The Science of the Total Environment, 121 (1992) 159–175
Elsevier Scientific Publishers B.V., Amsterdam

The chlorobenzene content of archived sewage sludges

M.-J. Wang[a], S.P. McGrath[b] and K.C. Jones[a]

[a]*Institute of Environmental and Biological Sciences, Lancaster University, Lancaster, LA1 4YQ, United Kingdom*
[b]*Soils and Crop Science Division, AFRC Institute of Arable Crops Research, Rothamsted Experimental Station, Harpenden, Herts, AL5 2JQ, United Kingdom*

(Received July 10th, 1991; accepted September 1st, 1991)

ABSTRACT

Chlorobenzenes in 40 anaerobically digested, lagoon dried sewage sludges were analysed by a Soxhlet extraction, Florisil clean-up and capillary gas chromatography method. These sludges had been applied to the plots of a long-term agricultural experiment from 1942 to 1961. Before application, the sewage sludges had been stored in lagoons at a sludge disposal works for about 1–5 years. Although some of the chlorobenzenes may have been lost during this period, substantial fractions remained at the time of field application. The mean concentration of the sum of the chlorobenzenes in the sludges was 43.7 μg/kg, with a range of 7.90–219 μg/kg. The five priority pollutants, i.e. 1,4-dichlorobenzene, 1,3-dichlorobenzene, 1,2-dichlorobenzene, hexachlorobenzene and 1,2,4-trichlorobenzene, were the most abundant. The concentrations of chlorinated benzenes generally decreased with increased chlorine substitution, although hexachlorobenzene and pentachlorobenzene were present at relatively high concentrations. 1,4-Dichlorobenzene and hexachlorobenzene increased over the period 1942–1961 in the sludges, whilst the other compounds analysed increased only from 1954 onwards. The relationship between organic matter contents and chlorobenzene recoveries from the sewage sludges was tested by experiments and the results are discussed. The results from the archived sewage sludges provide an outline of the chlorobenzene content in the environment of the West London area over a period when no monitoring was undertaken. Levels in the archived sludges are generally much lower, by perhaps an order of magnitude, than for contemporary samples.

Key words: sewage sludge; chlorobenzenes; organic pollution; gas chromatography; organic matter; environmental effects

---

Abbreviations: CB, chlorobenzene; MCB, monochlorobenzene; DCB, dichlorobenzene; TCB, trichlorobenzene; TeCB, tetrachlorobenzene; PeCB, pentachlorobenzene; HCB, hexachlorobenzene; ΣCBs, total concentration of CBs; TBB, tribromobenzene; OMC, organic matter content; GC, gas chromatography, ECD, electron capture detector; CS, centrifuged and sodium sulphate dried; CAS, centrifuged, air and sodium sulphate dried; CAO, centrifuged, air and 70°C oven dried.

INTRODUCTION

The chlorobenzenes (CBs) have a wide range of physico-chemical properties (Asher et al., 1985; Jones and Wild, 1991). They are known to be toxic to fish (Konemann, 1980; Galassi and Vighi, 1981; Dalich et al., 1982; Veith et al., 1983), water flea (LeBlanc, 1980; Calamari et al., 1983), shrimp (Mcleese and Metcalfe, 1980), algae (Galassi and Vighi, 1981; Figueroa and Simmons, 1991) and bacteria (Lui and Thomson, 1983; Wong et al., 1984). The toxicity of these compounds was reported to increase with increasing chlorine substitution (Galassi and Vighi, 1981; Black et al., 1982; Wong et al., 1984; Figueroa and Simmons, 1991). Three dichlorobenzenes (DCBs), 1,2,4-trichlorobenzene (1,2,4-TCB) and hexachlorobenzene (HCB) have been classified as priority pollutants by the United States Environmental Protection Agency (US EPA) and by the European Community (EC) (Jones and Wild, 1991). A technical mixture of trichlorobenzenes (TCBs) is also included on the EC priority pollutant list (Jones and Wild, 1991).

CBs have been found in waste soil (Shafer et al., 1984), waste water (Gaffney, 1976; Oliver and Nicol, 1982), lake water (Oliver and Nicol, 1982), river water (Wang and Lang, 1990), drinking water (Oliver and Nicol, 1982), sediments (Oliver and Nicol, 1982) and fish (Oliver and Niimi, 1983; Lang et al., 1988; Wang et al., 1990). Oliver et al. (1983) reported that the bioconcentration factor for these compounds increased dramatically as the degree of chlorine substitution on the aromatic ring became greater. CBs have also been reported in human tissues. In Slovenia, Yugoslavia, all of the chlorobenzene (CB) compounds except monochlorobenzene (MCB) were identified in samples of both human fat and milk (Jan, 1983). Pentachlorobenzene (PeCB) and HCB were found in the human adipose tissue samples collected from Kingston and Ottawa, Canada (Lebel and Williams, 1986). A further study showed the occurrence of HCB in human adipose tissue samples obtained in six municipalities around the Canadian Great Lakes (Williams et al., 1988). 1,4-DCB, 1,2,4,5-TeCB and HCB were found in Tokyo residents (EPA, 1985). HCB was also present in human adipose tissues collected from USA, Italy, UK, Germany, New Zealand and Sweden (EPA, 1985).

