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Estimates of the inputs of polychlorinated biphenyls and organochlorine insecticides to the River Thames derived from the sediment record

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Sediment deposited in the Tilbury Basin exhibited two distinct zones where contamination with organochlorine insecticides (OCL) and polychlorinated biphenyls (PCB) differed by up to an order of magnitude. The upper section of the core had an average concentration of 39 ng g^{-1} PCB and ΣDDT (sum of concentrations of DDT, DDD and DDE) 47 ng g^{-1} whereas in the lower section these were 309 and 87 ng g^{-1} respectively. This difference was attributed to improvements in waste water treatment technology, specifically the extension of activated sludge treatment at Beckton and its introduction at Crossness sewage treatment works (STW) between 1959 and 1964. At the time Beckton alone was the largest STW in Europe, treating waste from a population of 2.82 million in 1961, with a flow of $1.14 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ through the works making it the largest tributary of the Thames. The abruptness of change in pollutant concentrations observed in cored sediments at -5.82 m below Ordnance Datum Newlyn (OD) was linked to dredging activities within the basin and did not reflect rates of temporal changes in inputs. There was evidence to suggest that dechlorination of PCB had occurred within the deposited sediments. This was expressed as a change in the ratios of lower chlorinated (tri- and tetra-) congeners relative to those with 5 or more substituted chlorine atoms. An average ratio

of 0.23 from the sediment surface to -2.29 m OD changed to 0.32 and subsequently increased to 0.62 between -5.82 m to -9.55 m OD. A number of factors may account for changes in microbial dechlorination activity. However, the possibility that changes in input sources were responsible for such effects cannot be discounted.

1. Introduction

Chlorinated organic micropollutants such as polychlorinated biphenyls (PCB) and organochlorine insecticides (OCL) are widely distributed throughout the environment (Waid 1986). They have been implicated in increasing susceptibility to disease in marine mammals (Hall *et al.* 1992) although cause and effect has not been proven. The North Sea Task Force (1993*a*) expressed concern at concentrations of OCL and PCB in the North Sea and in its recommendations on organic contaminants emphasized the importance of locating input sources of these compounds. Municipal wastewaters have been identified as a significant source of OCL and PCB to receiving waters (Bedding *et al.* 1982) and the behaviour of hydrophobic organic compounds during wastewater treatment has been reported to be dominated by adsorption and sedimentation processes (Garcia-Gutierrez *et al.* 1982; Buisson *et al.* 1988; Morris & Lester 1994). The lack of qualitative information regarding the long-term fate of contaminants deposited in estuaries was recently highlighted in the overall conclusions of the North Sea Subregion 3b Assessment Report (North Sea Task Force 1993*b*).

The high affinity of non-polar anthropogenic pollutants such as the OCL and PCB for particulate matter within the hydrosphere results in their association with suspended solids (Schwarzenbach *et al.* 1994). In low flow rivers and at periods of slack tide in estuaries, such particulate material settles, taking with it the associated pollutant burden. As fluvial, marine, or estuarine sediments build up, it is not unreasonable to assume that their pollutant burden will reflect that of the period from which they were deposited. Once deposited, sediments may be resuspended or undergo reworking by benthic macroinvertebrates; however, such effects are most pronounced in areas where sediment deposition rates are low (Eisenreich *et al.* 1989). The retrieval of sediment cores and the use of geochronological techniques to assess the input histories of pollutants such as OCL and PCB has become well established (Paetzel *et al.* 1994; Huntley *et al.* 1995) and has recently been applied to major European estuaries such as the Rhine (Beurskens *et al.* 1993) and Scheldt (Van Zoest & Van Eck 1993).

During 1994 an opportunity arose to sample sediment that had accreted within the Tidal Basin at Tilbury Docks on the River Thames. This material had accreted over a unique period when significant improvements were made to Beckton and Crossness sewage treatment works (STW) which treated waste from populations of 2.82 and 1.6 million people respectively (Department of Scientific and Industrial Research 1964) and the flow from Beckton (1.14×10^6 m³ d⁻¹) made it the largest tributary to the Thames (Wood 1982).

The Tilbury Docks were built in the 1880s, 42 km downstream of London Bridge, on the Gravesend Reach of the river, one of the so-called 'Mud Reaches' (Inglis & Allen 1957). One feature of the new dock was a 19 acre tidal basin which was completely open to the river. At the time of construction it was noted that the site would be prone to siltation due to its location on the inside of a bend in the

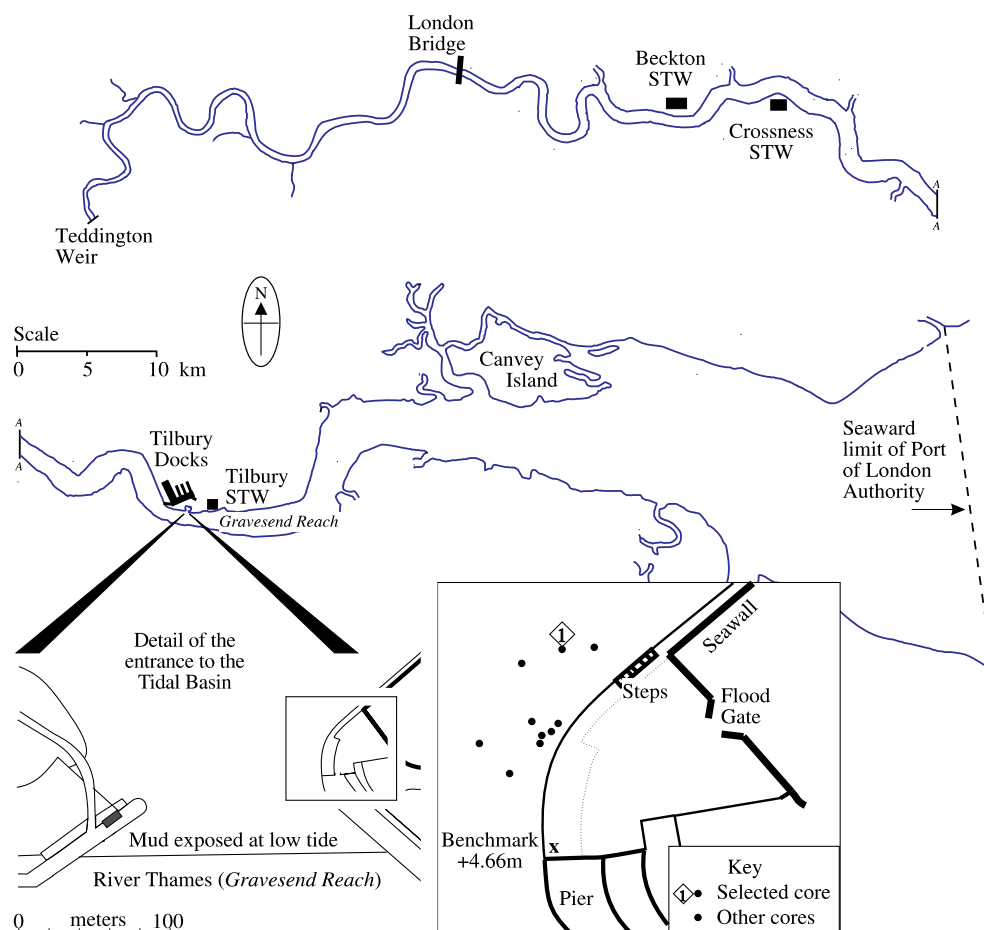


Figure 1. The Thames estuary and details of Tilbury Basin with location of sampling points.

river subject to slack heavily silted water (Broodbank 1921). The location of Tilbury Docks and the Tidal Basin in relation to the Thames tideway is indicated in figure 1.

