Bull. Environ. Contam. Toxicol. (1997) 58:871-878

Bulletin of Environmental Contamination and Toxicology

Heavy Metals and Organic Hydrocarbons in Sediments from the Waikareao Estuary, Tauranga Harbour, New Zealand

S. Burggraaf, A. L. Wilkins, A. G. Langdon, N. D. Kim

Chemistry Department, School of Science and Technology, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Received: 30 January 1997/Accepted: 12 February 1997

We have previously reported the levels of some organochlorine compounds (PCBs, DDT, DDE, chlordanes and dieldrin) in sediments and three species of shellfish from the Waikareao Estuary (Figure l), a small inlet of Tauranga Harbour, New Zealand (Burggraaf et al, 1994; Burggraaf et al. 1996). The detection of elevated levels of organochlorine compounds in some sediments and shellfish species prompted us to also determine the levels of some environmentally significant heavy metals (Cu, Pb, Zn and Cd) and three groups of organic hydrocarbons (PAHs, n-alkanes and hopane triterpenes) in sediments from eleven sites in the Waikareao Estuary.

MATERIALS AND METHODS

Samples were collected in February 1992 from sites (Figure 1) in the Waikareao Estuary, Tauranga Harbour, New Zealand (latitude 37°39'S, longitude 176°11'E). The organic carbon content of the sediment samples was determined using the loss on ignition procedure of Sansoni & Panday (1981), modified by the sample being heated to 450°C for 6 h. Heavy metal analyses were performed using a modified version of ASTM method 9.3.4 (Kimbrough & Wakakuwa 1992). Sediment material (2 g) was digested with 20 mL of 8 mol/L analar (AR) nitric acid in a 100 mL glass beaker capped with a watch glass. The digestate was then heated to 95°C and refluxed for 1 h. After cooling 30% AR hydrogen peroxide was added drop-wise (until the colour ceased to change) to dissolve any remaining organic matter. The sample was then filtered though a Whatman 541 filter paper and collected in a 100 mL volumetric flask. Zn levels were determined by flame atomic absorption spectrometry at $\lambda = 213.9$ nm with deuterium source background correction. The limit of detection for Zn was typically 2-3 µg/g (for the 2 g sample). Cu, Pb and Cd levels were established by graphite furnace atomic absorption spectroscopy at $\lambda = 324.7$, 217.0 and 228.8 nm, respectively, and with deuterium source background correction. Replicate analysis of five subsamples of the same sediment sample gave relative standard deviations of 4.7%, 5.4%, 3.3% and 7.8% for Pb, Cu, Zn and Cd respectively.