Undoubtedly, CBs should be regarded as a set of ubiquitous pollutants in the environment. Although no comprehensive studies have been conducted on the sources of these compounds released into the environment (EPA, 1985), it has been suggested that many operations, such as manufacture and transport of the chemicals, their use for both domestic and industrial purposes and the disposal of wastes from the manufacturing process will result in their release into the environment (EPA, 1985; Howard, 1989; Rogers et al., 1989; Jones and Wild, 1991). The chlorinated benzenes are produced in large quantities and utilised very widely (EPA, 1985; Howard, 1989; Rogers et al., 1989; Muganlinskii et al., 1990; Jones and Wild, 1991). 1,2-DCB has been used in cleaners, solvents, fuel additives and heat transfer media. 1,4-DCB is used industrially as a heat transfer medium and intermediate in the manufacture of pesticides and dyes and is also used domestically as a moth repellent and a toilet block deodorant. Besides being used by industry as a solvent, a coolant and an intermediate, 1,2,4-TCB is used as an insecticide against termites and for the treatment of waste water channels (Topp et al., 1989). Mixtures of the three TCBs are used as solvents and as degreasing agents. TeCBs, PeCB and HCB are used as flame retardants. HCB was formerly used as a dressing for wheat seed against Bunt fungi (FAO/WHO, 1970). Some of the CBs are formed as byproducts in various industrial processes (Born et al., 1989), so they may exist in many products as impurities which may therefore be important as sources of these compounds to the environment. CBs can also be formed during water disinfection by chlorine and during incineration of waste (Lahaniatis et al., 1981; Born et al., 1989).

Clearly, CBs can enter waste water from many possible sources. During the effluent treatment process a proportion of each CB compound may evaporate into the atmosphere (Wadden and Berrafato-Triemer, 1989; Govind et al., 1991), or biodegrade (Kirk et al., 1989), but sorption of the pollutants onto particulates of high organic matter content is a significant removal mechanism (Johnson and Young, 1983; Govind et al., 1991) because these compounds are lipophilic and hydrophobic. Chlorinated benzenes are therefore likely to be relatively concentrated in sewage sludge.

However, limited information is available about the CBs in sewage sludge. Table 1 summarises the concentrations of CBs in contemporary sewage sludges (Jacobs et al., 1987; Rogers et al., 1989). CB concentrations will vary significantly between waste water sources, sludge type and treatment technique. Generally, the data are insufficient to identify any trends in CB content in sludges, but sludges from industrial areas generally have higher concentrations (Wang and Jones, 1991). The concentrations in sludges are also very variable temporally and spatially. Most of the studies to date have analysed sewage sludges from different sewage treatment works (Jacobs et al., 1987; Rogers et al., 1989; Wang and Jones, 1991) although there is one report of analyses at a single sewage treatment plant over 14 months (Rogers et al., 1989). Analytical results from a study on 40 archived sewage sludges are presented in this paper. These sewage sludges were derived from a single sewage plant in London dating from 1942 to 1961. Since sewage sludges are produced from industrial and urban waste water, analysis of these sewage sludges may also give useful information about CB abundance in the environment at the time of sludge production.

TABLE 1

Concentrations of chlorobenzenes in contemporary sludges reported in the literature

Compound	USA (Jacobs et al., 1987)							UK (Rogers et al., 1989)				
	No. of sludges tested	% Occurrence	Conc. (mg/kg, dry wt)		No. of sludges tested	% Occurrence	Conc. (μg/l) range	No. of sludges tested	% Occurrence	Conc. (mg/kg, dry wt)		
			Range	Median						Range	Mean	Median
MCB	158	6	2.06–846	10.2	436	13	1–687					
1,3-DCB	215	54	0.0245–1650	1.76	437	9	14–1900	12	91.7	<0.2–40.2	4.9	1.9
1,4-DCB	215	66	0.0402–633	2.02	437	17	2–12 000	12	83.3	<0.2–33.9	11.9	9.8
1,2-DCB	215	47	0.029–809	0.645	437	16	3–1319	12	91.7	<0.2–13.6	6.9	7.9
1,3,5-TCB	217	33	0.00502–39.7	0.0632				12	91.7	<0.02–0.65	0.31	0.26
1,2,4-TCB	217	57	0.00551–51.2	0.274	437	13	2–8300	12	100	0.02–4.81	0.92	0.36
1,2,3-TCB	215	37	0.00278–152	0.0667				12	100	0.04–1.23	0.31	0.16
1,2,3(4),5-TeCBs	238	0	<detection limit					12	58.3	<0.01–0.21	0.07	0.01
1,2,3,4-TeCB	238	0	<detection limit					12	75.0	<0.01–0.22	0.1	0.07
PeCB								12	0	<0.01	<0.01	<0.01
HCB	237	43	0.000188–26.2	0.018	437	2	28–780	12	75.0	<0.01–0.42	0.07	0.02