The Basin became effectively redundant in 1926 when a new lock entrance was constructed. Subsequently limited dredging of the basin continued until it was finally halted in the 1960s. While still in use and being dredged, the basin was included in monthly sounding surveys carried out by the Port of London Authority (PLA), which date back to 1916. Following cessation of the dredging, inclusion of the basin in soundings surveys occurred once every six months when in use as a temporary refuge, falling to around once every four years after that time. Sediment within the Tidal Basin has built up to around or just above Ordnance Datum Newlyn (OD) (Ordnance Datum is the mean sea level at Newlyn measured over a six-year period during the 1920s as defined for the Government Survey of Great Britain) and is exposed at each low tide (figure 2). The archived soundings data provide a valuable record of sediment depths within the Basin.

The sediments that have accreted within Tilbury Tidal Basin, therefore, offer an opportunity to investigate changes in historical levels of contamination of the Thames by determining the concentrations of OCL and PCB. Within the time scale



Figure 2. Tilbury Basin at low tide showing sediment deposits.

of sediment accretion at Tilbury, usage of PCBs fell by 50% in five years from a peak in the early 1970s (Addison 1983) and the impact of their declining use and earlier improvements to wastewater treatment processes on the degree of environmental contamination may be reflected in the sediment record.

2. Materials and methods

The locations of the coring sites in relation to local features were fixed so that a correlation of sediment depth could be made with dates from historical sounding (depth) charts. The sampling area coincided with the area of the Basin last used and dredged. Since simple offset taping was not feasible for location fixing due to soft mud within the tidal basin, triangulation from a baseline using theodolites was chosen as the most practicable method of survey. The contemporary level of the top of the sediment at the coring location in relation to OD was taken from a benchmark located on the old quayside (figure 1)

The coring operation was planned to coincide with low tide on the mornings of 15 and 16 June 1994 so that the sediment in the tidal basin would be exposed to view. Sediment cores were taken by the British Geological Survey (BGS) using their Vibrocorer coring device, which was suspended without its support frame from a mobile crane positioned on the quayside. The vibrocorer has been frequently used to obtain core samples from under water, but this was the first time that BGS had used it to take sediment cores in this manner. The first core was taken using the BGS coring frame and a 6 m core tube, which is the more usual approach for river or sea coring. This method allowed for the slow extraction of the core using a reverse vibration technique; however, sediment depths were expected to exceed 6 m. Subsequent cores were therefore extracted using an extended (10 m) core barrel suspended from a crane without the lifting frame. These cores were retrieved by applying a gentle lifting force directly from the crane.

The coring tube contained a 10 cm inside diameter polycarbonate liner and a ‘catcher’ cap designed to allow the sediment to enter the core tube but be retained within the core tube when the tube was lifted clear. This cap consisted of flexible stainless steel fingers which closed to resist the sediment sample sliding back out of the tube. Cores were taken by allowing the Vibrocorer to sink under its own weight (*ca.* 1000 kg), followed by a period of vibration to achieve full penetration of the 10 m coring tube into the sediment.

Several approaches were followed in an attempt to obtain full recovery within the coring tube, i.e. a 10 m core sample. These included allowing penetration under self weight only to refusal, control by the crane to allow slow penetration in steps of around 1 m with periods where the corer was held fixed to allow equilibrium conditions to occur, and removal of the ‘catcher’ from the bottom of the core tube. However, the length of sediment cores within the tube never exceeded 6 m, probably due to compression of the soft sediments within the tube during the coring operation.

One of the cores (core 1, figure 1) was selected for analysis due to its greater length and location farthest into the basin, where it was expected that effects of reworking of sediments by tides and the wash from passing shipping would be less pronounced.

(a) *Soundings data*

The data on soundings within the Basin were collected from the PLA Hydrographic Department at Gravesend. Dredging operations within the basin would have taken place subsequent to soundings (which at times were taken monthly), but no record of the depth to which the Basin was actually dredged exist. These data consisted of charts of soundings surveys for the Tidal Basin with pre-1975 information stored on microfiche. Abstracts from 12 charts were obtained covering the following years: 1916, 1944 and 1965–93. 1916 and 1944 were selected to give a historical perspective and 1965 onwards to allow an evaluation of changes since dredging ceased.

To assess deposition rates, nine sounding points on a 17 m by 4 m grid were selected close to the location of core 7. Sounding depths were found for each point on the grid from each sounding survey or by interpolation where necessary. These were converted to elevations above OD (PLA Datum 3.12 m below OD) for each survey. The information that the Basin was constructed to a depth of 9.5 m below OD (Greeves 1980) was used to give a baseline from where sediment deposition began.

(b) *Core preparation*

Core samples were cut on site immediately following completion of coring at each location. The 10 m polycarbonate liner containing the sediment was laid out and cut into 0.9 or 1.0 m lengths. The core tubes were then capped and sealed. At the end of each day all the core tubes were returned to Imperial College and frozen at -18°C .

(c) *Laboratory methodology*

The procedure for analysis of the core samples was to defrost each core tube, in the case of Core 7 this involved pieces of 0.9 m length plus the shorter bottom end section, and to divide the core sample into subsamples of 5 cm length. This was achieved by splitting the polycarbonate core liner along two sides using a router and removing one half of the liner. The router fitted into a purpose-built frame with metal guide rails and an adjustable height arrangement. Before any subdivision of the core sample photographs were taken to record surface features.

The ends of each core section (*ca.* 1 cm) were discarded because of possible con-

tamination on site from the hacksaw blade. Samples were placed in solvent rinsed glass bottles with aluminium foil lined caps and re-frozen before analysis. Before removing material from any of the bottles for analysis the material was first thoroughly homogenized using a PTFE spatula to give an even consistency and uniform visual appearance.

(i) *Total solids and volatile solids*

Sub-samples were analysed for percent total solids (%TS) and volatile solids (%VS) using gravimetric analysis in accordance with methodology quoted by the Standing Committee of Analysts (1984). For volatile solids determination samples previously dried at 105 °C were muffled in a furnace at 500 °C for a period of 2 h.

(ii) *Total organic carbon*

Total organic carbon (TOC) percentage was determined using an adaptation of the titration method given in Gaudette *et al.* (1974). Use of a redox probe, rather than an indicator, to determine the end point was employed to give greater accuracy and reproducibility. Phthalate standard solution was used to verify the procedure, which was accurate up to a TOC content of 10%.

(iii) *Particle size distribution*

Determination of particle size distribution for sand, silt and clay fractions was carried out on all subsamples in order to determine any trends with depth. A pre-weighed sample was wet sieved through a 64 µm nylon mesh under vacuum (O'Reilly-Wiese *et al.* 1995); however, in this instance, reverse osmosis grade (RO) water was used as the wash medium.

Particle size distribution for the < 64 µm fraction was found by collecting a representative sample of the filtrate and subjecting it to analysis by a Malvern 2600/3600 Particle Sizer (Malvern Instruments Ltd, Malvern, UK) according to the manufacturer's instructions. Analysis was undertaken on samples in solution using a 63 mm lens.

(iv) *X-ray diffraction*

Total sediment samples were dried at 60 °C and then ground. Mineralogical composition was then characterized using a Philips scanning X-ray diffractometer measuring from 2–72°2θ. Separate analysis of the < 2 µm clay fraction was also undertaken.