Correspondence to: A. L. Wilkins

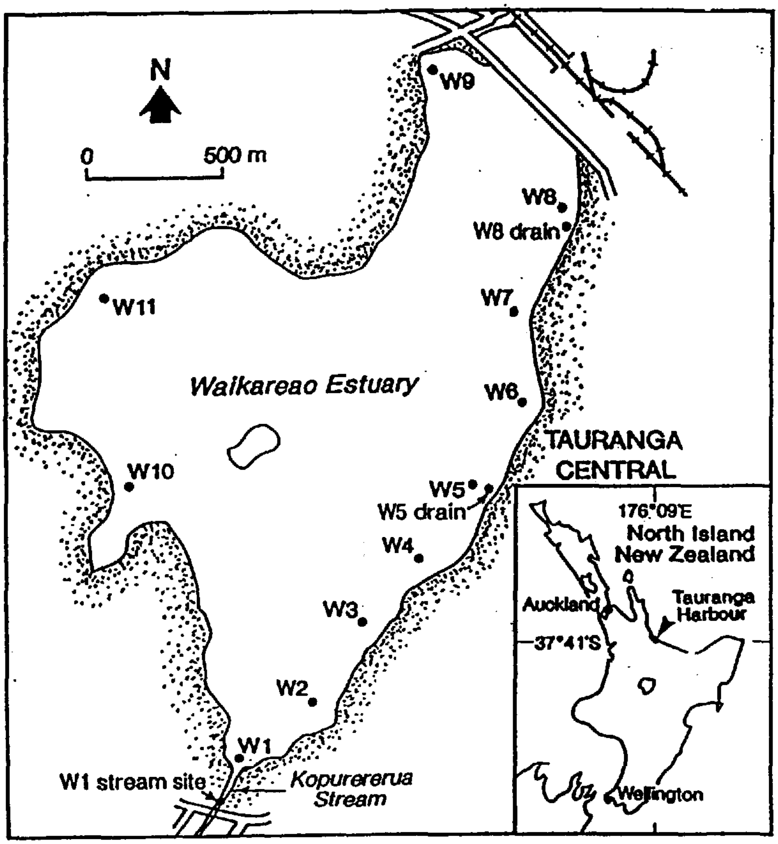

Figure 1. Location of survey sites in the Waikareao Estuary, Tauranga Harbour.

Sediment material (40 g) was dried, Soxhlet extracted, and prepared for combined gas chromatographic/mass spectrometric analysis (GC/MS) as described previously (Burggraaf et al. 1994), other than that diethylnaphthalene (added to the extracts, prior to florisil column chromatography) was utilised as the internal standard. Aliphatic, aromatic and triterpene hydrocarbons were quantified using a Hewlett Packard (HP) 5890 GC instrument fitted with a HP 7636A automatic injector and a DB-1 (J & W Ltd) fused silica capillary column (15 m x 0.25 mm), interfaced to a HP 5970B mass selective detector (MSD). Total ion GC/MS analyses established that pyrene and fluoranthene were the major PAH constituents of the non-polar organic fraction. Pyrene, fluoranthene and *n*-alkanes were identified by comparing their mass spectra (acquired in total ion chromatogram mode) and retention times with those of authentic standards and NBS library mass spectra. Recoveries of pyrene and anthacene from spiked sediment samples were 86% and 90% respectively. Hopane triterpenes were identified by comparison with published mass spectra, and a reference mixture of these triterpenes available in our laboratory. Quantification was performed using GC/MS data acquired in selected ion mode (SIM); quantification ions were *m/z* 141 (diethylnaphthalene),

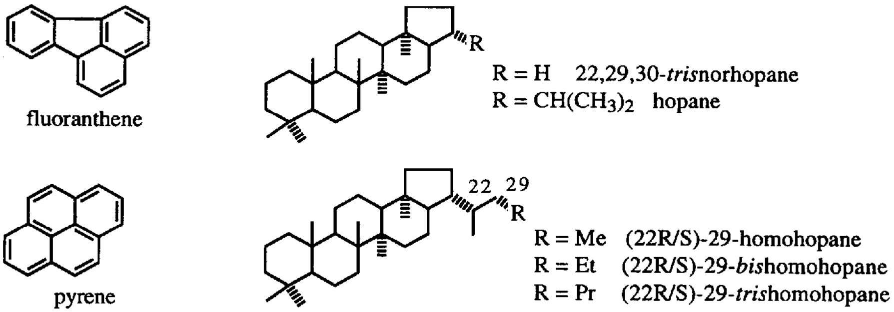

Figure 2. Chemical structures of some aromatic and triterpene hydrocarbons.

m/z 202 (pyrene and fluoranthene), *m/z* 191 (hopane triterpenes) and *m/z* 57 (*n*-alkanes). The Σ PAH, Σ hopane and Σ *n*-alkane levels represent the sums of the pyrene and fluoranthene; 22,29,30-*tris*norhopane, 29-norhopane, hopane, (22R/S)-29-homohopane, (22R/S)-29-*bis*homohopane and (22R/S)-29-*tris*homohopane, and C_{17}- C_{33} *n* -alkane contributions respectively.

RESULTS AND DISCUSSION

Concentrations of heavy metals are given in Table 1. Storm water water drains enter the harbour adjacent to the W5 and W8 sites, while the Kopurererua Stream enters the estuary adjacent to the W1 site (Figure 1). Heavy metal enrichments at the W5 and W8 sites are likely to be the result of enhanced concentrations in storm water water run off from the neighbouring residential and light industrial areas. Similarly the downward trend in heavy metal levels determined for sediments from the Wl, W2 and W3 sites implicate the Kopurererua Stream as a significant source of heavy metals in the southern portion of the estuary.