MATERIALS AND METHODS

Sludge samples

All the anaerobically digested sewage sludges were produced from the Isleworth Sewage Treatment Works and lagoon dried at Perry Oaks Disposal Works, where they were stored for some period and mixed with other batches before disposal. These sludges were applied to agricultural land at the Woburn Market Garden Experiment managed by Rothamsted Experimental Station from 1942, originally to assess the potential of organic manures as agricultural fertilizers. Perry Oaks only receives sludges from the Isleworth Works. The dates used for the sludge samples here are those when the sludges were applied to land but may actually have been produced 1–5 years earlier. Further details of the Woburn experiment can be found elsewhere (McGrath, 1987; Wild et al., 1990a; Wild et al., 1990b). When the sludges were applied to the field, the mean solid content was 52.9% with a range of 39.2–88.7%. A sample of the sludge was collected, dried at 70°C, ground and stored at the time of each application. The possible effects of this lagoon and 70°C oven drying treatment was estimated by comparing the CB concentrations in the subsamples from a large sewage sludge sample (solid content: 3%) using the following pretreatment techniques (Wang and Jones, 1991): (1) centrifuged (solid content: 12.4%) and mixed with anhydrous sodium sulphate (CS); (2) centrifuged, incompletely air dried (solid content: 52.1%) and mixed with anhydrous sodium sulphate (CAS); (3) centrifuged, incompletely air dried (solid content: 52.1%) and then 70°C oven dried (CAO, solid content: 95.2%). Obviously, the CAO subsamples were treated in a very similar way to the sludges taken from Isleworth about 30–40 years ago. This test was designed to broadly mimic the factors likely to influence the CB concentrations in the original fresh sludges, the lagoon dried sludges at the time of field application and the archived samples.

Analytical methods

All of the sewage sludge samples were analysed in duplicate. About 5 g of archived sludge was weighed, put into a pre-extracted cellulose extraction thimble and Soxhlet extracted in an all glass system with pesticide grade hexane for 6 h using a boiling water bath. Activated copper powder was put into the flask of the Soxhlet extractor to remove sulphur from the extract. The extract was then concentrated to about 2 ml in a Rotavapor without using the vacuum system. The samples were cleaned on a Sep-Pak cartridge containing 1 g Florisil, with the first 5 ml collected in a glass vial. The clean samples were then reduced under a gentle flow of nitrogen to 500 μl and dos-

TABLE 2

Concentrations of chlorobenzenes in sludges with different organic matter content using different extraction times (μg/kg)

Compound	Sample 1 (36.0%[a])			Sample 2 (47.4%[a])			Sample 3 (61.1%[a])		
	2 h	3 h	4 h	2 h	3 h	4 h	4 h	6 h	8 h
MCB	<5000	<5000	<5000	<5000	<5000	<5000	<5000	<5000	<5000
1,3-DCB	2.48	2.21	2.00	6.25	4.49	4.59	2.26	2.47	2.49
1,4-DCB	6.92	7.38	7.14	13.1	17.2	17.4	30.2	30.6	30.7
1,2-DCB	<2	<2	<2	<2	<2	<2	<2	<2	<2
1,3,5-TCB	0.52	0.55	0.51	<0.3	<0.3	<0.3	0.78	0.83	0.89
1,2,4-TCB	0.82	0.90	1.44	1.15	1.22	1.39	0.67	1.73	1.60
1,2,3-TCB	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.12	0.27	0.23
1,2,3,5-TeCB	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,2,4,5-TeCB	0.15	0.15	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
1,2,3,4-TeCB	4.54	3.77	3.02	0.36	0.43	0.64	0.27	0.33	0.33
PeCB	0.21	0.07	0.28	0.93	1.01	1.06	0.51	0.74	0.75
HCB	0.63	0.74	0.77	3.56	6.33	8.32	7.61	8.20	8.19
ΣCBs	16.3	15.8	15.3	25.3	30.7	33.4	42.5	45.2	45.1

[a] Organic matter content.

ed with 1 μl of 88 μg/ml 1,3,5-tribromobenzene (1,3,5-TBB) solution in hexane.

The extracts were analysed by gas chromatography (GC) with an electron capture detector (ECD) on DB Wax and Ultra-2 columns. Details of the GC analysis have been reported previously (Wang and Jones, 1991).

Recovery of CBs was tested by spiking samples at high and low concentrations. Recovery of MCB was 37% on average; MCB also gave a poor response on the ECD, so that the reported MCB concentration in all the sludges was less than the detection limit (5000 μg/kg). The recoveries of the other CBs were 80–98%, with coefficients of variation (% C.V.) less than 10%. The quantitative detection limits of the method were 0.05 μg/kg (HCB), 0.07 μg/kg (PeCB), 0.1 μg/kg (TeCBs), 0.3 μg/kg (1,3,5- and 1,2,3-TCB), 0.5 μg/kg (1,2,4-TCB), 2 μg/kg (1,3- and 1,2-DCB) and 3 μg/kg (1,4-DCB) separately. These values were estimated from the minimum peak area which could be accurately measured (approx. three times the background noise level).

Organic matter contents of the sewage sludges were determined by ashing the samples at 375°C in an electric furnace over night (approx. 14 h) after being dried at 105°C in an oven for 24 h.

RESULTS AND DISCUSSION

Extraction time

To optimise the Soxhlet extraction time, three sewage sludges were extracted for different periods. The results are shown in Table 2. The organic matter content (OMC) of the samples clearly has an effect on the recovery of these compounds. The OMC in sample 1 was 36.0% and the recoveries of CBs were not significantly different with extraction times of 2, 3 and 4 h. Sample 2 had an OMC of 47.4% and the compound recoveries were clearly different, suggesting that even a 4 h extraction might not be enough to recover these pollutants thoroughly. The sewage sludges used in this study had a mean OMC of 42.2% with a range of 26.1–49.8%. In order to ensure a thorough extraction of all sludges, a sewage sludge with an OMC of 61.1%, sample 3, was chosen to test the extraction time. The data from sample 3 illustrated that increasing the extraction time from 6 to 8 h resulted in no significant increase in CB recoveries. The effect of OMC on the recoveries of CBs implies that these compounds are present primarily in the organic matter of the sludges.