(v) *Polychlorinated biphenyls and organochlorine insecticides*

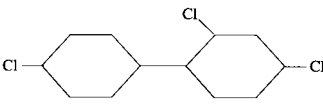
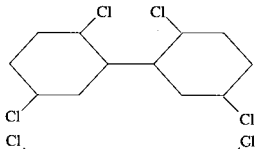
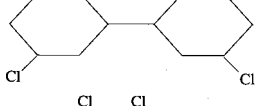
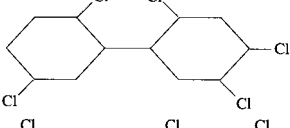
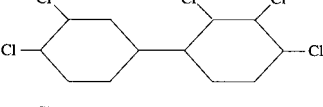
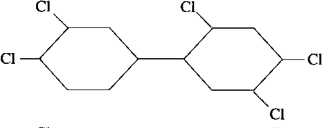
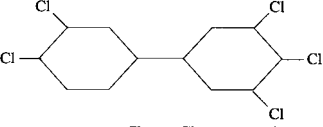
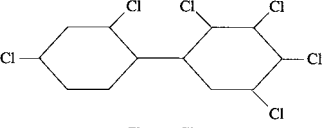
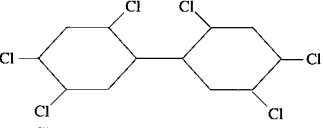
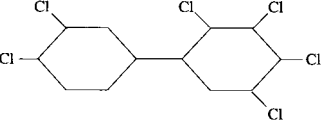
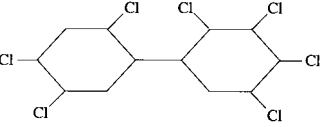
Sample extraction and clean-up procedures have been described previously (Scrimshaw *et al.* 1994). However, in this study, chlorinated biphenyls (CBs) were quantified against individual congener standards (CB 28, 52, 77, 101, 105, 118, 126, 138, 153, 156 and 180) and in some instances Aroclor 1248 to facilitate comparison with previous data. The names and structures of these congeners are listed in table 1.

The methodology for separation of CB congeners from the more polar organochlorine pesticides was modified from that previously reported. After clean-up the residue was dissolved in 100 µl of iso-octane and transferred, with 100 µl of rinsings, to a silica Sep-Pak cartridge (Waters Ltd, Watford, UK). The cartridge was then eluted with 4.5 ml of iso-octane (fraction 1) and subsequently 10 ml of 10% diethyl ether in hexane (fraction 2). Fraction 1 contained the CB plus HCB, aldrin, DDT and DDE isomers. The fractions were subsequently blown to dryness with oxygen free nitro-

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Table 1. *Chemical names and structural details of PCB congeners determined*

congener	chlorination	substitution	structure
28	2,4,4'-CBP	tri chlorinated	mono-ortho 
52	2,2',5,5'-CBP	tetra chlorinated	di-ortho 
77	3,3',4,4'-CBP	tetra chlorinated	non-ortho 
101	2,2',4,5,5'-CBP	penta chlorinated	di-ortho 
105	2,3,3',4,4'-CBP	penta chlorinated	mono-ortho 
118	2,3',4,4',5-CBP	penta chlorinated	mono-ortho 
126	3,3',4,4',5-CBP	penta chlorinated	non-ortho 
138	2,2',3,4,4',5-CBP	hexa chlorinated	di-ortho 
153	2,2',4,4',5,5'-CBP	hexa chlorinated	di-ortho 
156	2,3,3',4,4',5-CBP	hexa chlorinated	mono-ortho 
180	2,2',3,4,4',5,5'-CBP	hepta chlorinated	di-ortho 

gen and made to 0.8 ml with iso-octane containing 0.05 ppm δHCH as an internal reference peak for gas chromatographic retention times.

A reference material, IAEA 357 (Promochem, Welwyn, UK) sediment for chlorinated and petroleum hydrocarbons, was used to assess the method performance. Reagent blanks and spiked water were also extracted. To ensure that amounts of contaminants extracted were of the same order of magnitude as anticipated within the core sediments, 1 g subsamples of the reference material were extracted. The certified values and results for samples extracted in this study are presented in table 2.

3. Results

(a) *Dating of the core*

A number of inferences could be drawn from the soundings charts studied. In 1916 the Basin was dredged to depths of -9.0 to -10.5 m (all depths are relative to OD). By 1944, it is apparent that dredging was less extensive, with survey depths of around -6.6 m. The last occasion that surveys record a decrease in depth is between December 1965 (-4.3 m) and January 1966 when levels were -5.3 m. These are average levels, with an estimated error of ± 0.4 m. The level of sediment deposits in the Basin exhibited a rapid rise to -2.5 m (± 0.2 m) by October 1966 and subsequently accreted at a much reduced rate. Because no record was kept of the depth to which the Basin was actually dredged, we can only be certain that material deposited above -5.3 m is post January 1966, but material below this depth may date from a period substantially earlier than 1966.

Following the cessation of dredging, sediment appears to have accreted rapidly (over 300 cm a^{-1}) during 1966 followed by a lower rate of about 20 cm a^{-1} between mid 1966 and 1968. Subsequently the rate of accretion seems to have dropped to an average of 10 cm a^{-1} . However, soundings data for 1976 showed that the sediment surface was at -1.62 m which by 1980 had fallen to -1.8 m. The sediment surface level again fluctuated between 1984 and 1993. Such fluctuations in the sediment surface level indicate that the upper 1 m of sediment in the basin is constantly reworked through tidal and storm activity.

The sediment cores retrieved were all significantly shorter than expected given that the 10 m barrel of the Vibrocorer penetrated fully into the sediments in the Basin. It was apparent from examination of the retrieved sediment that undisturbed clay material was reached from the bed to which the Basin was constructed (see §3*b*) and that a degree of sediment compaction within the core barrel had occurred. The length of the core 5.13 m, was normalized to 10 m with the assumption that compression had been linear along the whole length.

(b) *Physico-chemical parameters*

The core was visually uniform throughout most of its depth, consisting of a grey-brown homogeneous sediment. The clearest physical change in features of the core occurred at between -9.55 and -10.33 m. This comprised of a band of grey-blue clay material, with some large pebbles (figure 3). Beneath this, the final 13 cm of material differed in character from the sediment above, being of a more peat like material.

These differences were reflected in the particle size and mineralogical composition of the sample. The percentage of silt particles decreased from predominantly $> 80\%$ above -9.55 m to $< 70\%$ from -9.55 to -10.33 m. X-ray diffraction indicated that

Table 2. Results (corrected for method recoveries) of the analysis of IAEA 357

		HCB	ppDDT	ppDDD	ppDDE	28	52	101	105	118	138	153	156	180
certified values	min	1.8	29.0	27.0	24.0	—	41.8	65.0	24.3	67.0	49.0	47.0	7.1	18.3
	max	5.2	63.0	40.0	40.0	—	52.2	81.0	33.7	117.0	99.0	81.0	12.9	35.7
	mean	3.5	46	32	32	14	47	73	29	92	79	64	10	27
this work	min	2.6	40.2	15.4	50.4	15.6	44.4	115.5	52.5	131.9	158.8	100.5	6.2	34.1
	max	7.8	60.2	31.5	62.3	20.5	56.7	135.7	67.6	154.3	182.1	122.7	14.8	47.2
	mean	4.3	53	21	56	18	52	125	57	144	178	111	12	39
$n = 5$	% rsd	56	17	27	9	12	9	7	11	6	8	7	28	13
recovery (%)		169	85	93	165	82	79	70	80	76	82	71	99	79



Figure 3. Bottom section of the core (–9.35 to –10.53 m) displaying clay and peat bands.

Table 3. *Composition (%) of the clay fraction in samples from the core*

depth below OD (m)	illite	kaolinite	chlorite	smectite
1.12–1.22	41	26	0	32
6.80–6.90	35	30	0	34
9.64–9.74	37	12	0	51

the clay minerals illite, kaolinite and smectite comprised 32% of mineral material in samples above –9.55 m and 55% in the range –9.55 to –10.33 m. Further analysis of the < 64 μm fraction itself (table 3) revealed that the base of the core was probably undisturbed London clay which is typically 50% smectite in the clay fraction, and sediment above this may contain re-worked London clay along with other sediments.