The levels of some aliphatic (*n*-alkane), hopane triterpene and polynuclear aromatic hydrocarbons (PAHs) identified in the sediment samples are reported in Table 2. A more detailed analysis of the levels of some individual aliphatic, triterpene and aromatic hydrocarbons identified in a sediment sample from the W8 site is given in Table 3. Although the sum of the concentrations of pyrene and fluoranthene is clearly an underestimate of the total level of PAHs in the sediment samples, it does however constitute a reliable basis for assessing the relative extent to which PAH contamination has occurred at each of the sample sites. For example, it is readily apparent (Table 2) that elevated levels of PAHs are present in sediments from the W5 and W8 sites (both of which are adjacent to storm water drains) and to a lesser extent also the Wl site (adjacent to the mouth of the Kopurererua Stream.

Numerous sources of PAHs have been identified, including the incomplete combustion of organic material in internal combustion engines and incinerators (Eiceman 1979). A small proportion of PAHs may be formed by digenesis of sediment organic material (Wakeham et al. 1980a). Triterpenes are often suggested as biogenic precursors of PAHs occurring in ancient sediments and petroleum, lignite and shale deposits (Peters & Moldowan 1993). Hopane triterpenes possessing between 27 and 35 carbon atoms are often encountered in sediment samples (Ourisson et al. 1979). Their presence is considered indicative of petroleum contamination in marine sediments.

Table 1. Concentrations of some heavy metals (µg/g dry wt) (ppm) in surficial sediment samples from the Waikareao Estuary, adjacent drains, and the Kopurererua Stream, Tauranga Harbour, New Zealand.

Site	Pb	Cu	Zn	Cd
W1	5.56	7.69	57.2	0.13
W2	3.29	3.78	49.3	0.13
W3	1.83	3.02	38.3	0.11
W4	2.33	3.01	41.5	0.14
W5	3.92	3.08	45.3	0.38
W6	0.54	2.85	16.2	0.14
W7	0.48	3.13	23.0	0.15
W8	7.56	13.4	46.3	0.16
W9	3.57	3.82	20.2	0.08
W10	0.38	2.41	9.02	0.09
W11	0.76	1.77	12.1	0.08
W5 drain	4.67	7.13	77.1	0.40
W8 drain	9.61	18.5	78.1	0.35
Kopurererua Stream	180	6.29	39.1	0.18

Table 2. Concentrations of some groups of hydrocarbons (ng/g dry wt) (ppb) in surficial sediment samples from the Waikareao Estuary, adjacent drains, and the Kopurererua Stream, Tauranga Harbour, New Zealand.

Site	Σ PAHS	Σ hopanes	Σ *n*-alkanes
W1	97	15	367
W2	37	9.3	264
W3	15	7.2	126
W4	23	11	135
W5	308	24	237
W6	10	4.2	116
W7	8.2	7.2	154
W8	127	39	280
W9	13	5.1	74
W10	4.2	2.2	66
W11	5.0	2.1	114
W5 drain	576	130	638
W8 drain	127	156	867
Kopurererua Stream	12	9.3	322

Σ PAHs = sum of pyrene and fluoranthene; Σ hopanes = sum of C_{27}-C_{33} hopane triterpenes;
Σ *n*-alkanes = sum of C_{17}-C_{33} *n*-alkanes

Three types of aliphatic hydrocarbon inputs were recognised in the majority of the *n*-alkane GC/MS profiles. Petroleum inputs typically give rise to a guassian-like *n*-alkane profile in the *n*-C_{15} to *n*-C_{22} region, on which may be superimposed a moderate *n*-C_{17} algae contribution, while terrigenous sources such as epicuticular plant waxes contribute the higher *n*-alkanes, with odd chain dominance in the *n*-C_{23} to *n*-C_{33} region. The levels of individual C_{17} to C_{33} n-alkanes identified in the W8 sediment sample are given in Table 3. Shorter chain length C_{10} to C_{16} *n*-alkanes were also present in some of the sediment extracts. However, a lower limit for quantification purposes of *n*-C_{17} was selected on the basis that whereas *n*-decane to *n*-hexadecane are liquids, *n*-heptadecane and higher homologues are solids; thus the higher chain homologues are likely to be retained in sediment for a longer time than would be the case for more volatile (liquid) shorter chain homologues.