Comment on the samples

Table 3 gives the concentrations of CBs in the subsamples from a large

TABLE 3

Concentrations of chlorobenzenes in a sludge sample treated by different techniques simulating the treatments of the archived sewage sludges

Compound	CS (Fresh[a]) Conc. (μg/kg)	CAS (Lagoon dried[a])		CAO (lagoon and oven dried[a])		
		Conc. (μg/kg)	CAS/CS (%)	Conc. (μg/kg)	CAO/CAS (%)	CAO/CS (%)
MCB	< 10 000	< 10 000	—	< 10 000	—	—
1,3-DCB	21.2	18.7	88.2	15.9	84.9	74.9
1,4-DCB	816	639	78.3	450	70.4	55.2
1,2-DCB	139	104	74.9	51.2	49.1	36.7
1,3,5-TCB	8.67	7.20	83.1	4.23	58.8	48.8
1,2,4-TCB	85.4	71.5	83.7	46.3	64.8	54.2
1,2,3-TCB	15.0	12.6	84.0	8.30	65.8	55.2
1,2,3,5-TeCB	5.43	5.08	93.6	3.59	70.7	66.1
1,2,4,5-TeCB	25.9	23.5	91.0	19.1	81.0	73.7
1,2,3,4-TeCB	15.3	13.6	88.6	11.8	86.8	76.9
PeCB	20.2	20.0	98.9	16.6	83.3	82.3
HCB	32.2	30.5	94.7	29.6	97.0	91.8

[a] Simulated treatment.

sludge sample treated by different methods described in the previous part of this paper. The CS, CAS and CAO treatments could basically represent the fresh, lagoon dried and 70°C oven dried sludge, respectively. The results in Table 3 show that about 75–99% (CAS/CS) of CBs originally present in the sludges still remained at the time of field application. The results also implied that the concentrations of CBs reported here could be 49–97% (CAO/CAS) of those in the lagoon dried sludges which had been applied to the land and 37–92% (CAO/CS) of those in the original fresh sludges.

Concentrations of CBs in sludges

Table 4 presents the concentrations of CBs in the archived sewage sludges applied to the Woburn Market Garden Experiment from 1942 to 1961. The occurrence, range, median and mean of these compounds in the sludges are listed in Table 5. 1,4-DCB, HCB and PeCB were identified in all the samples while MCB and 1,2,3,5-TeCB were below the detection limits in all the samples. The remaining compounds occurred in between 20 and 92% of the samples. To give a correct picture of the concentrations of CBs in the sludges, the means of those compounds with an occurrence between zero and 100% were calculated in two different ways: using either zero or the detection limits. The individual CBs occurred at concentrations between < 0.1 μg/kg and 86.1 μg/kg. The mean ΣCBs concentration in the samples was 43.7 μg/kg with a range of 7.90–219 μg/kg and a median of 32.5 μg/kg. 1,4-DCB was the most abundant compound with a mean concentration of 21.1 μg/kg. The mean concentrations of 1,2-DCB, 1,3-DCB, HCB, 1,2,4-TCB and 1,2,3,4-TeCB were 8.47–1.32 μg/kg, while those of 1,3,5- and 1,2,3-TCB, 1,2,4,5-TeCB and PeCB were lower than 1 μg/kg. The concentration of CBs generally decreased with increased chlorine substitution although HCB and PeCB had higher concentrations.

The CB concentrations in these archived samples were generally lower than those reported for contemporary sludges in Table 1, even allowing for the losses considered in Table 3. This may be due to several factors. Firstly, all of these sewage sludges were obtained from a single effluent treatment works which receives waste water from one area. This catchment may not be particularly contaminated with CBs. Secondly, CBs may not have been so widely used in the 1940s and 1950s as in more recent years. In 1989, a sludge sample was collected from Perry Oaks and dried at 70°C. The concentration of ΣCBs was 514 μg/kg which was higher than the maximum (219 μg/kg) of these archived samples and over an order of magnitude higher than the average value. Finally, the lagoon drying process may not have been simulated adequately by the tests reported in Table 3, so that a greater proportion of the CBs may have been evaporated and degraded (Wadden and

TABLE 4

Concentrations of chlorobenzenes in archived sewage sludges (μg/kg)

Year	MCB	1,3-DCB	1,4-DCB	1,2-DCB	1,3,5-TCB	1,2,4-TCB	1,2,3-TCB	1,2,3,5-TeCB	1,2,4,5-TeCB	1,2,3,4-TeCB	PeCB	HCB	ΣCBs
1942	<5000	18.3	9.90	15.9	<0.3	1.95	0.31	<0.1	<0.1	0.75	0.46	0.83	48.5
1943	<5000	38.8	25.2	31.0	0.47	7.67	0.85	<0.1	<0.1	3.84	0.79	3.02	112
1944	<5000	8.04	6.06	5.53	<0.3	1.88	0.34	<0.1	0.67	3.44	0.56	1.94	28.5
1945	<5000	10.1	27.3	9.13	0.30	2.10	0.57	<0.1	0.28	6.32	0.72	2.04	58.9
1947	<5000	2.23	7.15	<2	0.53	1.05	<0.3	<0.1	0.15	3.78	0.18	0.72	15.8
1948	<5000	3.25	4.11	<2	<0.3	0.74	<0.3	<0.1	<0.1	0.34	0.75	4.65	13.9
1948	<5000	<2	5.46	<2	<0.3	<0.5	<0.3	<0.1	<0.1	0.11	0.87	3.43	9.87
1949	<5000	10.4	14.8	9.05	0.45	1.62	<0.3	<0.1	0.29	2.91	0.54	1.75	41.9
1950	<5000	9.35	11.0	3.07	0.61	1.16	<0.3	<0.1	<0.1	0.73	0.41	3.85	30.2
1951	<5000	<2	6.58	<2	<0.3	1.37	<0.3	<0.1	0.32	5.26	0.61	1.84	16.0
1951	<5000	<2	5.87	<2	0.55	<0.5	<0.3	<0.1	0.43	<0.1	0.08	0.96	7.90
1951	<5000	<2	23.3	<2	0.44	0.76	<0.3	<0.1	0.20	<0.1	0.10	1.10	25.9
1952	<5000	<2	23.5	<2	<0.3	1.09	<0.3	<0.1	<0.1	<0.1	0.47	1.72	26.8
1952	<5000	<2	15.6	<2	0.45	0.55	<0.3	<0.1	0.38	0.18	0.12	1.61	18.9
1952	<5000	2.36	7.62	<2	<0.3	0.69	<0.3	<0.1	<0.1	0.13	0.39	2.03	13.2
1953	<5000	2.20	12.1	<2	0.92	<0.5	<0.3	<0.1	0.75	0.14	0.14	2.45	18.7
1953	<5000	86.1	50.6	61.9	0.38	9.36	0.50	<0.1	0.33	6.03	1.19	3.18	219
1954	<5000	<2	9.74	<2	<0.3	0.64	<0.3	<0.1	<0.1	0.16	0.25	1.10	11.9