The distribution of organochlorine pollutants exhibited a dramatic shift at –5.82 m (see §3 *c, d*). To assess if significant changes also occurred to physico-chemical parameters the t-test was applied to values for %volatile solids and %TOC above and below –5.82 m (ending at –9.55 m). The hypothesis that the mean of the volatile solids in samples below –5.82 m is greater than that of those above (table 4) is true

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Table 4. Means and standard deviations (std dev) of %TOC and %VS in the core above and below -5.82 m

	%TOC	%VS
mean above -5.82 m OD	2.82	11.49
mean below -5.82 m OD	2.89	12.11
std dev above -5.82 m OD	0.86	1.00
std dev below -5.82 m OD	1.30	1.64

at the 99.99% confidence level, however, such a hypothesis is not true for TOC (64% confidence).

Volatile solids within a sample may consist of a number of components, however carbon and sulphur species are likely to predominate within estuarine sediments. Mineralogical analysis by X-ray diffraction revealed the presence of pyrite (iron sulphide) in the core sediments. It is possible that there was a change in inputs or diagenetic processes at the time the sediment level rose above -5.82 m which may account for the observed change in volatile solids content above and below this level.

(c) Polychlorinated biphenyl distribution

The profile of Σ CB contamination (sum of congeners 28, 52, 77, 101, 105, 118, 126, 138, 153, 156 and 180) against depth within the sediment core is displayed in figure 4. Values for individual congener concentrations are listed in table 5. An increase of almost an order of magnitude in Σ CB concentrations was observed at -5.82 m, from an average of 39 (-0.53 to -5.82 m) to 309 ng g⁻¹ (-5.82 to -9.55 m). Between -9.55 and -10.33 m, within the layer of clay, the least contamination (< 1 ng g⁻¹) was observed. Immediately below this clay layer was a peaty material which exhibited a degree of contamination about half of that measured in the sediment above.

Between -5.82 and -5.92 m (Σ CB concentration was 149 ng g⁻¹, table 5) contaminant concentrations may be intermediate between the high and low values due to disturbance and mixing of sediments subsequent to the final dredging operation in December 1965. Subsequently the section of the core above, from -0.53 to -5.82 m, had been deposited contiguously since January 1966 and the concentration of Σ CB with depth in sediment from this section is displayed in figure 4. The sediments between -5.82 and -4.65 m exhibit a decline in Σ CB concentrations, however, the time scale over which this occurred is short as sediment had accreted to a depth of -2.5 m by October 1966. Such a decline in concentrations could be an artefact of mixing with the more heavily contaminated sediment below after the final dredging operation. Since late 1966, however, there has been no significant decrease in total Σ CB concentrations within the core (figure 4).

All 11 congeners determined displayed an increase in concentrations below -5.82 m; however, the degree of increase varied. The change in ratio of the concentration of tri- and tetra-CB (28, 52 and 77) to the penta-, hexa- and hepta-CB (101, 118, 126, 138, 153, 156 and 180) congeners is displayed in figure 4. The less chlorinated congeners are relatively enhanced in the lower part (below -5.82 m OD) of the core, where the ratio of tri- plus tetra- to penta-, hexa- and hepta-CB averaged 0.62, but which decreased to 0.32 between -2.29 to -5.82 m and subsequently a more subtle change occurs from -2.29 m OD to the sediment surface (-0.53 m OD) where the

Table 5. Concentrations of CB congeners and total CB (Σ -CB) ng g⁻¹ dry weight
(A blank space indicates < 1 ng g⁻¹; Σ -CB is the sum of 11 congeners.)

depth cm below OD	CB 28	CB 52	CB 101	CB 77	CB 118	CB 153	CB 105	CB 138	CB 126	CB 156	CB 180	Σ - CB
53-63	4	3	4	1	3	7	2	11				36
63-73	3	3	4		3	6	2	10				31
73-82	3	3	3		2	6	1	10				29
82-92	3	2	3		2	5	1	8				24
92-102	4	4	5		4	9	2	14			1	43
102-112	4	3	4		3	7	1	11		1		35
112-122	4	3	5		4	9	2	14		1	1	43
122-131	5	4	6		4	9	2	14			1	45
131-141	4	4	5		4	9	2	13		1	1	44
141-151	3	3	4		3	7	1	11		1		33
151-161	5	4	6		4	9	2	13		1	1	45
161-171	4	4	6		4	8	2	13		1	1	41
171-180	4	3	5		4	8	1	12			1	39
180-190	4	4	6		4	9	2	13		1	1	44
190-200	3	4	6		4	9	2	15		1	1	45
200-210	3	3	5		3	8	1	12				37
210-220	4	4	7		5	10	2	16	1	1	2	50
220-229	4	4	7		4	10	2	15		1	1	49
229-239	4	4	4		2	5	1	9				30
239-249	2	2	2		1	3	1	6				18
249-259	5	5	5		3	6	1	9				34
259-269	6	5	5		3	6	1	11				39
269-278	5	5	5		3	6	1	11				38
278-288	5	4	4		2	5	1	8				29
288-298	6	5	4		2	5	1	8				30
298-308	6	5	5		3	6		11				39
308-318	5	6	6		3	7	1	12				41
318-327	4	4	5		2	6	1	10				32
327-337	4	4	5		2	7	1	11				34
337-347	4	5	5		3	7	1	12				39
347-357	3	4	4		2	5	1	9				28
357-367	4	4	5		4	10	2	14		1	1	46
367-376	4	5	7		3	10	1	15			1	47
376-386	3	4	4		2	5	1	8				26
386-396	4	5	5		3	7	1	11				37
396-406	3	4	4		2	5	1	8				27
406-416	3	3	4		2	5	1	9				27
416-425	3	4	1	1	2	5	1	10				28
425-435	3	4	4		2	6	1	11				32

Inputs of organochlorine micropollutants to the River Thames

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Table 5. *Cont.*

depth cm below OD	CB 28	CB 52	CB 101	CB 77	CB 118	CB 153	CB 105	CB 138	CB 126	CB 156	CB 180	Σ - CB
435–445	3	3	4		2	5	1	9				27
445–455	2	2	2		1	3		6				17
455–465	3	4	4		2	7	1	11		1		33
465–474	2	3	3		1	5	1	7				22
474–484	4	5	5		3	7	1	12				37
484–494	5	6	6		3	8	1	13		1	1	44
494–504	5	6	7		4	9	3	16		1	1	50
504–514	5	5	7		4	10	3	18		1	2	54
514–523	4	4	5		3	7	2	13			1	38
523–533	8	14	7		6	9	2	15		1	1	63
533–543	5	5	6		4	7	1	12				42
543–553	5	5	9		5	13	2	23		1	4	68
553–563	5	5	7		4	10	1	17		1	2	52
563–572	6	6	10		6	15	2	26		1	5	76
572–582	4	4	8	1	0	11	2	20	1	1	4	73
582–592	29	21	20		17	18	1	31	1	2	8	149
592–602	90	61	41	2	41	34	20	56	2	6	18	372
602–612	117	65	46	2	45	38	23	66	3	7	21	432
612–621	111	57	41	2	40	32	20	58	2	7	18	387
621–631	124	87	45	2	44	37	23	63	3	7	20	454
631–641	107	58	38	1	36	32	18	53	3	6	18	371
641–651	94	61	34	3	34	28	17	47	2	5	14	339
651–661	96	49	37	2	36	30	18	50	2	5	14	340
661–670	61	40	30	1	28	24	12	39	1	4	11	251
670–680	65	38	32	1	31	28	13	41	2	5	12	266
680–690	85	38	44	1	41	37	18	60	3	7	21	355
690–700	64	34	30	2	31	29	12	44	2	4	15	268
700–710	34	22	19	1	19	18	7	28	1	2	7	158
710–719	55	44	32	2	32	29	14	44	2	4	13	271
719–729	46	30	22	1	18	15	6	25		2	3	168
729–739	40	21	23		22	21	10	34	1	3	9	185
739–749	52	33	24	1	25	22	10	35	1	3	9	218
749–759	85	33	41	1	39	36	19	59	2	6	19	341
759–768	82	42	45	3	44	39	20	63	3	6	20	325
768–778	79	69	47	2	46	41	20	63	3	7	20	397
778–788	76	47	37	2	37	31	16	51	2	6	15	321
788–798	66	49	38	1	35	30	16	48	2	5	13	304
798–808	75	49	39	1	37	32	16	53	2	5	15	325
808–817	74	46	34	2	33	28	16	44	2	5	13	296
817–827	105	63	46	2	47	40	23	65	3	8	20	421