Table 3. **Concentrations of some aliphatic, aromatic and triterpene hydrocarbons (ng/g dry wt) (ppb) identified in the surficial sediment sample from the W8 site, Waikareao Estuary, Tauranga Harbour, New Zealand.**

aliphatic hydrocarbons		aromatic hydrocarbons	
n-heptadecane (C_{17})	32.8	fluoranthene	62.1
n-octadecane (C_{18})	17.0	pyrene	65.1
n-nonadecane (C_{19})	25.2		
n-cosane (C_{20})	22.3	triterpene hydrocarbons	
n-heneicosane (C_{21})	21.7	22,29,30-*tris*norhopane (C_{27})	2.3
n-docosane (C_{22})	15.0	30-norhopane (C_{29})	11.2
n-tricosane (C_{23})	17.5	hopane (C_{30})	7.3
n-tetracosane (C_{24})	14.7	(22S)-29-homohopane (C_{31})	5.0
n-pentacosane (C_{25})	22.6	(22R)-29-homohopane (C_{31})	4.6
n-hexacosane (C_{26})	13.4	(22S)-29-*bis*homohopane (C_{32})	2.8
n-heptacosane (C_{27})	18.4	(22R)-29-*bis*homohopane (C_{32})	2.1
n-octacosane (C_{28})	8.7	(22S)-29-*tris*homohopane C_{33})	1.9
n-nonacosane (C_{29})	21.3	(22R)-29-*tris*homohopane C_{33})	1.3
n-triacontane (C_{30})	4.1		
n-hentriacontane (C_{31})	14.4	Σ n-alkanes	280
n-dotriacontane (C_{32})	2.5	Σ PAHs	127
n-tritriacontane (C_{33})	8.0	Σ hopane triterpenes	39

The decreasing trends in the levels of PAHs, hopanes and *n*-alkanes determined for the Wl, W2 and W3 sediments (Table 2) is consistent with these sites being increasingly distant from the mouth of the Kopurererua Stream. It is also apparent that the W5 and W8 sediments are strongly influenced by PAH, hopane and *n*-alkane inputs from the W5 and W8 drains, respectively.

It is well known that sorption of neutral organic compounds is dependant on the amount of organic matter in the sediment, and that the carbon content of sediment fractions can be correlated with weight loss on ignition (LOI). An analysis of the organic hydrocarbon content of fractionated sediment from the W5 site identified

Table 4. Sample descriptions, concentrations of organic compounds (ng/g dry wt) (ppb), and loss on ignition (LOI) of sediment fractions from the W5 site, Waikareao Estuary, Tauranga Harbour, New Zealand.

fraction size (mm)	description	fraction frequency (% by wt)	Σ PAHs	Σ hopanes	Σ *n*-alkanes	LOI (% by wt)
< 0.0625	silt	2.8	157	63	361	6.1
0.0625 - 0.125	very fine sand	13.4	116	30	163	3.3
0.125 - 0.250	fine sand	48.4	90	25	130	2.7
0.250 - 0.500	medium sand	28.8	250	25	132	3.2
> 0.500	coarse sand	6.6	702	75	283	3.6
-	particulate organic matter	nq	80 030	998	28 270	98

Σ PAHs = sum of pyrene and fluoranthene; Σ hopanes = sum of C_{27}-C_{33} hopane triterpenoids; Σ *n*-alkanes = sum of C_{17}-C_{33} *n*-alkanes; LOI = loss on ignition; nq = not quantified.