1954	<5000	3.88	16.9	<2	0.36	0.55	<0.3	<0.1	<0.1	0.23	0.93	2.97	25.8
1954	<5000	<2	6.52	<2	<0.3	0.76	<0.3	<0.1	<0.1	0.12	0.51	1.93	9.83
1955	<5000	2.52	19.8	<2	0.43	0.55	<0.3	<0.1	0.63	0.20	0.35	2.47	27.0
1955	<5000	5.11	15.9	<2	<0.3	1.26	<0.3	<0.1	<0.1	0.48	1.00	6.07	29.8
1955	<5000	<2	28.8	<2	1.08	0.70	<0.3	<0.1	0.31	0.21	0.39	3.10	34.6
1956	<5000	<2	11.1	<2	<0.3	<0.5	<0.3	<0.1	<0.1	0.83	1.76	3.30	17.0
1956	<5000	19.3	24.0	18.6	<0.3	1.26	0.32	<0.1	0.78	5.74	2.36	3.23	75.5
1957	<5000	<2	32.6	<2	0.86	1.57	<0.3	<0.1	<0.1	0.28	0.75	6.66	42.7
1957	<5000	<2	34.2	2.69	1.98	1.25	0.33	<0.1	0.58	0.25	0.93	5.34	47.6
1957	<5000	13.5	37.9	15.9	3.14	1.62	<0.3	<0.1	0.89	3.20	0.53	4.32	80.9
1958	<5000	<2	18.0	<2	1.29	0.75	<0.3	<0.1	0.59	0.22	0.37	3.20	24.4
1958	<5000	3.53	18.7	2.76	1.15	0.86	<0.3	<0.1	<0.1	0.23	0.68	5.39	33.3
1958	<5000	7.80	26.1	9.11	1.75	1.02	<0.3	<0.1	<0.1	0.23	0.62	1.29	47.9
1958	<5000	4.65	22.3	3.58	0.75	0.74	<0.3	<0.1	<0.1	0.21	0.54	4.59	37.3
1959	<5000	3.80	16.3	3.24	1.25	1.31	<0.3	<0.1	<0.1	0.19	1.04	4.40	31.6
1959	<5000	12.2	49.7	23.5	1.89	2.85	<0.3	<0.1	0.83	2.33	0.55	3.15	97.0
1960	<5000	2.57	31.0	8.61	0.90	1.82	<0.3	<0.1	<0.1	0.18	0.45	4.18	49.7
1960	<5000	<2	29.2	6.52	0.89	1.05	<0.3	<0.1	<0.1	0.18	0.55	5.22	43.6
1960	<5000	<2	47.8	19.7	2.30	1.74	<0.3	<0.1	<0.1	0.21	0.46	2.60	74.8
1961	<5000	<2	33.7	11.8	1.03	2.49	<0.3	<0.1	<0.1	0.16	0.51	2.84	52.5
1961	<5000	<2	36.6	11.5	1.40	1.94	<0.3	<0.1	0.12	0.23	0.44	1.77	53.9
1961	<5000	27.9	22.7	27.9	0.54	3.52	0.36	<0.1	1.74	2.83	0.69	6.89	95.0

TABLE 5

Occurrence, range, median and mean of the concentrations of CBs in sewage sludges

Compound	Occurrence (%)	Range (μg/kg)	Median (μg/kg)	Mean[a] (μg/kg)
MCB	0	<5000	<5000	<5000
1,3-DCB	57.5	<2–86.1	2.44	7.45[b]–8.30[c]
1,4-DCB	100	4.11–50.6	19.3	21.1
1,2-DCB	52.5	<2–61.9	2.73	7.52[b]–8.47[c]
1,3,5-TCB	70.0	<0.3–3.14	0.50	0.70[b]–0.79[c]
1,2,4-TCB	90.0	<0.5–9.36	1.13	1.56[b]–1.61[c]
1,2,3-TCB	20.0	<0.3–0.85	<0.3	0.09[b]–0.33[c]
1,2,3,5-TeCB	0	<0.1	<0.1	<0.1
1,2,4,5-TeCB	47.5	<0.1–1.74	<0.1	0.26[b]–0.31[c]
1,2,3,4-TeCB	92.5	<0.1–6.32	0.23	1.32[b]–1.33[c]
PeCB	100	0.08–2.36	0.54	0.63
HCB	100	0.72–6.89	3.00	3.08
ΣCBs		7.90–219	32.5	43.7[b]

[a]Undetected values were treated as [b]zero and [c]detection limit separately.

