERC = 0.72 ng/g

DL = 0.5 ng/g

Sites: Anns, Awaruku, Big Muddy, Browns, Cheltenham, Hellyers, Henderson Upper, Hobson Newmarket, Lucas Upper, Mangere Cemetery, Meola Inner, Middlemore, Motions, Oakley, Pahurehure Papakura, Pakuranga Lower, Pakuranga Upper, Paremoremo, Puhinui Upper, Pukaki at Airport, Te Matuku, Te Tokaroa (Meola Reef), Vaughans, Weiti, Whau Lower, Whau Upper, Whau Wairau

Median dieldrin at SoE sites in 2003

Chart: Dieldrin (ng/g d.w. at 1% TOC in <500 μm fraction)

Sandy sites with very low TOC (<0.2%) not plotted as TOC-normalisation not valid

ERC = 0.72 ng/g

Legend:
- >D.L. at 1% TOC (orange)
- <D.L. at 1% TOC (blue)

Sites: Anns, Awaruku, Big Muddy, Browns, Cheltenham, Hellyers, Henderson Upper, Hobson Newmarket, Lucas Upper, Mangere Cemetery, Meola Inner, Middlemore, Motions, Oakley, Pahurehure Papakura, Pakuranga Lower, Pakuranga Upper, Paremoremo, Puhinui Upper, Pukaki at Airport, Te Matuku, Te Tokaroa (Meola Reef), Vaughans, Weiti, Whau Lower, Whau Upper, Whau Wairau
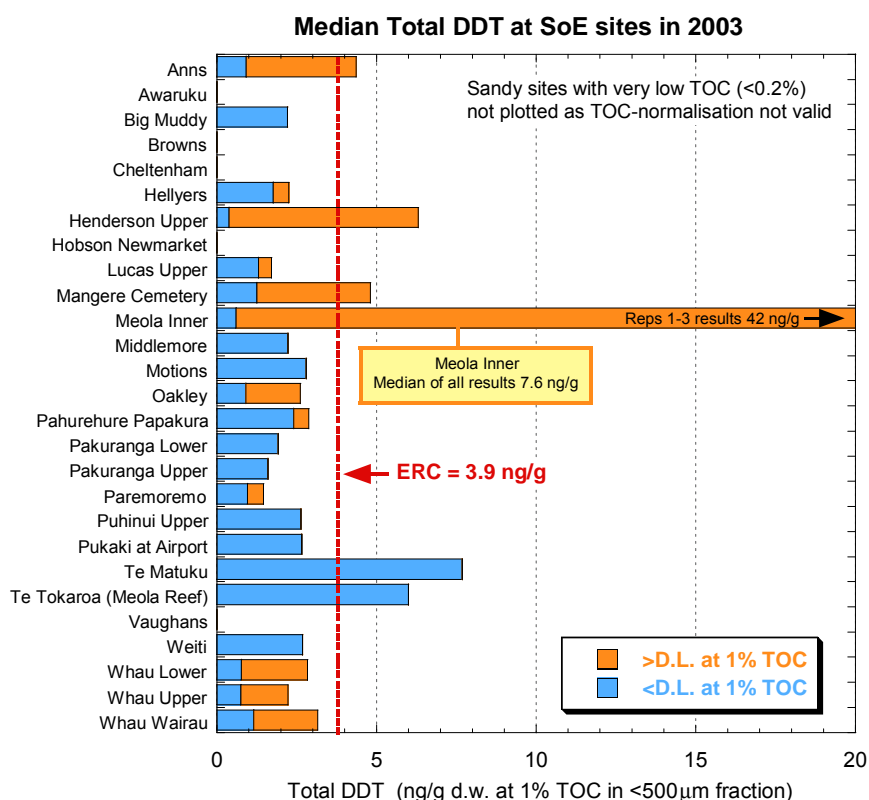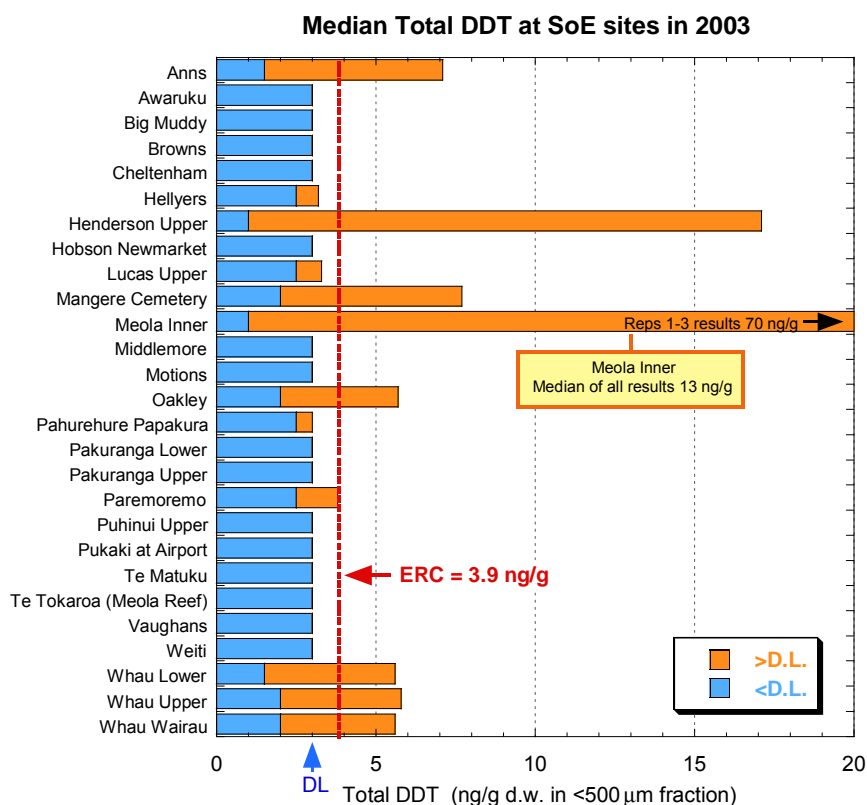
Figure 3-2 Dieldrin and 1%TOC-normalised dieldrin concentrations at SoE sites sampled in 2003. Concentrations below detection limits (DL; 0.5 ng/g d.w.) are shown at DL in blue. Concentrations above DL are shown in orange.
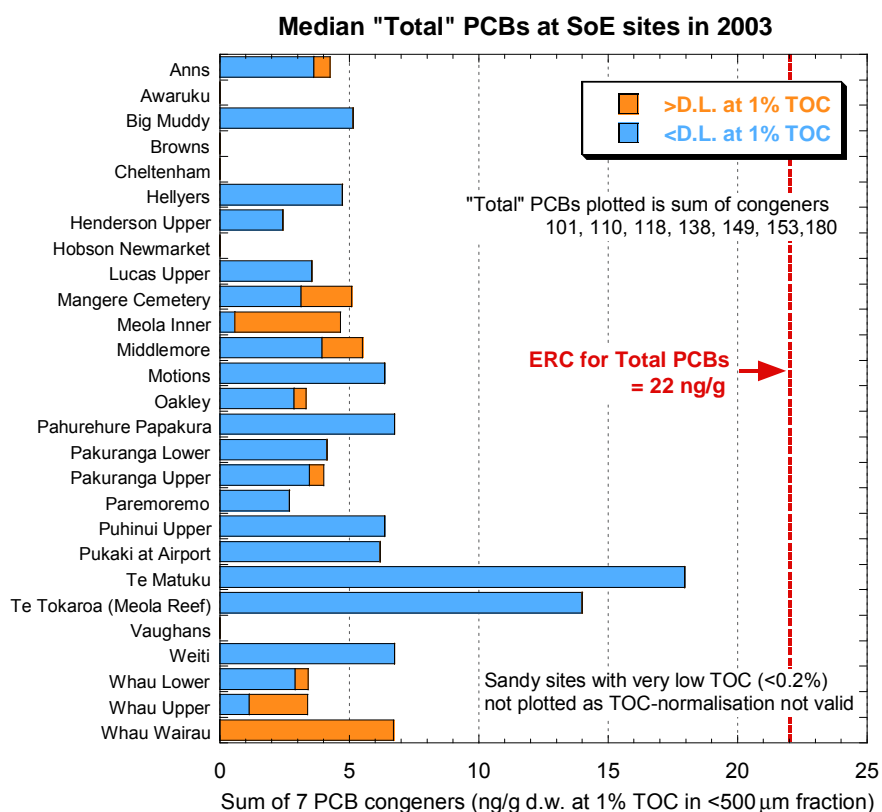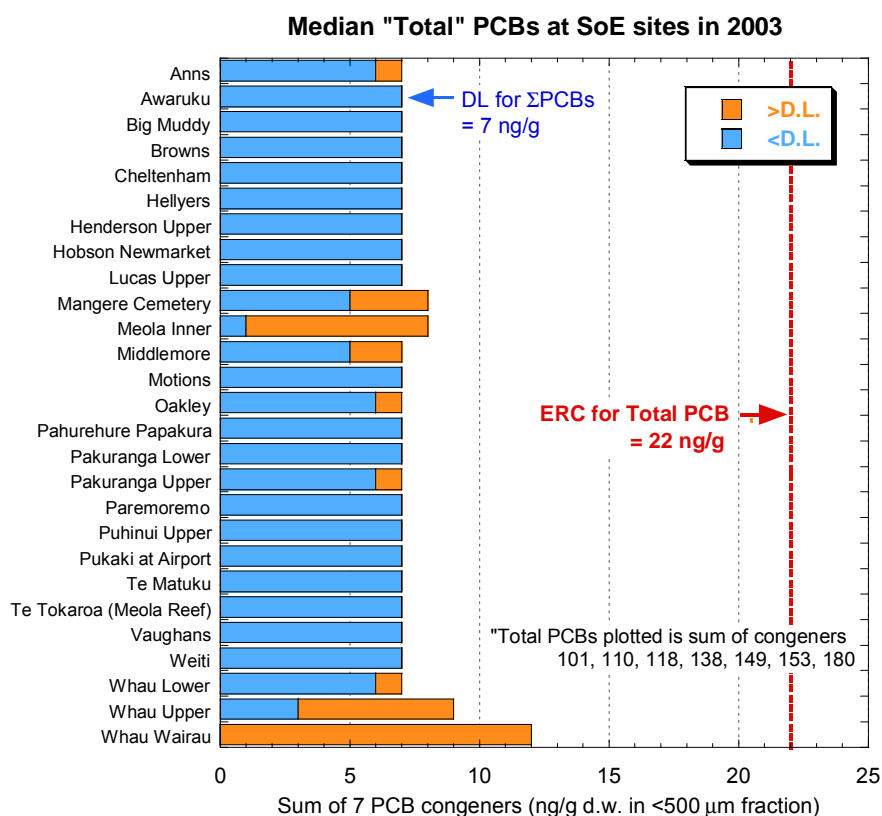
Figure 3-3 Total PCBs and 1%TOC-normalised Total PCB concentrations (sum of 7 major congeners). SoE sites sampled in 2003 (n = 3 for each congener). Concentrations below detection limits (DL; 1 ng/g per congener) are shown in blue. Concentrations above DL are shown in orange. The total bar heights therefore represent total concentrations where < DL values have been treated as equal to the DL.