Table 5. *Cont.*

depth cm below OD	CB 28	CB 52	CB 101	CB 77	CB 118	CB 153	CB 105	CB 138	CB 126	CB 156	CB 180	Σ - CB
827–837	67	43	36	1	34	30	14	49	2	5	15	296
837–847	33	30	36		33	31	14	47	3	5	16	248
847–857	82	61	45	1	40	38	19	58	3	7	19	373
857–866	115	85	38	3	38	32	18	50	2	5	14	401
866–876	98	59	38	2	40	34	19	56	2	6	18	372
876–886	70	36	28	1	29	25	13	42	2	4	13	265
886–896	84	61	36	2	37	30	18	49	2	5	15	340
896–906	90	45	37	2	38	32	20	54	3	6	17	344
906–915	62	39	31	1	29	25	13	40	2	4	12	258
915–925	84	48	36	2	32	30	16	44	2	5	15	312
925–935	55	36	24	1	21	18	9	33		2	6	204
935–945	89	50	39	1	36	33	16	55	3	6	19	346
945–955	77	52	34	2	29	25	10	41		3	9	283
955–964	2	1						1				4
964–974												
974–984												1
984–994												
994–1004												
1004–1013												
1013–1023												
1023–1033	1	1				1		1				4
1033–1043	38	20	18		17	16	7	25	1	2	6	150
1043–1053	39	24	19	1	19	16	8	26	1	2	6	161

ratio averages 0.23. This effect may be due to changes in the ability of sediment microbiota to dehalogenate the PCB congeners or to a change in the distribution of congeners at the sources of contamination.

Several extracts were also quantified as Aroclor 1248. The average concentration of PCB as Aroclor 1248 in the four samples from the top 20 cm of the core was 26.1 ng g⁻¹. At 5.72–5.82 m below OD the CB concentration was 23.9 ng g⁻¹. This had increased to 79.3 ng g⁻¹ at –5.82 to –5.92 m and subsequently to 136 ng g⁻¹ at 5.92–6.02 m below OD, reflecting the results obtained by congener specific analysis.

(d) Organochlorine insecticide distribution

Of the insecticides determined aldrin was the only compound observed at less than the method detection limit of 0.1 ng g⁻¹. There were two patterns to the dispersion of the remaining compounds through the sediment core. HCB, the HCH isomers and endrin were present throughout the core at sediment concentrations approximating to 1 ng g⁻¹, displaying constant distributions with depth. Low sediment concentrations of the HCH isomers probably reflect their greater solubility compared to the other compounds studied and it is likely that aldrin residues would have been trans-

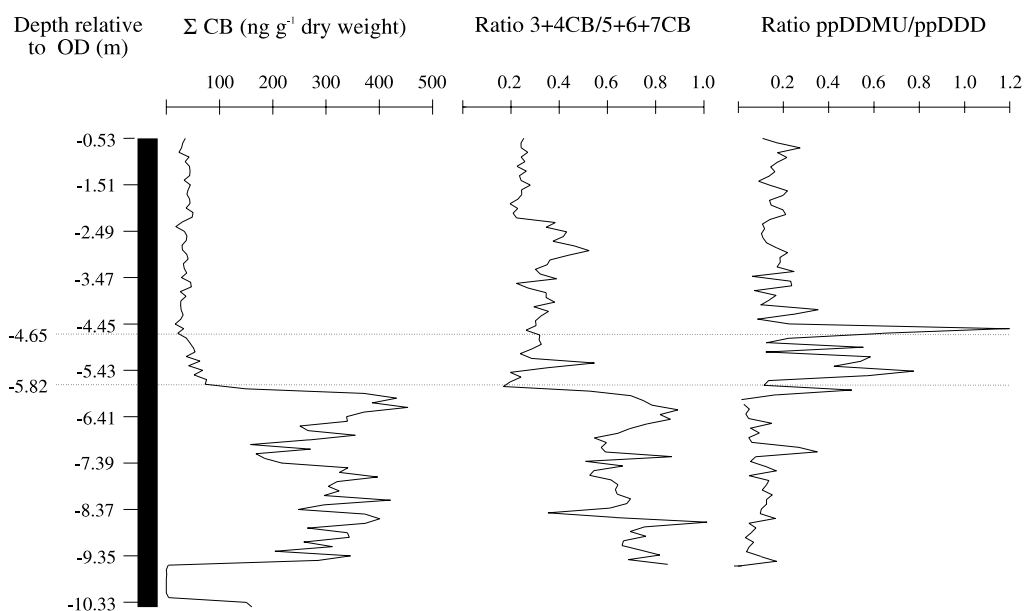


Figure 4. Distribution of contaminants within the sediment core.

formed to dieldrin, its epoxide, either before or subsequent to deposition. Dieldrin exhibited similar behaviour to the HCH compounds, though at relatively enhanced concentrations of 10–41 ng g^{-1} (table 6).

DDT (and its degradation products) were also consistently observed at levels above 1 ng g^{-1} ; however, the behaviour of ppDDT and its breakdown products ppDDE and ppDDD mirrored that of PCB, with average sediment concentrations in the lower part of the core of 87 ng g^{-1} dropping to 47 ng g^{-1} above -5.82 m OD. Sediment concentrations of ΣCB correlated most strongly with those of ppDDE (0.990) and ppDDT (0.871). Such correlations may be the result of common input sources.

Not all the DDT related compounds displayed a clear increase in concentrations within the sediment at depths greater than -5.82 m; however, the relative proportions of some ppDDT degradation products in the upper and lower parts of the core showed distinct trends. A secondary degradation product of ppDDT, ppDDMU, was detected in the sediments. This compound is produced via ppDDD. The ratio of ppDDMU to ppDDD showed a shift at -5.82 m (figure 4) similar to that already noted for CB congeners.

The results of a *t*-test on the ppDDMU/ppDDD ratio indicates that there is a 99.99% probability that there are two populations present. It may be that a greater proportion of ppDDD has been degraded to ppDDMU in the top of the core, or that further breakdown of ppDDMU has occurred at depth. Such changes may be related to improvements in river water quality occurring between the deposition of sediments in the upper and lower parts of the core. Sediment exposure to the atmosphere at low tide is another possible influence on oxygen availability. An increase in sediment concentrations of ppDCBP was observed below -5.82 m. This compound is a subsequent degradation product, although the number of pathways by which it may be produced make inferences regarding its presence difficult.