Table 5. Pearson product-moment correlation matrix (R values) for log normalised (L) concentrations of heavy metals (Pb, Cu, Zn and Cd) and for groups of hydrocarbon, PCB and DDT compounds identified in Waikareao Estuary, adjacent drains, and the Kopurererua Stream sediments (n = 14 samples). R values in the ranges 0.65-0.75 and 0.76-0.99 represent very significant ($p < 0.01$) and highly significant ($p < 0.001$) correlations respectively.

	L Pb[a]	L Cu	L Zn	L Cd	L Σ PAHs	L Σ hopanes	L Σ *n*-alkanes	L Σ PCBs[b]	L Σ DDTs[b]
L Pb	1.00								
L Cu	0.79	1.00							
L Zn	0.86	0.73	1.00						
L Cd	0.52	0.55	0.72	1.00					
L Σ PAH	0.82	0.64	0.84	0.82	1.00				
L Σ hopanes	0.79	0.83	0.88	0.86	0.89	1.00			
L Σ n-alkanes	0.73	0.81	0.87	0.80	0.78	0.89	1.00		
L Σ PCB[b]	0.84	0.67	0.93	0.78	0.89	0.93	0.86	1.00	
L Σ DDT[b]	0.89	0.76	0.75	0.63	0.72	0.83	0.86	0.90	1.00

Σ PAHs = sum of pyrene and fluoranthene; Σ hopanes = sum of C_{27}-C_{33} hopane triterpenoids; Σ *n*-alkanes = sum of C_{17}-C_{33} *n*-alkanes; Σ PCBs = total PCB expressed as an Arochlor 1260 equivalent; Σ DDTs = *p,p*'-DDT + *p,p*'-DDE + *p,p*'-DDD; [a] For n = 13 samples, Kopurererua stream value for Pb (180 µg/g) was omitted from the correlation matrix because it was unusally high; [b] Levels from Burggraaf et al. 1994 two trends in the LOI and organic hydrocarbon results (Table 4). The LOI values and organic hydrocarbon levels determined for the silt, very fine sand and fine sand fractions decreased with increasing particle size, while the medium and coarse sand fractions exhibited increasing LOI values and organic hydrocarbon levels with increasing particle size. While the trend exhibited by the silt, very fine sand and fine sand fractions was as expected, given that the smallest particles possess the largest surface areas (for adsorption), that exhibited by the medium and coarse sand fractions was not. Close inspection revealed the coarse sand fraction to include contributions from shell fragments, pumice, stones, quartz material and small black particulate matter of globular morphology and uncertain origin. GC/MS analysis of the organic extracts of a subsample comprised mainly of shell fragments, pumice and stones established the presence of only low levels of PAHs, hopanes and *n*-alkanes. However, very high levels (Table 2) of these compounds were detected in black particulate matter recovered from the coarse sand fraction (Table 4). The black particulate matter appeared to include appreciable quantities of carbonaceous components such as charcoal, coal and roading asphalt. The high LOI value (98%; Table 4) determined for this material is also indicative of a high organic content. The presence of PAH enriched organic particulates in sediment samples has been observed by others (Wakeham et al. 1980b), who attributed their origin to asphalt particles in road run off. The upward trend in the levels of organic hydrocarbons (especially PAHs) in the medium and coarse sand fractions can therefore be attributed to the presence of organic rich particulate matter.

The data from Tables 1 and 2, and the organochlorine compound concentrations reported in Burggraaf et al. 1994, were log-normalised prior to the derivation of the Pearson product-moment correlation matrix (Table 5). The correlation matrix shows that the organic compounds were highly ($p<0.001$) correlated. Heavy metal levels were either highly correlated ($p<0.0011$, or very correlated ($p< 0.01$) to each other, except for Cd/Pb and Cd/Cu. Each of the four heavy metals were also highly, or very correlated, to the organic constituents. Strong associations between these metals and the organic fractions of sediments have been reported previously (Fergusson 1990).