Table 3-2 Organochlorine pesticide (OCP) status for SoE sites sampled in 2003.

Values are medians of n = 3 replicates, except for Meola Inner (see footnote). Red shaded values exceed ERC in both ng/g and TOC-normalised concentrations. Pale red values are within 10% of ERC. (Bracketed values) indicate exceedance in only one of the concentration units, including values within 10% of the ERC-Red. Pale blue shading indicates analytical detection limits (DL) higher than ERC-Red, while "n/a" indicates sites where TOC-normalisation is inappropriate because of very low TOC content (< 0.2%). Chlordane is sum of cis- and trans-chlordane. Total DDT treats < DL values = 0, because the sum of DLs for the six DDT components = 3 ng/g, which is close to the ERC (3.9 ng/g). A Total DDT of < 3 ng/g indicates all DDT components were < DL (< 0.5 ng/g). All other OCPs were either < DL, or have no ERC values.

Site	Compounds exceeding ERC	TOC (%)	Lindane ERC = 0.3 ng/g	at 1% TOC	Dieldrin ERC = 0.72 ng/g	at 1% TOC	Chlordane (<DL = 0) ERC = 2.3 ng/g	at 1% TOC	4,4'-DDE ERC = 2.1 ng/g	at 1% TOC	4,4'-DDD ERC = 1.2 ng/g	at 1% TOC	4,4'-DDT ERC = 3.2 ng/g	at 1% TOC	Total DDT (<DL = 0) ERC = 3.9 ng/g	at 1% TOC
Anns	Dieldrin, DDE, (DDD), (Total DDT)	1.63	< 0.5	< 0.3	1.3	0.8	< 1	< 0.6	3.4	2.1	1.2	0.7	1.1	0.7	5.6	3.4
Awaruku		0.09	< 0.5	n/a	< 0.5	n/a	< 1	n/a	< 0.5	n/a	< 0.5	n/a	< 0.5	n/a	< 3	n/a
Big Muddy		1.36	< 0.5	< 0.4	< 0.5	< 0.4	< 1	< 0.8	< 0.5	< 0.4	< 0.5	< 0.4	< 0.5	< 0.4	< 3	< 2.2
Browns		0.08	< 0.5	n/a	< 0.5	n/a	< 1	n/a	< 0.5	n/a	< 0.5	n/a	< 0.5	n/a	< 3	n/a
Cheltenham		0.15	< 0.5	n/a	< 0.5	n/a	< 1	n/a	< 0.5	n/a	< 0.5	n/a	< 0.5	n/a	< 3	n/a
Hellyers		1.48	< 0.5	< 0.3	< 0.5	< 0.3	< 1	< 0.6	0.7	0.5	< 0.5	< 0.3	< 0.5	< 0.3	0.7	0.5
Henderson Upper	(Dieldrin), DDE, (DDD), (DDT), Total DDT	2.77	< 0.5	< 0.2	0.7	0.3	< 1	< 0.4	6.8	2.5	3.1	1.1	5.7	2.0	16.1	5.9
Hobson Newmarket		0.16	< 0.5	n/a	< 0.5	n/a	< 1	n/a	< 0.5	n/a	< 0.5	n/a	< 0.5	n/a	< 3	n/a
Lucas Upper		1.98	< 0.5	< 0.3	< 0.5	< 0.3	< 1	< 0.6	0.8	0.4	< 0.5	< 0.3	< 0.5	< 0.3	0.8	0.4
Mangere Cemetery	Dieldrin, (DDE), (DDD), (Total DDT)	1.59	< 0.5	< 0.3	1.5	1.0	< 1	< 0.6	3.6	2.4	1.2	0.8	< 0.5	< 0.3	5.7	3.6
Meola Inner	DDD, DDT, Total DDT	1.72	< 0.5	< 0.3	< 0.5	< 0.3	< 1	< 0.3	1.8	1.1	4.3	2.5	7.1	4.1	13.1	7.6
Middlemore	(Dieldrin)	1.35	< 0.5	< 0.4	0.7	0.5	< 1	< 0.8	< 0.5	< 0.4	< 0.5	< 0.4	< 0.5	< 0.4	< 3	< 2.2
Motions	Dieldrin	1.07	< 0.5	< 0.5	1.0	1.0	< 1	< 1	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 3	< 2.8
Oakley	(DDD), (Total DDT)	2.23	< 0.5	< 0.2	< 0.5	< 0.2	< 1	< 0.4	1.7	0.8	1.8	0.8	< 0.5	< 0.2	3.7	1.7
Pahurehure Papakura		1.04	< 0.5	< 0.5	< 0.5	< 0.5	< 1	< 1	0.5	0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.5	0.5
Pakuranga Lower		1.30	< 0.5	< 0.4	< 0.5	< 0.4	< 1	< 0.8	< 0.5	< 0.4	< 0.5	< 0.4	< 0.5	< 0.4	< 3	< 1.8
Pakuranga Upper		1.74	< 0.5	< 0.3	< 0.5	< 0.3	< 1	< 0.6	< 0.5	< 0.3	< 0.5	< 0.3	< 0.5	< 0.3	< 3	< 1.6
Paremoremo		2.61	< 0.5	< 0.2	< 0.5	< 0.2	< 1	< 0.4	1.3	0.5	< 0.5	< 0.2	< 0.5	< 0.2	1.3	0.5
Puhinui Upper		1.10	< 0.5	< 0.5	< 0.5	< 0.5	< 1	< 1	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 3	< 2.7
Pukaki at Airport		1.13	< 0.5	< 0.4	< 0.5	< 0.4	< 1	< 0.8	< 0.5	< 0.4	< 0.5	< 0.4	< 0.5	< 0.4	< 3	< 2.7
Te Matuku		0.39	< 0.5	n/a	< 0.5	< 1.3	< 1	< 2.6	< 0.5	< 1.3	< 0.5	< 1.3	< 0.5	< 1.3	< 3	< 7.7
Te Tokaroa (Meola Reef)		0.50	< 0.5	< 1	< 0.5	< 1	< 1	< 2	< 0.5	< 1	< 0.5	< 1	< 0.5	< 1	< 3	< 6.0
Vaughans		0.08	< 0.5	n/a	< 0.5	n/a	< 1	n/a	< 0.5	n/a	< 0.5	n/a	< 0.5	n/a	< 3	n/a
Weiti		1.04	< 0.5	< 0.5	< 0.5	< 0.5	< 1	< 1	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	<0.5	< 3	< 2.9
Whau Lower	(Total DDT)	2.02	< 0.5	< 0.3	0.6	0.3	< 1	< 0.6	0.8	0.4	1.1	0.5	2.2	1.1	4.1	2.1
Whau Upper	(Dieldrin), (DDD), (Total DDT)	2.66	< 0.5	< 0.2	1.7	0.6	< 1	< 0.4	2.0	0.8	1.4	0.5	< 0.5	< 0.2	3.8	1.5
Whau Wairau	(Dieldrin), (DDD)	1.74	< 0.5	< 0.3	1.0	0.6	< 1	< 0.6	2.0	1.1	1.6	0.9	< 0.5	< 0.3	3.6	2.0

Footnote: Very high DDT results (244 and 70 ng/g) were obtained for 2 of the 3 replicates initially analysed from Meola Inner. Replicates 4 and 5 (archived samples) were analysed, giving much lower results. The values given in the table above are medians from all sample analyses (n = 7).