Table 6. Concentrations of dieldrin, DDT plus degradation products and sum of DDT (Σ -DDT) ng g⁻¹ dry weight(A blank space indicates < 0.1 ng g⁻¹ Σ -ppDDT sum of all pp isomers. Σ -DDT sum of all isomers of DDT, DDE and DDD.)

depth cm	op below OD	pp dieldrin	op DDT	pp DDT	op DDE	pp DDE	op DDD	pp DDD	pp DDMU	pp DCBP	Σ -pp DDT	Σ - DDT
53-63	18.0	26.6	8.6	1.0	4.6	0.3	3.1	0.5	0.4	17.2	43.2	
63-73	17.4	19.2	7.5	0.9	3.7	0.4	3.5	0.7	0.4	15.8	34.3	
73-82	17.5	19.0	7.2	0.8	3.4	0.4	4.0	0.9	0.4	16.0	34.0	
82-92	17.2	16.8	6.1	0.7	2.8	0.2	2.2	0.5	0.4	12.1	28.2	
92-102	19.4	35.5	10.3	1.3	5.1	0.5	3.7	1.1	0.6	20.9	55.1	
102-112	17.0	17.0	8.4	1.1	4.4	0.3	3.1	0.8	0.5	17.2	33.3	
112-122	18.8	33.5	9.9	1.3	5.3	0.3	3.3	0.8	0.5	19.8	52.3	
122-131	21.8	37.4	9.7	1.2	5.7	0.3	3.9	0.9	0.3	20.7	57.2	
131-141	19.5	31.8	10.2	1.2	5.3	0.4	3.3	0.7	0.5	19.9	50.8	
141-151	17.6	25.9	8.1	1.0	3.9	0.2	2.4	0.4	0.4	15.2	40.6	
151-161	22.3	21.1	9.7	1.2	5.4	0.6	3.2	0.8	0.3	19.5	40.0	
161-171	21.7	23.3	8.7	1.2	5.1	0.6	3.6	1.1	0.6	19.0	41.3	
171-180	20.1	19.4	9.1	1.1	4.6	0.5	2.8	0.9	0.4	17.8	36.3	
180-190	21.1	25.6	10.5	1.3	5.3	0.6	3.3	0.7	0.5	20.3	45.3	
190-200	24.0	22.9	10.0	1.2	5.3	0.6	3.4	0.8	0.8	20.3	42.2	
200-210	20.1	18.6	7.9	1.1	4.5	0.4	2.9	0.9	0.4	16.6	34.3	
210-220	20.8	22.2	11.5	1.5	5.8	0.5	4.1	1.2	0.4	23.0	44.1	
220-229	18.7	31.7	10.1	1.5	5.9	0.4	3.3	0.8	0.3	20.4	51.4	
229-239	32.3	7.1	7.1	0.8	4.0	0.9	4.5	0.4	1.4	17.5	23.6	
239-249	20.3	13.1	3.2	0.5	2.1	0.4	1.7	0.2	0.8	8.1	20.6	
249-259	37.6	15.7	5.8	1.0	4.3	0.6	4.0	0.5	1.1	15.6	30.4	
259-269	37.5	7.5	6.6	1.1	5.1	0.8	4.2	0.6	1.2	17.6	24.2	
269-278	39.3	7.4	6.8	1.1	5.0	0.8	5.1	0.6	1.2	18.7	25.1	
278-288	36.6	9.2	5.0	1.0	3.9	0.6	4.1	0.7	1.1	14.8	22.8	
288-298	33.4	12.1	5.4	0.9	3.8	0.6	3.4	0.8	1.1	14.6	25.3	
298-308	38.3	13.4	7.0	1.3	5.4	0.8	4.7	1.0	1.4	19.5	31.2	
308-318	32.4	24.1	7.6	1.4	5.5	0.9	3.8	1.0	0.2	18.1	41.8	
318-327	31.7	10.6	5.5	1.2	4.7	0.9	4.8	0.8		15.8	26.5	
327-337	28.7	26.2	6.7	1.3	4.8	0.7	4.1	1.2		16.7	42.5	
337-347	26.9	19.8	7.7	1.4	5.4	1.1	6.9	0.3	0.7	20.9	40.8	
347-357	24.4	19.0	5.5	1.0	4.1	0.8	4.6	0.9	1.1	16.2	34.0	
357-367	18.3	37.4	11.3	1.3	5.7	0.4	5.2	1.4		23.6	60.0	
367-376	23.7	33.1	9.4	1.7	7.1	0.7	9.2	0.5	0.4	26.7	59.6	
376-386	22.1	19.1	5.9	0.9	3.6	0.7	4.8	0.6	0.1	15.1	34.2	
386-396	25.5	26.8	7.4	1.3	5.5	1.2	6.6	0.8	0.3	20.6	47.6	
396-406	23.8	15.9	5.5	1.1	3.9	0.6	4.2	0.4	0.8	14.8	30.1	
406-416	10.0	17.1	5.5	0.9	3.6	1.1	3.0	1.3	0.5	13.9	30.3	

Inputs of organochlorine micropollutants to the River Thames

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Table 6. *Cont.*

depth cm below OD	dieltrin	op DDT	pp DDT	op DDE	pp DDE	op DDD	pp DDD	pp DDMU	pp DCBP	Σ -pp DDT	Σ - DDT
416–425	21.1	22.0	11.9	1.3	4.1	0.8	4.8	1.0	0.9	22.7	43.7
425–435	23.1	20.1	6.4	1.2	4.5	0.8	6.6	0.4	0.5	18.3	38.3
435–445	19.2	21.6	5.6	1.0	3.7	0.6	3.7	0.8	0.2	14.0	35.2
445–455	11.8	11.6	3.7	0.6	2.1	0.8	2.1	2.5	0.4	10.9	20.3
455–465	14.5	18.7	7.0	1.2	4.5	1.2	3.9	2.8	0.4	18.6	35.3
465–474	19.7	18.0	4.9	0.7	3.0	0.6	3.9	0.7	0.2	12.6	30.4
474–484	31.2	14.1	7.5	1.2	5.3	1.0	8.9	0.7	0.9	23.4	36.9
484–494	16.0	45.4	8.4	1.6	6.2	1.2	4.3	3.4	0.5	22.9	65.5
494–504	27.8	31.6	13.4	1.4	6.8	0.9	5.3	0.8	0.7	27.0	58.0
504–514	15.0	36.4	16.1	1.5	6.9	1.1	5.1	4.0	0.4	32.4	65.5
514–523	13.0	38.8	18.1	1.1	4.4	1.0	3.9	2.4	0.3	29.1	66.3
523–533	14.7	34.6	9.7	2.7	7.6	1.2	4.0	3.2	0.3	24.8	57.1
533–543	13.9	32.9	8.4	1.3	4.8	1.0	3.7	3.7	0.4	20.9	50.7
543–553	13.6	107.0	22.0	2.0	7.7	1.2	4.2	4.4	0.4	38.6	142.0
553–563	20.4	95.9	15.4	1.6	6.0	0.8	5.5	0.8	0.6	28.3	123.6
563–572	20.9	104.2	23.7	2.5	8.8	1.0	5.8	1.0	1.2	40.5	143.5
572–582	13.1	47.3	11.1	3.4	6.2	1.1	3.3	3.1	0.6	24.3	69.0
582–592	17.2	29.0	14.7	6.0	12.9	1.1	5.1	2.2	1.2	36.0	62.9
592–602	17.0	19.3	34.1	13.8	27.7	0.9	6.2	0.4	2.9	71.2	88.2
602–612	21.9	26.5	33.1	15.2	30.3	1.4	6.5	0.8	3.6	74.3	97.8
612–621	21.7	23.4	25.0	15.2	26.4	1.6	4.9	1.3	3.7	61.3	81.3
621–631	20.7	22.4	29.3	17.8	29.6	1.2	4.7	1.0	3.1	67.7	87.2
631–641	20.5	22.7	26.7	13.3	24.3	1.2	3.2	1.2	3.1	58.5	78.1
641–651	27.9	22.4	37.7	6.7	21.5	0.5	4.0	3.2		66.5	86.1
651–661	23.9	24.9	31.2	14.2	23.8	1.3	5.0	1.3	2.2	63.5	86.1
661–670	21.3	15.7	17.8	9.6	18.0	0.7	5.6	1.7	1.7	44.8	57.9
670–680	20.9	18.8	26.0	10.3	20.1	0.9	9.5	1.0	2.7	59.2	75.3
680–690	22.5	26.7	29.8	13.3	27.0	0.9	11.2	1.7	3.3	72.9	95.5
690–700	22.8	19.6	38.8	6.1	18.8	0.2	5.0	5.0		67.6	82.4
700–710	15.1	13.5	22.1	3.8	11.4	0.2	3.8	4.0	1.0	42.3	51.0
710–719	23.1	20.3	36.5	6.5	18.9	0.6	8.2	1.5		65.1	84.5
719–729	27.5	3.7	59.6	4.7	16.0	1.6	21.3	0.9	2.1	99.8	102.1
729–739	12.1	12.3	16.9	5.4	16.1		6.5	1.9	1.8	43.3	51.8
739–749	17.1	11.6	28.7	4.9	17.6	0.3	6.3	3.0	2.1	57.7	64.4
749–759	19.6	26.0	35.3	12.7	26.7	1.1	6.6	1.3	3.4	73.4	95.6
759–768	26.4	30.4	49.0	9.0	27.2	1.1	8.4	3.7	3.2	91.6	116.2
768–778	27.4	31.2	50.1	10.4	29.0	0.9	9.0	3.6	3.1	94.8	120.2
778–788	25.2	25.5	58.2	7.2	23.4	1.0	8.0	2.5	2.9	95.0	116.2
788–798	19.9	19.5	38.0	7.4	23.0	0.4	7.1	3.5	2.2	73.7	88.0
798–808	18.6	24.4	39.9	8.1	23.4	0.4	7.9	3.0	2.6	76.8	96.1