Comparison with the results of an earlier study (BOPCC 1983) showed that the heavy metal levels determined in this study are not significantly different from those determined a decade previously. Our results therefore indicate that only modest contamination of the estuary has occurred during the past decade. The levels of Cu, Pb and Zn detected in sediments from the eleven Waikareao Estuary sites are lower than the mean values (143,21 and 43 ppm respectively) reported in a survey of sediment samples from 24 New Zealand harbours and estuaries (Smith 1986). The PAH levels presented in Table 2 can be compared with those reported in other recent Australasian studies of marine sediments (Maber & Aislabie 1992; Wilcock & Northcote 1995; Holland et al. 1993; Kingett Mitchell & Associates 1989). In general the levels of PAHs detected in these investigations, and in the Waikareao Estuary sediments (Table 2), were less than the level of 2000 ng/g dry weight considered harmful to aquatic organisms (Long & Morgan 1991).

Acknowledgments. We thank Dr R J Wilcock and Mr G L Northcott, National Institute of Water and Atmospheric Research, Hamilton, New Zealand for technical assistance and gifts of standards.

REFERENCES

BOPCC (1983) Intertidal sediments of the Tauranga Harbour. Bay of Plenty Catchment Commission (BOPCC). Report available from Environment Bay of Plenty, Whakatane, New Zealand.

Burggraaf S, Langdon AG, Wilkins AL (1994) Organochlorine contaminants in sediments of the Tauranga Harbour, New Zealand. NZ J Mar Freshwater Res **28:**291-298.

Burggraaf S, Wilkins AL, Langdon AG, Wilcock RJ (1996) Organochlorine compounds in three species of shellfish from Waikareao Estuary, Tauranga Harbour, New Zealand. Bull Environ Contam Toxicol **57**:111-117.

Eiceman GA (1979) Analysis of fly ash from municipal incinerators for trace organic compounds. Anal Chem **51**:2343-2350.

Fergusson JE (1990) The heavy elements: chemistry, environmental impact, and health effects. Pergamon Press, New York, USA.

Holland PT, Hickey CW, Roper DS, Trower TM (1995) Variability of organic contaminants in inter-tidal sandflat sediments from Manukau Harbour, New Zealand. Arch Environ Contam Toxicol **25**: 456-463.

Kingett Mitchell & Associates (1989) Ports of Auckland environment studies 3: Assessment of dredged material at the Purukau Channel spoil ground. Ports of Auckland Ltd, Auckland, New Zealand.

Kimbrough DE, Wakakuwa J (1992) A study of the linear ranges of several acid digestion procedures. Environ Sci Technol **26**:173-178.

Long ER, Morgan LG (1991) The potential for biological effects of sediment-sorbed contaminants tested in the national standards and trends programme. Technical memorandum NOS OMA 52. National Oceanic and Atmosphere Administration, Seattle, Washington, USA.

Maher WA, Aislabie J (1992) Polycyclic aromatic hydrocarbons in nearshore marine sediments of Australia. Sci Total Environ **112**:143-164.

Ourisson G, Albrecht P, Rohmer M (1979) The hopanoids. Palaeochemistry and biochemistry of a group of natural products. Pure and Applied Chem **51**:709-729.

Peters KE, Moldowan JM (1993) The biomarker guide. Interpreting molecular fossils in petroleum and ancient sediments. Prentice-Hall Inc, Eaglewood Cliffs, New Jersey, USA.

Sansoni B, Panday VK (1981) Heavy metals in biological fluids. Lectures of a course held at the Joint Research Centre, Ispra, Italy, 22-26th June. Elsevier Science Publishers BV, Amsterdam, The Netherlands.

Smith GD (1986) Heavy metals in the New Zealand aquatic environment: A review. Water and soil miscellaneous publication No 100, National Water and Soil Conservation Authority, Water and Soil Directorate, Ministry of Works and Development, Wellington, New Zealand.

Wakeham SG, Schaffner C, Giger W (1980a) Polycyclic aromatic hydrocarbons in recent lake sediments 2: Compounds derived from biogenic precursors during early diagensis. Geochim Cosmochim Acta **44**:415-430.

Wakeham SG, Schaffner C, Giger W (1980b) Polycyclic aromatic hydrocarbons in recent lake sediments 1: Compounds having anthropogenic origins. Geochim Cosmochim Acta **44**:403-414.