3.3   Status from 2007 sampling at SoE sites

The initial analyses of the 2007 samples were undertaken at screening level, with DLs of 10 ng/g. This was too high for any meaningful assessments of spatial distribution or status. However, the results did "confirm" that the very high DDT concentrations recorded at Meola Inner in 2003 were unlikely to be real (or at least present on anything other than a very localised spatial scale, less than a few square metres).

A sub-set of nine sites (six of which were assessed as ERC-Red in 2003) were reanalysed for OCPs, using quantitative methods with lower DLs. The status of these sites is shown in Table 3-3. A comparison of the 2007 and 2003 non-normalised results are shown in Figure 3-4. Note the comparisons shown in Figure 3-4 use < DL = 0, to improve comparability of the two sets of data, since the DLs for the 2007 data set were much lower than those for 2003.

The 2007 reanalysis data showed generally lower concentrations than were found in 2003. Only Whau Upper, Mangere Cemetery, and possibly Anns Creek approached or exceeded ERC-Red (for DDTs or dieldrin). Lindane and chlordanes were well below ERC-Red thresholds at all nine sites.

These results, while limited to only a few sites, suggest that the results obtained in 2003 may have been higher than "real". Four 2003 sites with ERC-Red OCP concentrations (Henderson Upper, Meola Inner, Oakley, and Whau Wairau) were not reanalysed in 2007 at low DLs. It is not known whether reanalysis of these sites would have also found lower concentrations.

It is possible that OCP concentrations had decreased substantially in the 4 years between the 2003 and 2007 surveys, but given the persistence of these compounds, this seems unlikely to be the major reason for the difference in concentrations reported.

Given the marked difference in results obtained for most sites in 2007 compared with 2003, and consequently the difference in ERC status, further analysis of the data is not considered warranted. To obtain a more quantitatively robust picture of OCP (and PCB) distribution and ERC status across the region's estuaries, reanalysis of archived samples, or analysis of freshly sampled sediments, from a wider range of sites is required.

Total DDT in 2003 and 2007

ERC = 3.9 ng/g

<3 ng/g in 2003

<D.L. values = 0

Total DDT (ng/g, <500 μm fraction)

Dieldrin in 2003 and 2007

<0.5 ng/g in 2003

<0.5 ng/g in 2003
<0.51 ng/g in 2007

<0.5 ng/g in 2003

<D.L. values = 0

ERC = 0.72 ng/g

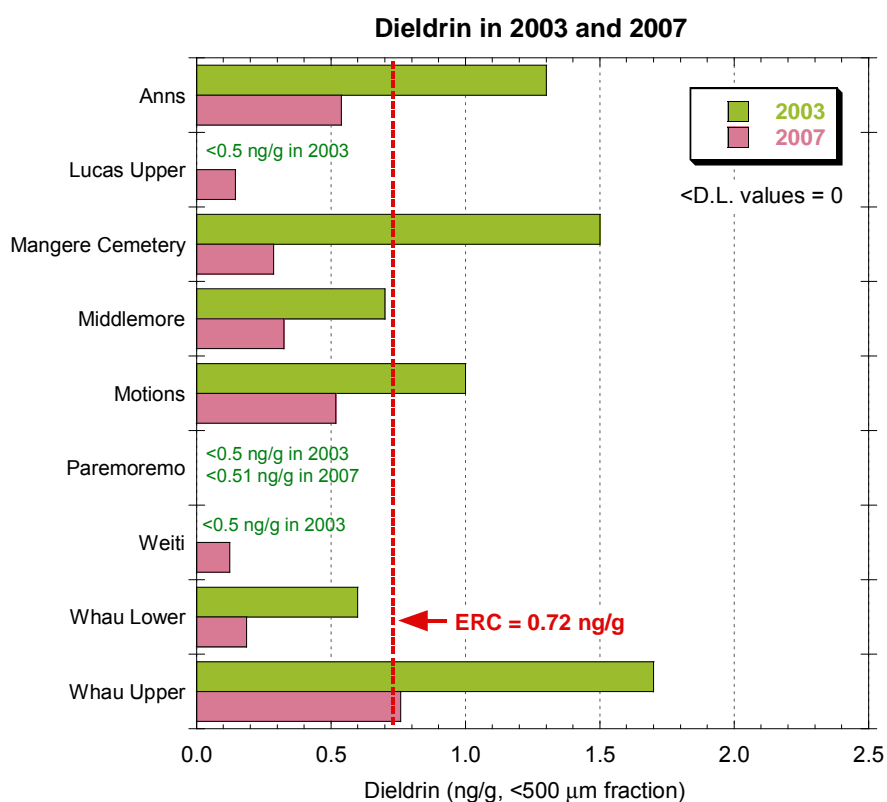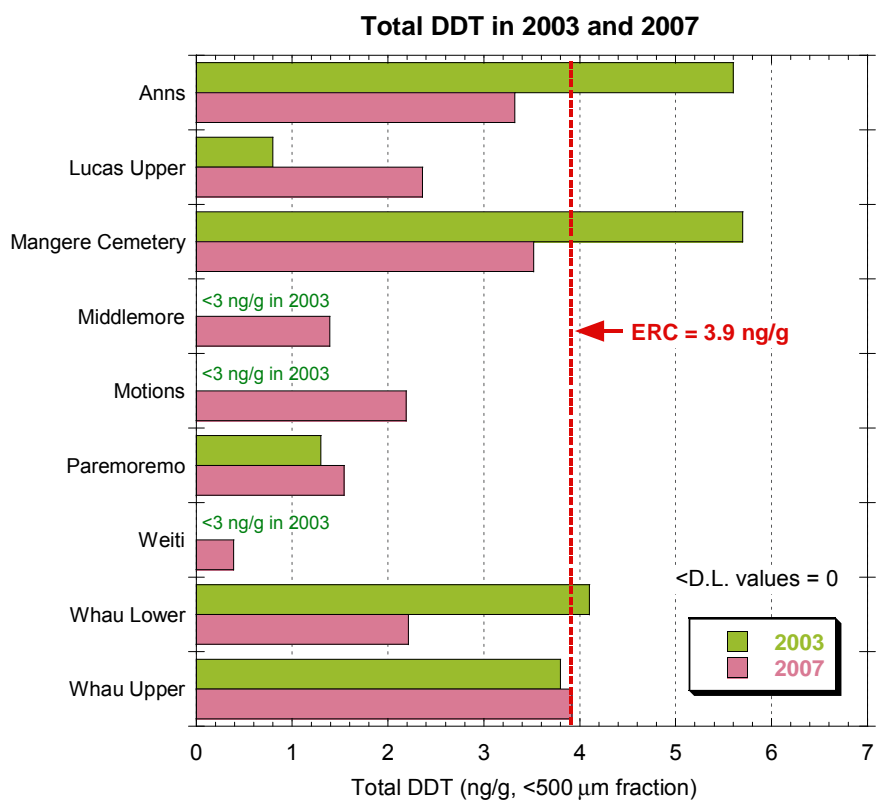Dieldrin (ng/g, <500 μm fraction)

Figure 3-4 Total DDT and dieldrin concentrations at SoE sites sampled in 2003 and 2007.
The 2007 results are for the nine sites reanalysed at lower DLs. Values below detection limits (DL; 0.5 ng/g)
were treated as equal to zero for calculating Total DDT.

Table 3-3 Organochlorine pesticide (OCP) status for SoE sites sampled in 2007.