Berrafato-Triemer, 1989; Kirk et al., 1989; Govind et al., 1991). Nevertheless, data from the archived sludges provides some information about the abundance of CBs in the environment during the time course of sludge production and application.

The ranking of abundance of individual CBs in relation to the ΣCBs content of the samples is given in Table 6. This shows 1,4-DCB to be consistently the most abundant compound with the TCBs and TeCBs consistently of low abundance. The ranking of HCB and PeCB decreased as the ΣCBs content in sludges increased, whereas those of 1,3-DCB and 1,2-DCB showed the opposite trend. This is illustrated very clearly in Fig. 1, which gives the percentage abundance of each CB in different overall concentrations of ΣCBs.

Figure 2 shows the concentrations of the five most abundant CBs (a–e) and the overall ΣCBs (f) through the time course. All of the concentrations varied substantially during the period. There were two samples which had significantly larger concentrations than the rest, those from 1953 (219 μg/kg) and 1943 (112 μg/kg). Both these sludges had particularly high concentrations of 1,3-DCB, 1,2-DCB and 1,2,4-TCB. Although 1,4-DCB was also

TABLE 6

Ranking of abundance for individual chlorobenzene compounds in sewage sludges with different ΣCBs values[a]

Compound	ΣCBs (μg/kg)				
	0–20 *n* = 11	20–40 *n* = 12	40–60 *n* = 10	>60 *n* = 7	7.90–219 *n* = 40
1,3-DCB	4	2	3	3	3
1,4-DCB	1	1	1	1	1
1,2-DCB	9	4	2	2	2
1,3,5-TCB	7	6	7	7	6
1,2,4-TCB	5	5	5	4	5
1,2,3-TCB	9	10	10	10	10
1,2,4,5-TeCB	8	9	9	9	9
1,2,3,4-TeCB	3	8	6	6	8
PeCB	6	7	8	8	7
HCB	2	3	4	5	4

[a] For example, HCB was the second most abundant compound (ranking = 2) in the sludges which had low ΣCBs (0–20 μg/kg), but was ranked fifth in the most polluted sludges (ΣCBs > 60 μg/kg) and fourth overall (in all the 40 sludges).

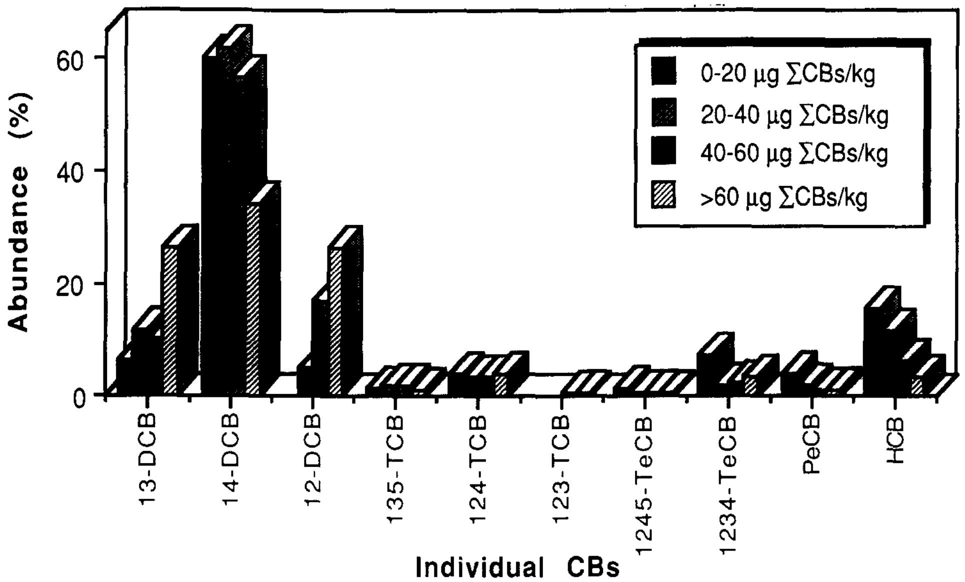

Fig. 1. Percentage abundance of individual CBs in sewage sludges with different ΣCBs categories.

present at large concentrations in these two samples its contribution to the ΣCBs loading was not as significant as in other samples. HCB was not a major contributor to the ΣCBs content of the two most contaminated sludges. 1,4-DCB is now widely used for domestic purposes. HCB is a relatively persistent pollutant.