Table 6. *Cont.*

depth cm below OD	dieltrin	op DDT	pp DDT	op DDE	pp DDE	op DDD	pp DDD	pp DDMU	pp DCBP	Σ -pp DDT	Σ - DDT
808–817	24.1	20.1	33.7	6.9	20.9			2.6	3.9	61.1	74.6
817–827	37.4	29.0	52.2	9.5	28.6	1.2	10.8	2.9	4.9	99.5	121.8
827–837	27.1	22.2	36.0	7.5	22.7	1.3	10.7	2.2	3.8	75.5	93.0
837–847	23.2	22.9	36.7	6.8	24.3	0.5	5.9	4.0	3.6	74.5	90.4
847–857	29.0	30.3	48.3	9.1	28.7	1.0	11.5	1.4	4.7	94.6	119.8
857–866	25.2	27.3	36.2	8.0	23.0	0.9	8.4	1.8	3.0	72.4	95.8
866–876	27.7	24.5	37.7	9.9	25.6	1.2	11.3	1.5	4.8	80.8	100.3
876–886	23.4	18.0	27.4	11.1	19.2	0.9	6.4	0.6	2.9	56.6	71.9
886–896	21.7	22.3	34.5	13.8	23.2	0.9	6.0	1.6	2.7	67.9	86.8
896–906	23.2	22.0	37.7	11.8	25.0	1.1	6.4	1.2	2.8	73.1	92.2
906–915	20.8	16.8	21.3	11.4	19.4	0.9	8.2	0.7	2.8	52.5	66.7
915–925	21.4	20.4	34.4	7.4	21.8	0.6	8.0	2.2	3.0	69.5	85.2
925–935	13.8	10.3	28.7	4.6	17.7	0.6	5.9	3.0	1.6	56.9	63.3
935–945	41.1	21.6	30.1	13.2	25.3	0.8	18.6		2.5	76.6	96.5
945–955	39.6	8.1	26.4	7.8	22.8	0.8	16.4		2.4	68.0	74.4
955–964	0.8					0.1			0.2	0.2	0.1
964–974						0.1			0.2	0.2	0.1
974–984			0.1					0.3		0.4	0.1
984–994					0.1				0.2	0.3	0.1
994–1004								0.1	0.2	0.3	0.0
1004–1013		0.3							0.4	0.4	0.3
1013–1023					0.1				0.2	0.3	0.1
1023–1033	0.4		0.8		0.1		0.1	0.6		1.6	1.0
1033–1043	8.3	10.1	13.7	4.9	11.3	0.4	4.2	0.2	1.2	30.5	39.7
1043–1053	14.2	9.0	19.5	4.0	11.1	0.3	7.1	16.0	1.3	55.0	47.0

4. Discussion

The procedure used to correct for compression of the sediment core is verified by the corrected depth of the clay layer starting at -9.55 m, with peat material beneath. The presence of a biogenic deposit, Tilbury II, below olive green to blue/grey silt clays, occurring between -9 m and -11.5 m has been noted by Devoy (1979) along a transect crossing the Tilbury Basin. Given that there has been some variation in the relationship between levelling benchmarks, due to errors and subsequent settling over the years, this also fits well with the reported construction depth of the basin of -8.1 m (Greeves 1980) and the recorded depth to which the basin was dredged in 1916 (-9.5 to -10.1 m). Peat deposits taken from the Tilbury Docks area at depths between -9 and -12 m have been dated between 5790 and 7700 (± 120) B.P. (Churchill 1965). This confirms that the peat and clay materials retrieved from the basin are of Holocene age. Such deposits, rich in organic material, may therefore act as sinks for hydrophobic anthropogenic compounds when hydraulic connectivity to

more recent, contaminated material, occurs. While such links between deposits may occur naturally, it is also possible that the extensive engineering works at Tilbury, or disruption of the clay layer within the basin through dredging activity may have contributed to contaminant mobility.

Above the bottom clay layer, the distribution of organochlorine contaminants within the sediment core displayed two distinct zones. The most plausible explanation for the abruptness of the change in concentrations at around 6 m below OD (figure 4) is that it has resulted from dredging operations within the Basin. Such operations, which in post war years have not dredged to the bottom of the Basin, appear to have left base sediments dating from sometime between 1929 (when the new entrance lock was built) and the date dredging ceased in late 1965. The presence of residues of DDT throughout the lower sediments does, however, indicate that they have accreted since the mid 1940s, when DDT became readily available. Hence the upper and lower sections of the core represent sediments deposited post and pre 1966 respectively.

There are few historical data available on organochlorine concentrations within sediments of the river Thames sediments. Recent work indicates, however, that the concentrations of Σ PCB from 0 to 20 cm depth in the core from Tilbury Basin, 26 ng g^{-1} (expressed as Aroclor 1248) are comparable with those observed in sediments from the same depth (although temporal relationships are not clear) in surrounding areas of the river, at Grays (110 ng g^{-1}) and East Tilbury (15 ng g^{-1}) (Scrimshaw & Lester 1995).

One possible explanation for the observed decrease in sediment contamination with PCB and insecticides in the more recent (upper) sediments is the major improvements made to London's large sewage treatment works (STW) at Beckton and Crossness during the late 1950s and early 1970s. The change in quality based on the effective oxygen load (EOL) of the effluent from these two works is shown in figure 5. Changes in effluent quality were a result of improvements to the STW (Cockburn 1979). The most significant improvements in treatment with respect to discharges of organochlorine micro pollutants from these works are likely to have been the introduction of activated sludge treatment plants. By 1959 between a third and half of Beckton's output was treated in this manner, and in 1963 full treatment was introduced at Crossness. Subsequently, the commissioning of a full activated sludge treatment plant at Beckton in 1972 led to a further fall in the EOL in the river (Cockburn 1979).