The 2003 status from the same sites is also shown for comparison. The 2007 concentrations are from single composite samples reanalysed in 2009 using more sensitive analytical methods than in the initial screening analysis undertaken at all 27 SoE sites. Red shaded values exceed ERC in both ng/g and TOC-normalised concentrations. Pale red values are within 10% of ERC. (Bracketed values) indicate exceedance in only one of the concentration units, including values within 10% of the ERC-Red. Chlordane is sum of cis- and trans-chlordane. Total DDT refers to the sum of all six o,p'- and p,p'- DDE, DDD, and DDT components. All other OCPs were either < DL, or have no ERC values. The Lab Blank is assumed to have a TOC of 1% for comparison with TOC-normalised sample data.

A. Lindane, dieldrin, and chlordane

A. Lindane, dieldrin, and chlordane	2007 Status	2003 Status		Lindane		Dieldrin		Chlordane (<DL = 0)		Chlordane (<DL = DL)	
Site	Compounds exceeding ERC	Compounds exceeding ERC	TOC (%)	ERC = 0.3		ERC = 0.72		ERC = 2.3		ERC = 2.3	
				ng/g	at 1% TOC	ng/g	at 1% TOC	ng/g	at 1% TOC	ng/g	at 1% TOC
Lab Blank			1.00	< 0.020	< 0.02	< 0.057	< 0.06	0.00	0.00	0.17	0.17
Anns	None	Dieldrin	1.50	0.081	0.05	0.54	0.36	0.21	0.14	0.39	0.26
Lucas Upper	None		2.00	< 0.021	< 0.010	0.15	0.07	0.00	0.00	0.25	0.13
Lucas Upper	None	Dieldrin	1.30	0.071	0.05	0.29	0.22	0.00	0.00	0.23	0.18
Middlemore	None	(Dieldrin)	1.60	0.028	0.02	0.33	0.20	0.00	0.00	0.15	0.09
Motions	None	Dieldrin	0.98	0.032	0.03	0.52	0.53	0.79	0.81	1.46	1.49
Paremoremo	None		2.90	< 0.098	< 0.034	< 0.51	< 0.177	0.00	0.00	1.75	0.60
Weiti	None		1.30	0.023	0.02	0.12	0.10	0.00	0.00	0.22	0.17
Whau Lower	None		1.80	0.032	0.02	0.19	0.10	0.00	0.00	0.33	0.19
Whau Upper	(Dieldrin)	(Dieldrin)	2.30	0.034	0.01	0.76	0.33	0.20	0.08	0.40	0.18

B. DDE, DDD, DDT, and Total DDT

B. DDE, DDD, DDT, and Total DDT	2007 Status	2003 Status		4,4'-DDE		4,4'-DDD		4,4'-DDT		Total DDT (<DL = 0)		Total DDT (<DL = DL)	
Site	Compounds exceeding ERC	Compounds exceeding ERC	TOC (%)	ERC = 2.1		ERC = 1.2		ERC = 3.2		ERC = 3.9		ERC = 3.9	
				ng/g	at 1% TOC	ng/g	at 1% TOC	ng/g	at 1% TOC	ng/g	at 1% TOC	ng/g	at 1% TOC
Lab Blank			1.00	< 0.031	< 0.03	< 0.020	< 0.02	< 0.022	< 0.02	0.00	0.00	0.14	0.14
Anns	None	DDE, (DDD), (Total DDT)	1.50	1.71	1.14	0.71	0.47	0.57	0.38	3.32	2.22	3.32	2.22
Lucas Upper	None		2.00	1.02	0.51	0.66	0.33	0.50	0.25	2.36	1.18	2.38	1.19
Mangere Cemetery	(Total DDT)	(DDE), (DDD), (Total DDT)	1.30	1.59	1.22	0.51	0.39	0.48	0.37	3.52	2.71	3.52	2.71
Middlemore	None		1.60	0.54	0.34	0.54	0.34	0.14	0.09	1.39	0.87	1.39	0.87
Motions	None		0.98	0.57	0.58	0.99	1.01	0.40	0.41	2.19	2.23	2.21	2.25
Paremoremo	None		2.90	0.85	0.29	0.44	0.15	0.15	0.05	1.54	0.53	1.69	0.58
Weiti	None		1.30	0.12	0.09	0.15	0.12	0.07	0.05	0.39	0.30	0.44	0.34
Whau Lower	None	(Total DDT)	1.80	0.92	0.51	0.85	0.47	0.22	0.12	2.21	1.23	2.23	1.24
Whau Upper	(DDD), (Total DDT)	(DDD), (Total DDT)	2.30	1.65	0.72	1.33	0.58	0.52	0.22	3.92	1.70	3.92	1.70

3.4 Status of rural harbours and estuaries sampled in 2009 and 2010

Status for OCPs and PCBs for the Whangateau Harbour (7 sites, collected in 2009), Kaipara Harbour (6 sites collected in 2009), Mahurangi Harbour (2 sites collected in 2009), and the "7 estuaries" programme (one site in each of Puhoi, Orewa, Okura, Waikopua, Waiwera, Mangemangeroa, and Turanga estuaries, collected in 2010) were all ERC-Green.

Concentrations of OCPs and PCBs at all sites were very low, at most sites being comparable with laboratory blanks (Figure 3-5, Figure 3-6, Figure 3-7). Because these concentrations were so low (and not greatly above blank levels) no detailed analysis of TOC-normalised concentrations for these sites has been presented. Nine of the 22 sites also had TOC levels below 0.2%, the lower threshold adopted for TOC-normalisation.

The analytical protocols and instrumental output from AsureQuality sample analysis (used in 2009-2010 sample analysis) provide a high level of precision while also presenting an instrument calculated DL for each individual sample. As a result, the previously mentioned variability of DLs between samples and analytes (section 2.3.2) can result in not only differing DLs for batch runs, but also a blank value coming in either above or below the DL (e.g. Figure 3-5). In addition, the very low levels of contaminants in some locations can result in sample values being less than those of the analytical blank (e.g. Figure 3-6).

Noticeably higher concentrations of DDTs and PCBs were recorded at Whangateau Site 6 (Wh6), a muddy site (TOC = 0.61%) which is possibly influenced by leachate from a nearby landfill. Dry weight concentrations of Total DDT at Wh6 were 0.87 ng/g (< DL values = 0) or 0.91 ng/g (< DL = DL). The TOC-normalised concentrations of Total DDT at Wh6 were 1.42 ng/g (< DL values = 0) or 1.50 ng/g (< DL = DL). All concentrations were well below the ERC-Red threshold of 3.9 ng/g. Individual DDT components (p,p'-DDE, DDD and DDT) were also below ERC-Red. The Total PCB concentration at Wh6 (1.1–1.2 ng/g d.w., depending on how < DL values were treated) was also well below the ERC-Red threshold (22 ng/g).