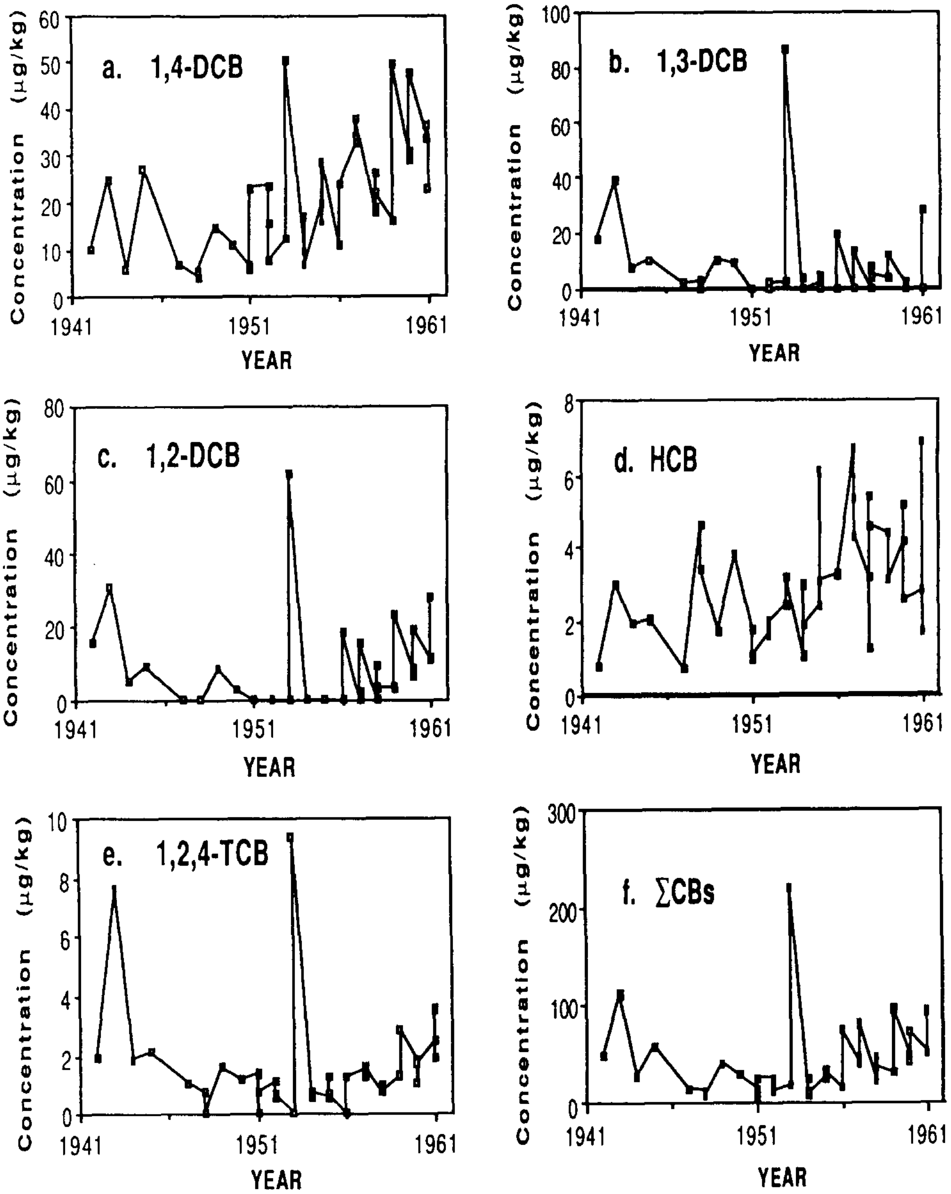

Fig. 2. Concentrations of CBs in sludges with time.

The changes observed in CB concentrations during the period are not easy to interpret since the exact sludge production dates are not available and the sludges had been mixed at Perry Oaks when samples were collected. However, it is likely that the sludges might have been produced 1–5 years earlier than the date of field application and samples from mixed sludges over several years possibly give more representative results.

The 1,4-DCB and HCB content in the sludges generally increased through time, reflecting an increase in use of these two compounds. The concentrations of 1,3-DCB, 1,2-DCB, 1,2,4-TCB and ΣCBs showed an obvious increase from 1954 to 1961.

It was notable that the ΣCBs concentrations were significantly lower from 1947 to 1952 than the other periods. Considering the sewage sludges had been kept at Perry Oaks for several years before land application, the samples dated 1947–1952 were probably produced during or slightly after the Second World War when the production and use of CBs may have been somewhat smaller.

CONCLUSIONS

CBs in sewage sludges are mainly absorbed or adsorbed by the organic matter. Tests of the recovery of these compounds from sludges showed that the organic matter content may influence the efficiency of extraction.

The five priority pollutants, 1,4-DCB, 1,3-DCB, 1,2-DCB, HCB and 1,2,4-TCB, were the most abundant individual CBs in the sewage sludges applied to the Woburn Market Garden Experiment.

1,4-DCB and HCB in sludges increased over the period 1942–1961, whilst the other compounds analysed increased only from 1954 onwards.

It is difficult to deduce the various sources of CBs; the exact dates of production and treatment of these samples are not known. However, the results from these archived sewage sludges provide an outline of the CB content in the environment of the West London area during the period when no monitoring was made. These results suggest that the CB content of modern sludges is somewhat higher than those sampled during the 1940s and 1950s.

REFERENCES

Asher, S.C., K.M. Lloyd, D. Mackay, S. Paterson and J.R. Roberts, 1985. A Critical Examination of Environmental Modelling — Modelling the Environmental Fate of Chlorobenzenes Using the Persistence and Fugacity Models. Pub. No. NRCC 23990 of the Environmental Secretariat, NRCC, Ottawa, Canada.

Black, J.A., W.J. Birge, W.E. McDonnell, A.G. Westerman and B.A. Ramey, 1982. The Aquatic Toxicity of Organic Compounds to Embryo-larval Stages of Fish and Amphibians. Kentucky Water Resources Research Inst., Lexington.

Born, J.G.P., R. Louw and P. Mulder, 1989. Formation of dibenzodioxins and chlorobenzenes in fly ash catalyzed reactions of monochlorophenols. Chemosphere, 19: 1629–1633.