The effect of primary sedimentation and subsequent activated sludge treatment on PCB and organochlorine insecticides has been studied by several workers and recently reviewed (Meakins *et al.* 1994). Primary sedimentation is known to remove a significant proportion of organochlorine contaminants (McIntyre *et al.* 1981; Garcia-Gutierrez *et al.* 1982); however, such treatment has been used at Beckton and Crossness since 1891 (Stanbridge 1977). The introduction of secondary waste water treatment processes, is however, likely to have had a significant impact on the discharge of organochlorines passing through primary sedimentation tanks.

Studies have observed the removal of PCB by activated sludge treatment ranging from 69 to 88% (Kaneko *et al.* 1976) and at greater than 90% (Buisson *et al.* 1988). This degree of removal by the treatment technologies introduced at Crossness and Beckton relates well to the observed decline in PCB concentrations of 87% between the lower and upper (above -5.82 m) parts of the core. The decrease in the concentration of ppDDE (72%) observed in the core was less than that of the PCB. This is

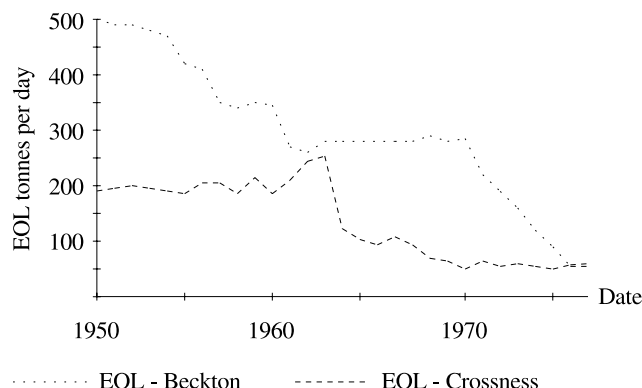


Figure 5. Effective oxygen loads from Crossness and Beckton STW 1950–1976 (Cockburn 1979).

Table 7. Correlation matrix for ppDDT, ppDDE and Σ CB against metals normalized against lithium

	Ag/Li	Cd/Li	Cu/Li	Hg/Li	Ni/Li	Pb/Li	Zn/Li
ppDDT	0.858	0.73	0.878	0.87	0.604	0.741	0.828
ppDDE	0.915	0.817	0.933	0.929	0.631	0.816	0.902
Σ CB	0.898	0.797	0.922	0.917	0.604	0.806	0.888

reflected in the less efficient removal of ppDDE (of up to 65%) compared to that of PCB by activated sludge treatment (Buisson *et al.* 1988).

Further evidence that effluent inputs and improvements in waste water treatment may be the most significant factors in explaining the difference in the degree of contamination in the core has been found from the determination of metallic elements (O'Reilly-Wiese *et al.* 1996) in the core sediments. Many metals are derived from anthropogenic sources, and at Tilbury Basin they display a similar pattern of change in concentrations within the sediment of the core as the organochlorines (table 7). The strong correlations of the sediment concentrations of metals of anthropogenic origin with those of the synthetic organochlorine compounds indicates that common events are responsible for their distribution in the core sediments.

The consequences of the introduction of activated sludge treatment may not have been confined to influencing the total inputs of contaminants to the estuary. Degradation of chlorinated organic pollutants has been noted to occur in STW (Meakins *et al.* 1994). The increase in the proportion of higher chlorinated PCB congeners in the upper section of the core may be due to preferential biodegradation of lower chlorinated PCB in the activated sludge process. Several workers (Tucker *et al.* 1975; Rockind-Dubinsky *et al.* 1987; Havel & Reineke 1991) have shown that PCB congeners with less than five chlorine atoms are extensively degraded, whereas more highly chlorinated molecules tend to persist.

Changes in sewage treatment processes may, therefore, have been a major influence on the concentrations of contaminants within the sediment core taken from Tilbury Basin. However, subsequent diagenetic processes may also have been affected by the

change in the level of the accreting sediment within the Basin and/or the significant improvement in river water quality that occurred with the introduction of new STW.

The percentage saturation of dissolved oxygen 30 km downstream of London Bridge, for example, increased from around 5% in the 3rd quarter of 1965 to 12% by 1970 and to > 25% by 1975. Ammonia concentrations at the same point fell from up to 4 mg l⁻¹ in 1960–61 to an average of < 1 mg l⁻¹ between 1967 and 1971 (Wood 1982). Such changes in river water quality, which were a direct result of improvements to treatment processes at major sewage treatment works along the Thames, may have caused changes in the community structure of microbes, or in their ability to dechlorinate, PCBs within the sediments.

Anaerobes in particular are predominantly associated with reductive dehalogenation (Mohn & Tiedje 1992), and dehalogenation by these organisms may have been inhibited by such changes. Laboratory studies have demonstrated that even subtle changes in sediment chemistry can significantly effect dehalogenation, for example, the enrichment of sediment with biphenyl (at 1000 µg g⁻¹) resulted in the accumulation of 2,4,4'-CB (PCB28), whereas in non-enriched sediment this congener was further dechlorinated (Rhee *et al.* 1993). The three plateaux observed in figure 4 may, therefore, represent different zones of dechlorinating activity within the Tilbury core, however further work is required to elucidate the dominant processes that may be occurring.

The concentrations of PCB within the sediment may also be at or approaching values which are below optimum for microbial dechlorination. In laboratory studies dechlorination activity by microbes isolated from Hudson river sediment has been observed to be greatest at a sediment concentration of 160 µg g⁻¹ of PCB. This concentration, noted by Abramowicz *et al.* (1993) is three to four orders of magnitude above that of PCB in the Tilbury core sediments. The dechlorination of PCB in Hudson river sediments has also led to the conclusion that there may be a threshold concentration below which no dechlorination will occur. Concentrations of PCB used in batch experiments by Rhee *et al.* (1993), were at 400 µg g⁻¹. The concentration of PCB138 had reached approximately 2 mol. percent when dechlorination of this congener stopped. The total molar PCB concentration remained constant at 400 µg g⁻¹, yielding 8 µg g⁻¹ PCB138 in the sediment, which is significantly above the concentration range of < 1–66 ng g⁻¹ observed in the sediments from the Thames estuary. Further information on the ability of microbes to reductively dechlorinate PCB at such low (ng g⁻¹) concentrations would facilitate understanding their fate along the UK Essex coast where contamination at such concentrations is ubiquitous (Scrimshaw *et al.* 1995).

The consistency in the proportion of DDT relative to its breakdown products, DDD and DDE within the sediment indicates that degradation of this group of compounds is not occurring. In anaerobic conditions DDT degradation occurs via DDD in preference to DDE (Kuhn & Suffita 1989). This implies that DDE residues within the sediments have not been formed *in situ*. Enhancement of ppDDMU relative to ppDDD may also be due to pre-depositional transformations. Although anaerobes are able to convert ppDDD to ppDDMU (Kuhn & Suffita 1989), the relative depletion of tri- and tetra-CB in the upper part of the core implies that less anaerobic activity is occurring than at depth. The observed relative increase of ppDDMU to ppDDD in the upper section of core sediments may be due to metabolism in invertebrates (Thompson 1973) (facilitated by improvements in the quality of the water in the Thames) before deposition in the sediment.

5. Conclusions

The contamination with OCL and PCB of sediments that have accreted in Tilbury Basin reflects historic levels of these compounds discharged to the Inner Thames Estuary.

The available evidence implies that changes to sewage treatment processes at Beckton and Crossness STW between 1963 and 1974 have been significant in reducing inputs of these compounds to the Thames as recorded by the drop in concentrations within the sediment core.

It is probable that dechlorination of PCB congeners is occurring within the sediment. It is however, unclear whether lower chlorinated congeners are accumulating as end products, or if higher chlorinated congeners are present at concentrations below which degradation does not occur.

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