Site 1 in the Waiwera Estuary, which is located in the muddy lower reaches influenced by urban runoff and the municipal wastewater discharge (which enters the estuary approximately 1 km upstream), had a noticeably higher (but still very low) PCB concentration compared with other "7 estuary" sites. The Total PCB concentration at Waiwera S1 was 1.1–1.2 ng/g d.w. (depending on how < DL values were treated), which was well below the ERC-Red threshold (22 ng/g).
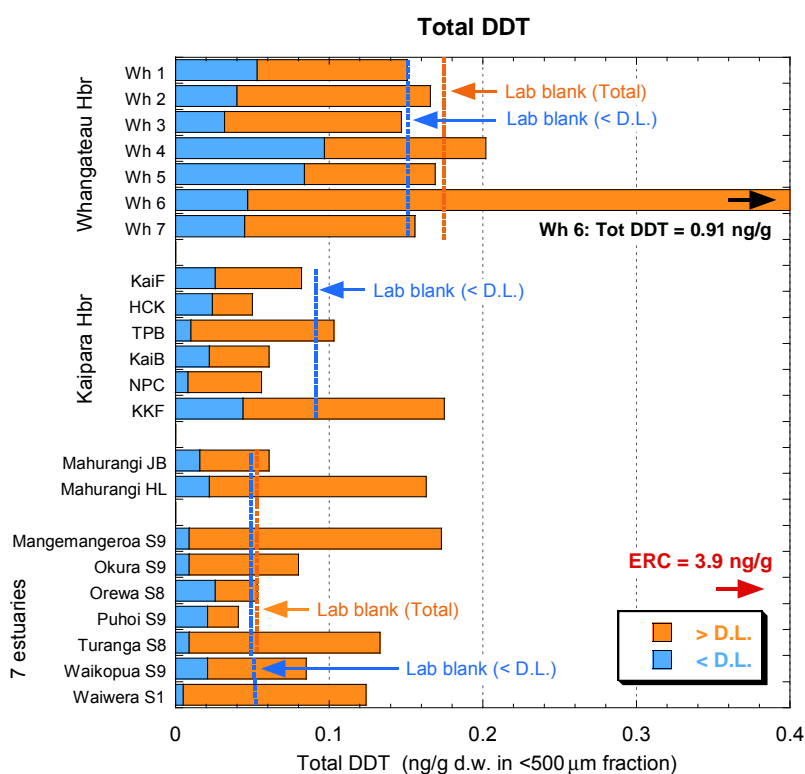
Figure 3-5 Total DDT concentrations at rural harbour sites sampled in 2009/10.
Total DDT refers to the sum of all six o,p'- and p,p'-DDE, DDD, and DDT compounds (n = 1 for each compound). Values less than detection limits (< DL) are shown in blue, while values above DL are shown in orange. The total bar heights therefore represent maximum total concentrations where < DL values have been treated as equal to the DL.
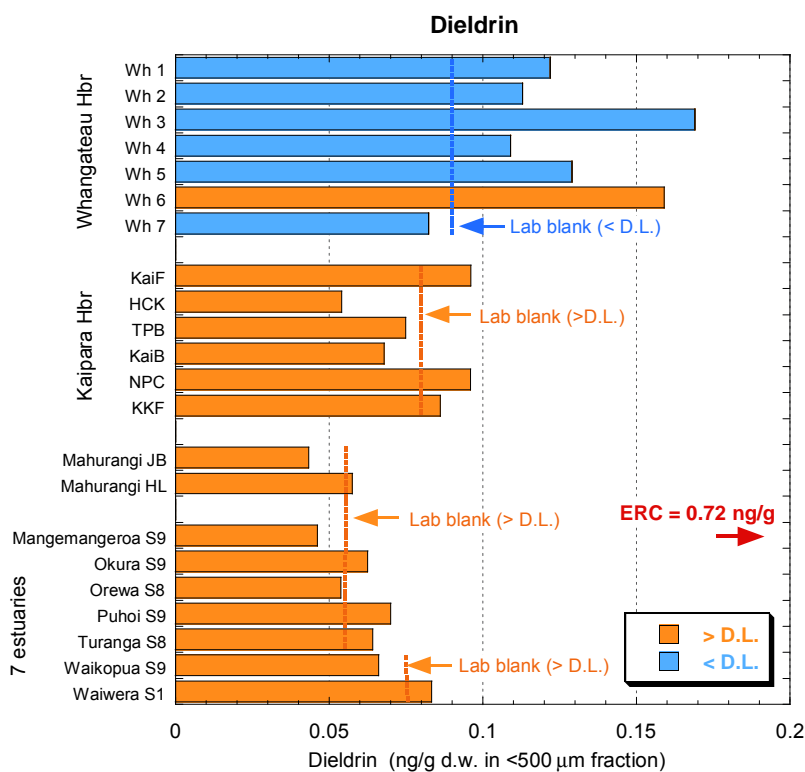

Figure 3-6 Dieldrin concentrations at rural harbour sites sampled in 2009/10 (n = 1).
Values less than detection limits (< DL) are shown in blue, while values above DL are shown in orange.
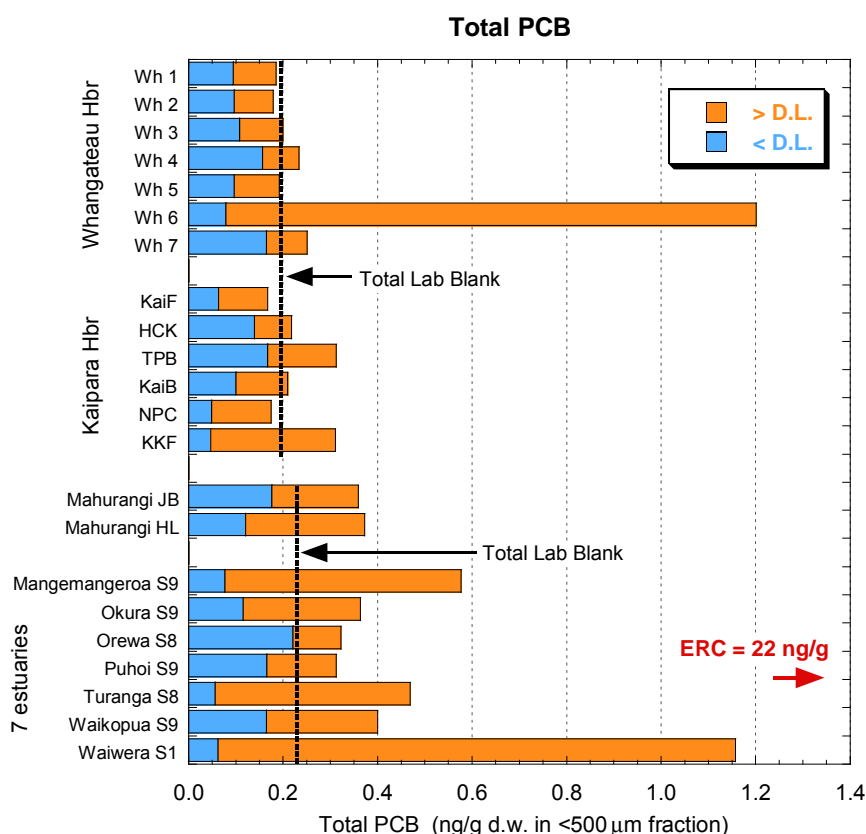
Total PCB

Figure 3-7 Total PCB concentrations at rural harbour sites sampled in 2009/10.

Totals are the sum of 7 major congeners (n = 1 for each congener). Values less than detection limits (< DL) are shown in blue, while values above DL are shown in orange. The total bar heights therefore represent maximum total concentrations where < DL values have been treated as equal to the DL.

3.5   Overall Status: Comparison of OCP, PAH, and metals' status

The OCP results from the 2003 and 2007 surveys at the SoE sites have been combined with the metals and PAH data (Mills et al. 2012). The results are summarised in Table 3-4. This provides an assessment of whether OCPs are present at elevated levels at sites not adversely affected by other contaminants, and could therefore be contributing to ecological stress unaccounted for by metals or PAH data.

Using the 2003 OCP survey results, the combined status data indicate that OCPs (and probably PCBs also) only exceed ERC-Red thresholds at sites that have elevated metals' concentrations (in particular Zn). The only exception may be at Mangere Cemetery (Mangere Inlet), where the metals' concentrations are ERC-Amber (rather than Red as at other sites with ERC-Red OCPs).

Using the 2007 survey OCP data (at a limited range of sites), suggests that OCPs may be even less important than metals. Only two of the nine sites analysed approached or exceeded ERC-Red concentrations – Whau Upper, which has ERC-Red Zn concentrations, and Mangere Cemetery (ERC-Amber Cu and Zn). Note that four sites with ERC-Red OCP levels in 2003 were not reassessed in 2007.

Overall, it appears that OCPs, and possibly PCBs, are unlikely to markedly influence the established ERC status of SoE sites. Overall status based on the most recent available metals, PAH and organochlorines data from Table 3-4 is shown in Figure 3-8.

Table 3-4 Overall status summary for SoE sites.
Red shaded values exceed ERC in one or both ng/g and 1%TOC-normalised concentrations for the analysed OCs (DDTs PCBs and dieldrin). Pale red values are within 10% of ERC. (Bracketed values) indicate exceedance in only one of the concentration units, including values within 10% of the ERC-Red. Grey cells indicate sites not reanalysed in 2007. Metals and HWPAH (high molecular weight PAH) status follows standard green, amber, and red classification given in ARC (2004).

| Site	Organochlorines Status 2003 Compounds exceeding ERC	Organochlorines Status 2007 Compounds exceeding ERC	Metals' status 2011			HWPAH 2005
			Cu	Pb	Zn	
Anns	Dieldrin, DDE, (DDD), (Total DDT)	None	22.4	26.5	153.1	0.154
Awaruku			2.0	3.3	23.0	0.070
Big Muddy			10.0	10.2	57.6	0.156
Browns			n/a	n/a	n/a	n/a
Cheltenham			6.7	19.1	47.3	1.689
Hellyers			16.9	26.3	108.2	0.201
Henderson Upper	(Dieldrin), DDE, (DDD), (DDT), Total DDT		33.0	32.0	169.1	0.169
Hobson Newmarket			22.7	40.2	117.5	1.366
Lucas Upper		None	19.6	22.4	106.1	0.204
Mangere Cemetery	Dieldrin, (DDE), (DDD), (Total DDT)	(Total DDT)	20.2	24.5	125.5	0.152
Meola Inner	DDD, DDT, Total DDT		29.6	56.0	240.0	2.330
Middlemore	(Dieldrin)	None	23.2	27.3	196.0	0.530
Motions	Dieldrin	None	17.8	38.4	242.4	2.045
Oakley	(DDD), (Total DDT)		27.1	40.6	153.6	0.335
Pahurehure Papakura			5.7	9.8	60.6	0.071
Pakuranga Lower			17.5	24.2	184.8	0.235
Pakuranga Upper			23.5	31.3	252.5	0.145
Paremoremo		None	21.9	25.0	97.9	0.130
Puhinui Upper			9.2	12.3	107.1	0.052
Pukaki at Airport			8.1	10.7	63.9	0.055
Te Matuku			2.8	6.7	30.3	0.019
Te Tokaroa (Meola Reef)			19.4	32.3	113.5	0.463
Vaughans			1.8	2.9	21.0	0.043
Weiti		None	9.3	8.1	46.5	0.196
Whau Lower	(Total DDT)	None	22.7	35.1	157.7	0.338
Whau Upper	(Dieldrin), (DDD), (Total DDT)	(Dieldrin), (DDD), (Total DDT)	28.6	49.0	234.7	0.379
Whau Wairau	(Dieldrin), (DDD)		32.0	46.9	199.0	0.424
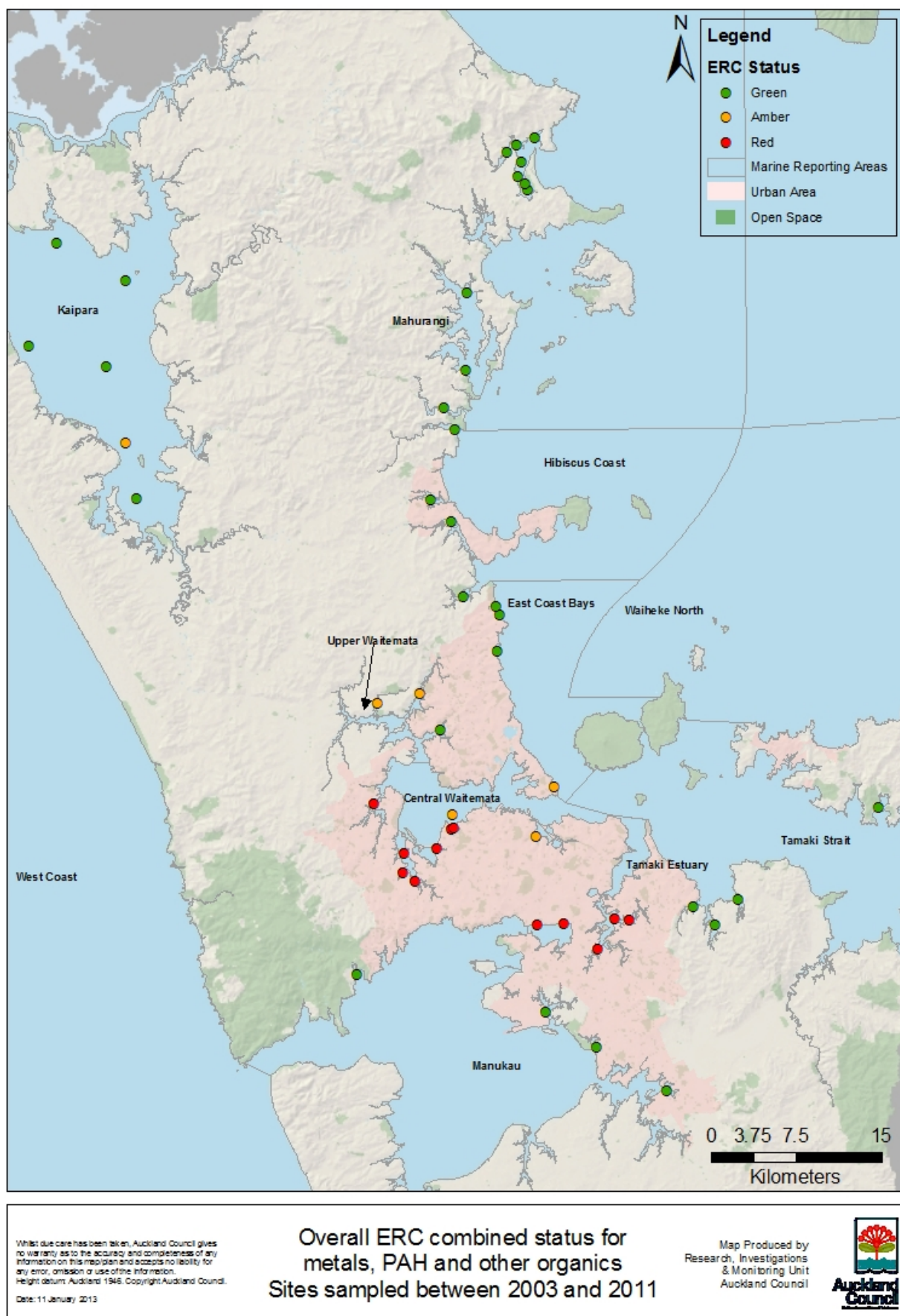
Figure 3-8 Overall status based on the most recent available metals, PAH and organochlorines data from Table 3-4

4.0 Other pesticides

4.1 Endosulfan

Endosulfans (I and II) and endosulfan sulphate (a key degradation product) were detected in the 2003 survey of SoE sites at relatively low concentrations (0.6 – 2.6 ng/g per component) at Awaruku, Pakuranga Lower, Weiti, Paremoremo, and Whau Upper. Concentrations above the DLs in all 3 replicates per site were found only at Weiti and Paremoremo, where median total endosulfans were 4.7 ng/g and 4.9 ng/g respectively. Endosulfan sulphate (but not endosulfan I or II) was detected at Lucas Upper (median concentration of 0.6 ng/g) and at Whau Upper (2.4 ng/g).

The ecological implications of these endosulfan residues are unknown because there are no known sediment quality guidelines for endosulfan.

Analysis of nine SoE sites sampled in 2007 found no endosulfans above DLs, except for a very low concentration of endosulfan I (0.14 ng/g) at Anns Creek. The endosulfan analyses in 2007 had high analytical blank DLs (< 0.15 – < 0.73 ng/g), and samples also had relatively high DLs (0.13 – 4.4 ng/g) compared with other OCPs. The endosulfan sulphate results were either < DL (< 0.49 – < 3.4 ng/g) or had "estimated maximum possible concentrations" (EMPC) of 0.52 – 2.73 ng/g. The EMPC values indicate difficulty in unambiguously quantifying the compound at concentrations below these levels, probably due to matrix interference.

Overall, the endosulfan data provide no clear picture of contamination levels or spatial distribution. The available data indicate that most sites have no significant endosulfan residues, being near or below the DLs of the analytical methods.

4.2 Hexachlorobenzene and other pesticides

Hexachlorobenzene (HCB) was found at low concentrations (0.06 – 0.36 ng/g) at eight of the nine SoE sites analysed in 2007. No HCB was detected at Motions (< 0.11 ng/g). The highest concentration was found at Whau Upper (0.36 ng/g). Median HCB levels were < 0.5 ng/g (< DL) at all SOE sites in 2003.

There were no other targeted OCPs consistently detected in the SoE or rural estuary sediments.

5.0 Emerging contaminants

Sediments from 13 estuarine locations around Auckland were taken in March 2008, and analysed for 34 of the key "chemicals of potential environmental concern" (CPEC) that could be analysed by commercial laboratories at the time (Stewart et al. 2009). Sites included seven that were close to SoE or Regional Discharge Project (RDP) monitoring sites:

- SoE locations – Meola Inner, Motions, Hobson Bay Newmarket, Pakuranga Upper, and Whau Upper; and
- RDP locations – Cox's Bay and Shoal Bay, Hillcrest.

Other sites included three marinas (Milford, Westhaven and Half Moon Bay), Puketutu Island (Manukau Harbour, near the Mangere sewage treatment plant), the Taihiki River estuary (Southern Manukau Harbour, primarily agricultural catchment) and the upper reaches of the Mahurangi Harbour (immediately below the Warkworth sewage treatment plant discharge).

The CPECs analysed included:

- polybrominated diphenylether (PBDE) flame retardants
- phthalate ester plasticisers ("phthalates")
- biocides, including common antifoulants, herbicides (including glyphosate), and various pesticides (including dithiocarbamates, diazinon, and pyrethroids)
- triclosan (disinfectant)
- oestrogens, and
- nonylphenols.

Results indicated:

- PBDE residues are widespread, being detected at all 13 sites, at concentrations totalling up to 570 ng/g (at Puketutu Island, Manukau Harbour). The highest concentration at the SoE or RDP locations was found at Pakuranga Upper (140 ng/g total PBDE). Interestingly, the Whau Upper site, which has high concentrations of other contaminants (metals, OCPs, and probably PCBs), had relatively low PBDE concentrations (5 ng/g).
- Glyphosate residues were detectable at most sites, up to 1000 ng/g. The highest of the SoE/RDP locations was Meola Inner (950 ng/g) and the lowest were at Cox's Bay (< 40 ng/g) and Pakuranga Upper (90 ng/g).
- Dithiocarbamates were detectable at close to DL levels at 4 of the SoE/RDP sites, with Shoal Bay, Hillcrest having highest concentrations (110 ng/g as carbon disulphide).
- Phthalate concentrations were generally below analytical detection limits. Of the SoE/RDP sites, only Hobson Bay Newmarket was above DL (4800 ng/g and 560 ng/g for two major phthalate esters).

The CPEC data indicated that residues of some emerging contaminants are found, at widely varying concentrations, in Auckland's estuarine sediments.

It is too early yet to assess the environmental significance of these residues, but these initial data suggest that sewage discharges (as indicated by Puketutu Island data) – perhaps historically, rather than current – may be significant sources of some key contaminants (e.g. PBDE).

The significance of CPECs with respect to urban runoff impacts is yet to be determined, but elevated concentrations (i.e. above DLs) of PBDEs, phthalates, glyphosate, and possibly dithiocarbamates have been reported at SoE and RDP monitoring sites.

Stewart et al. (2009) also pointed out that the failure to detect many of the CPECs in their initial study does not mean that there is no cause for concern, as the detection limits were often higher than concentrations reported elsewhere in the international literature. Therefore, future studies utilising improved analytical methods are still warranted to improve the quality and coverage of the CPEC database.

The sediment samples collected in 2008 from these sites were subsequently analysed for 46 pharmaceuticals (an EU suite of compounds), 33 of which are listed in the NZ Pharmac 2007 schedule. The results have been reported by Stewart (2013) and summarised here (Figure 5-1 and **Error! Reference source not found.**).

Of the 46 compounds analysed, 21 were quantified at one or more sites. Eighteen of these 21 detected compounds were in the Pharmac (2007) schedule. Fifteen of the Pharmac schedule drugs were not detected at any site (concentrations were below limits of quantitation).

The concentrations of detected pharmaceuticals were in the parts per billion (ppb or ng/g) range. Average concentrations across all sites ranged from 7.7 ng/g (for acetaminophen, the common painkiller paracetamol) to 0.16 ng/g (for Bezafibrate, a cholesterol lowering drug).

A preliminary examination of the spatial distribution of these chemicals (Figure 2-1) suggests that sites potentially influenced by treated wastewater discharge or wastewater overflows (Puketutu, Mahurangi, Cox's Bay), and possibly historical landfills (Meola), may have higher concentrations of most pharmaceuticals.

Stewart (2013) recommended further investigation of pharmaceuticals in raw and treated wastewaters, development of analytical capability for testing residues of pharmaceuticals most relevant to NZ, and toxicological studies to determine the effects of key chemicals on NZ biota.
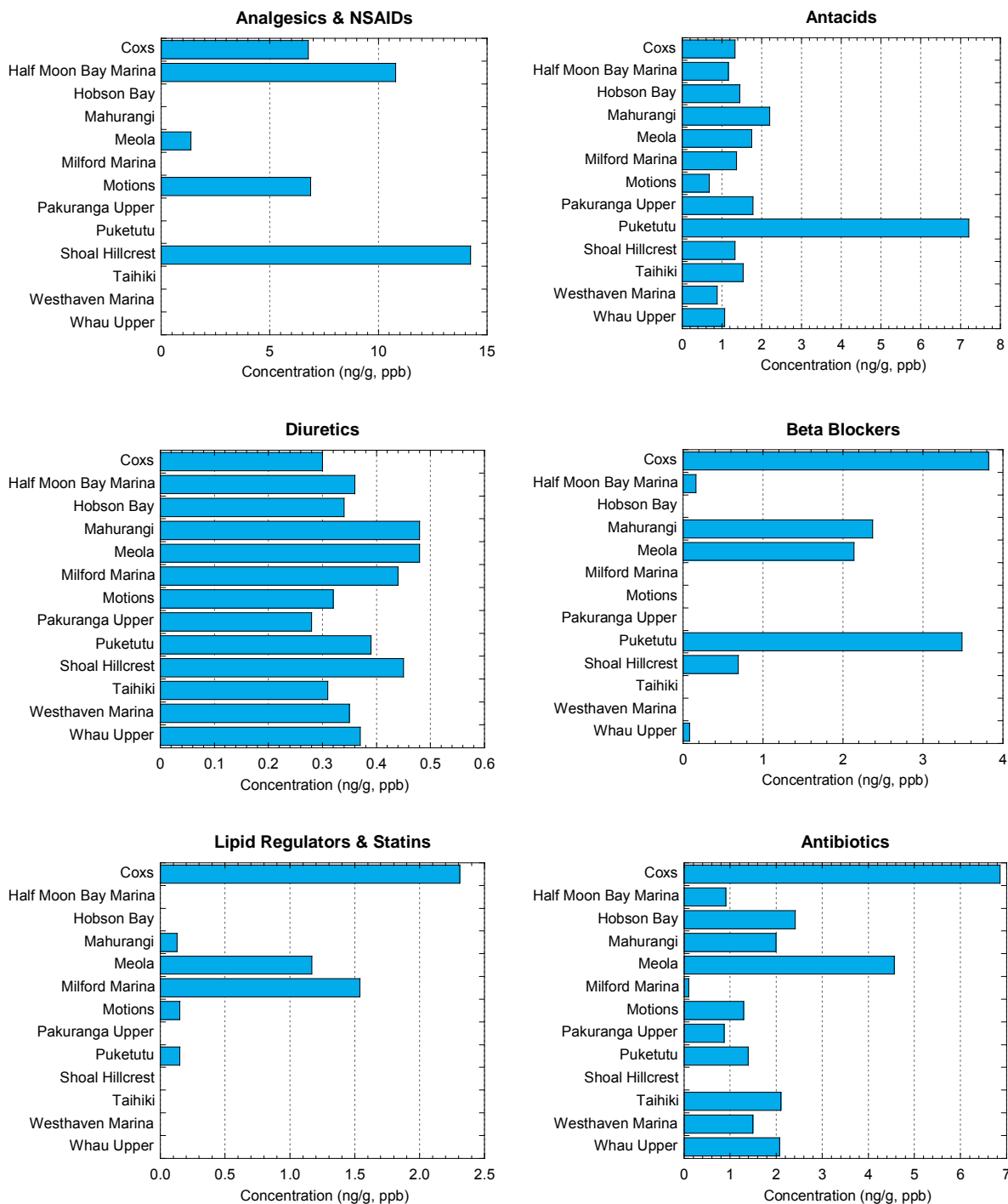
Figure 5-1 Pharmaceuticals in sediments from 13 Auckland sites sampled in 2008.

Data are means of aggregated compound groups, using data reported in Appendix 1 of Stewart (2013).
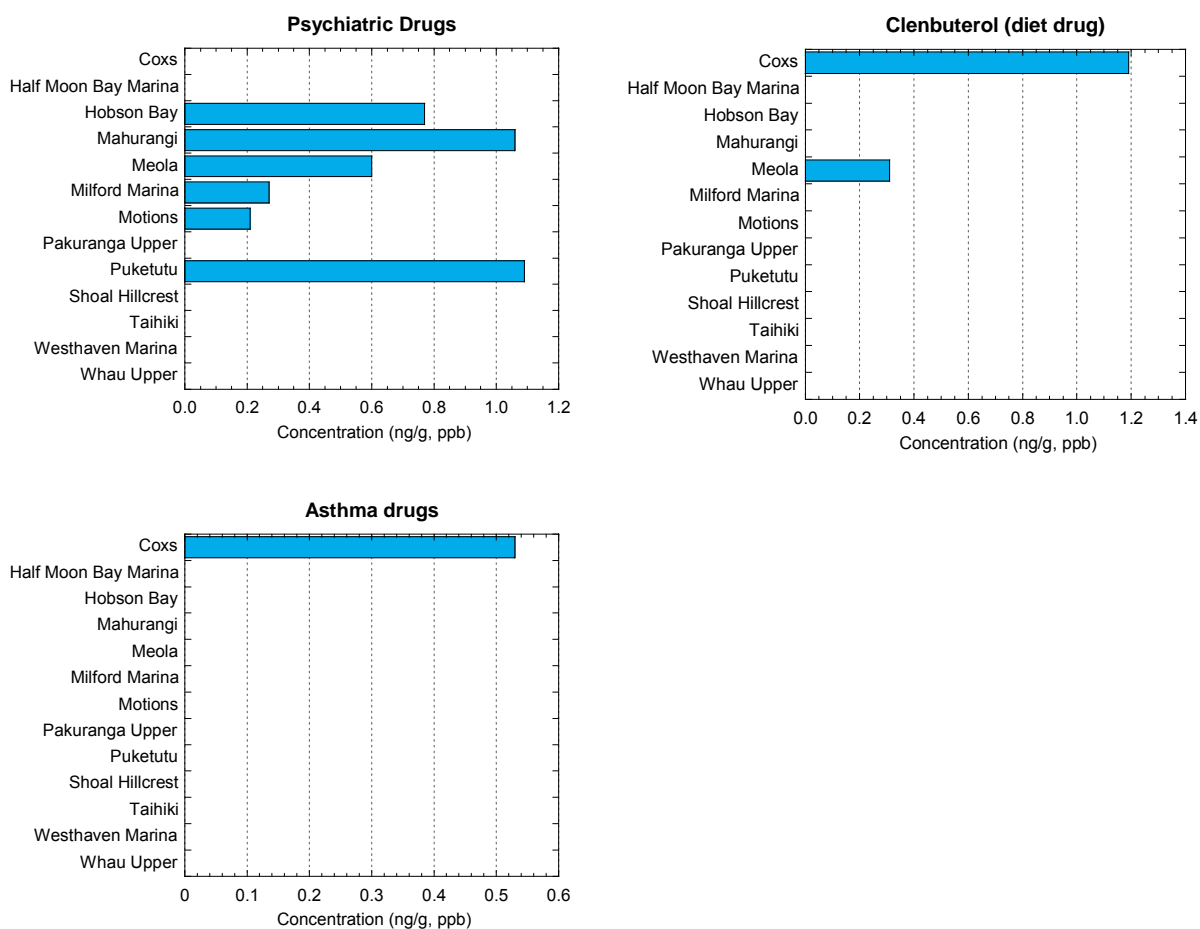
Figure 5-2 continued. Pharmaceuticals in sediments from 13 Auckland sites sampled in 2008.

Data are means of aggregated compound groups, using data reported in Appendix 1 of Stewart (2013).

6.0 Trends

In theory, OCP concentrations from the nine SoE sites sampled in both 2003 and in 2007 could be compared to assess indicative "trends" over time – or at least differences in concentrations that might indicate the general direction of trends in OCP concentrations. However, these comparisons are unlikely to be reliable, mainly because of the large differences in analytical methodologies and DLs between surveys. With this reservation, OCP status in 2003 and 2007 was summarised in Table 3-4, and concentrations of Total DDTs and dieldrin compared in Figure 3-4. These comparisons indicate that OCP concentrations were generally lower in the 2007 samples, and the number of ERC-Red sites was also lower in 2007 (one, possibly two, of the nine sites) than in 2003 (five, possibly six, of the nine sites). Any future trend assessment would need to start from a high quality baseline. At this stage, no such baseline exists across a wide range of sites.

An alternative approach to assessing changes over time at SoE sites would be to analyse archived samples[1] from 1998 (the first SoE sampling) and 2011 (the most recent SoE sampling). An intermediate year (say 2005) could also be assessed to obtain a basic time series (n = 3). Analysis should target key OCPs (dieldrin and DDTs) and PCBs at reference site(s), representative rural sites, and a selection of urban sites. Analysis of all samples in the same analytical batch would reduce the potential effects of between-batch variability, and hence improve the comparability of the time series data.

Because of the expense associated with this, and the likelihood of generally declining levels in the environment, the value of undertaking these analyses at a wide range of sites is uncertain. Auckland Council would need to consider this when assessing the priority such a study would hold relative to other needs.

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[1] Auckland Council regional marine sediment contaminant monitoring programme (RSCMP) sediment samples are currently archived to allow for future analyses. Samples in freeze dried form are stored in the dark, at room temperature, in air-tight glass jars. This is considered the best practical option currently available, given the large numbers of samples in the archive and Council resources. However, the stability of organic contaminants in these storage conditions has not been tested. It is likely that persistent chemicals such as PCBs, OCPs, and PAH should be stable. The stability of the "emerging contaminants" is unknown and would need to be considered for each compound if future analysis of archived samples is to be used for "retrospective" trend assessment.

7.0 Summary and Recommendations

7.1 Summary

Organochlorine pesticide and PCB data from surveys carried out in 2003 and 2007 at former SoE monitoring programme sites, and at rural/low density urban estuary sites sampled in 2009 and 2010, were assessed to determine ERC status.

Nine, possibly 10, of the 27 SoE sites had OCP concentrations in the ERC-Red range in 2003. Limited analysis of nine SoE sites in 2007 found lower concentrations than reported in 2003, suggesting that there may be fewer than nine or 10 SoE sites in the ERC-Red range for OCPs. DDTs and dieldrin were the only OCPs consistently detected, and were the only compounds that reached ERC-Red levels.

The usefulness of the PCB data for assessing concentrations or ERC status at SoE sites was limited by the high analytical DL in the 2003 survey. Based on very limited results it is conceivable that there may be sites in the more heavily contaminated estuary zones around Auckland (e.g. muddy industrial Tamaki Estuary sites, muddy Waitemata Harbour sites in older developed catchments) that would approach, or exceed, ERC-Red for PCBs.

Pesticide and PCB levels at the rural/low density urban estuary sites sampled in 2009 and 2010 were very low, well below ERC-Red levels and at many sites little higher than analytical blank levels. This indicates no ecologically significant contamination by these OCs at these locations.

Status assessment at the SoE sites showed that sites with elevated (ERC-Red) concentrations of OCPs (DDTs and/or dieldrin) also had high metals' concentrations, in particular Zn. The addition of the OCP data therefore did not change the ERC status of any sites, except possibly increasing Mangere Cemetery from ERC amber to red.

Studies of emerging contaminants are in their infancy, and information collected to date is "research phase" rather than "monitoring" data. Some emerging contaminants have been found, at widely varying concentrations, in Auckland's estuarine sediments. The environmental significance of these residues is currently unknown, but the initial data obtained from samples collected in 2008 suggest that treated sewage discharges and overflows (as indicated by Puketutu Island, Cox's Bay, and Mahurangi, and historical landfills (as indicated by data from Meola) may be significant sources of emerging contaminants (e.g. PBDE and some pharmaceuticals). The significance of urban runoff as a source of emerging contaminants is yet to be determined, but elevated concentrations (i.e. above DLs) of PBDEs, phthalates, glyphosate, and possibly dithiocarbamates were found at SoE and RDP monitoring sites.

7.2 Recommendations for future monitoring

There are currently few robust quantitative data for OCPs and PCBs at urban monitoring sites. Therefore there is little baseline from which to assess contaminant distributions (status) or trends. Conducting baseline analysis at a broad range of sites, in particular "high risk" urban sites (as indicated by metals' concentrations) might seem to be worth considering.

However, because of the high analytical cost associated with such as survey, the apparent correlation between metals concentrations and OCP levels, and the likelihood of generally declining levels in the environment, the value of undertaking these analyses at a wide range of sites is uncertain.

Shellfish bioaccumulate OCs, and therefore contain higher concentrations than their surrounding environment (water or sediment). These higher concentrations therefore provide a more sensitive indicator of ambient concentrations. Continued use of shellfish monitoring may be a better alternative to sediment analysis for tracking broad-scale trends over time in OCP and PCB levels. However, to date there are no ecological guidelines (as exist for sediment) for putting organic contaminant levels found in shellfish into an ecological effects context.

Overall, while the existing data are fairly limited, some general conclusions about the probable relevance of OCPs in Auckland's marine sediments were reached. The data suggest that the OCP concentrations are likely to follow similar spatial patterns to metals (particularly Zn), and therefore OCP data add little extra beneficial information for contaminant status assessment. From this point of view, it seems there is no great value in conducting further OCP analyses. However, targeted sampling of sites where benthic ecology is worse than would be expected from the concentrations of key metal contaminants (or sediment texture) may still be of some benefit.

PCB data are very limited. Analysis of key "high risk" sites (urban sites with elevated metals' concentrations) would be worthwhile to provide a better perspective on the probable importance of this group of contaminants As recommended for OCPs, high sensitivity analytical methods, with good quality assurance, are required to obtain reliable PCB data.

Continued investigation of emerging contaminants is warranted. Development of analytical capability for testing residues of compounds most relevant to NZ, and toxicological studies to determine the effects of key chemicals on NZ biota, should be undertaken. Initial focus should probably be given to understanding the composition and concentrations of emerging contaminants in key contaminant sources (e.g. raw and treated wastewaters, landfill leachates), and at receiving environment sites directly affected by these sources. As analytical capabilities are developed and demonstrated to be capable of producing reliable results at lower concentrations, monitoring a broader range of sites could be undertaken.

8.0 Acknowledgements

9.0 References

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