Calamari, D., S. Galassi, F. Setti and M. Vighi, 1983. Toxicity of selected chlorobenzenes to aquatic organisms. Chemosphere, 12: 253–262.

Dalich, G.M., R.E. Larson and W.A. Gingerich, 1982. Acute and chronic toxicity studies with monochlorobenzene in rainbow trout. Aquatic Toxicol., 2: 127–142.

EPA, 1985. Health Assessment Document for Chlorinated Benzenes. EPA 600/8-84-015F.

FAO/WHO, 1970. Hexachlorobenzene. In: 1969 Evaluations of Some Pesticide Residues in Food: The Monographs. FAO/FOOD ADD./70.38, Rome, pp. 161–175.

Figueroa, I.C. and M.S. Simmons, 1991. Structure-activity relationships of chlorobenzenes using DNA measurement as a toxicity parameter in algae. Environ. Toxicol. Chem., 10: 323–329.

Gaffney, P.E., 1976. Carpet and rug industry case study I: water and wastewater treatment plant operation. J. Water Pollut. Control Fed., 48: 2590–2598.

Galassi, S. and M. Vighi, 1981. Testing toxicity of volatile substances with algae. Chemosphere, 10: 1123–1126.

Govind, R., P.A. Flaherty and R.A. Dobbs, 1991. Fate and effects of semivolatile organic pollutants during anaerobic digestion of sludge. Water Res., 25: 547–556.

Howard, P.H., 1989. Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Vol. I, Large Production and Priority Pollutants. Lewis Publishers, Michigan, USA.

Jacobs, L.W., G.A. O'Connor, M.A. Overcash, M.J. Zabik and P. Rygiewicz, 1987. Effects of trace organics in sewage sludges on soil-plant systems and assessing their risk to humans. In: A.L. Page, T.J. Logan and J.A. Ryan (Eds.), Land Application of Sludge — Food Chain Implications. Lewis Publishers, Michigan, USA, pp. 101–143.

Jan, J., 1983. Chlorobenzene residues in human fat and milk. Bull. Environ. Contam. Toxicol., 30: 595–599.

Johnson, L.D. and J.C. Young, 1983. Inhibition of anaerobic digestion by organic priority pollutants. J. Water Pollut. Control Fed., 55: 1441–1449.

Jones, K.C. and S.R. Wild, 1991. Organic Chemicals Entering Agricultural Soils in Sewage Sludges: Screening for Their Potential to Transfer to Crop Plants and Livestock. Foundation for Water Research Report Number FR0169, Water Research Centre, Medmenham, UK.

Kirk, P.W.W., H.R. Rogers and J.N. Lester, 1989. The fate of chlorobenzenes and permethrins during anaerobic sewage sludge digestion. Chemosphere, 18: 1771–1784.

Konemann, H., 1980. Structure-activity relationships and additivity in fish toxicities of environmental pollutants. Ecotoxicol. Environ. Safety, 4: 415–421.

Lahaniatis, E.S., R. Roas, D. Bieniek, W. Klein and F. Korte, 1981. Bildung von chlorierten organischen Verbindungen bei der Verbrennung von Polyethylen in Gegenwart von Natriumchlorid. Chemosphere, 10: 1321–1326.

Lang, P.-Z., M.-J. Wang, F.-S. Long and X. Yuan, 1988. Analysis of organic pollutants in the bodies of fish by gas chromatography. Bull. Anal. Testing, 7: 38–40.

Lebel, G.L. and D.T. Williams, 1986. Determination of halogenated contaminants in human adipose tissue. J. Assoc. Off Anal. Chem., 69: 451–458.

LeBlanc, G.A., 1980. Acute toxicity of priority pollutants to water flea (*Daphnia magna*). Bull. Environ. Contam. Toxicol., 24: 684–691.

Lui, D. and K. Thomson, 1983. Toxicity assessment of chlorobenzenes using bacteria. Bull. Environ. Contam Toxicol., 31: 105–111.

McGrath, S.P., 1987. Long-term studies of metal transfers following application of sewage sludge. In: P.J. Coughtrey et al. (Eds.), Pollutant Transport and Fate in Ecosystems, British Ecological Society Special Publication No. 6. Blackwell, Oxford. pp. 301–317.

Mcleese, D.W. and C.D. Metcalfe, 1980. Toxicities of eight organochlorine compounds in sediment and seawater to *Grangon Septemspinosa*. Bull. Environ. Contam. Toxicol., 25: 921–928.

Muganlinskii, F.F., V.L. Sandler, V.B. Kakhramanov and D.D. Guseinova, 1990. Possibilities of activation of the reaction of chlorobenzenes with potassium phenolate. J. Appl. Chem. USSR, 63: 854–856.

Oliver, B.G. and K.D. Nicol, 1982. Chlorobenzenes in sediments, water and selected fish from Lakes Superior, Huron, Erie and Ontario. Environ. Sci. Technol., 16: 532–536.

Oliver, B.G. and A.J. Niimi, 1983. Bioconcentration of chlorobenzenes from water by rainbow trout: Correlations with partition coefficients and environmental residues. Environ. Sci. Technol., 17: 287–291.

Rogers, H.R., J.A. Campbell, B. Crathorne and A.J. Dobbs, 1989. The occurrence of chlorobenzenes and permethrins in twelve U.K. sewage sludges. Water Res., 23: 913–921.

Shafer, K.H., T.L. Hayes, J.W. Brasch and R.J. Jakobsen, 1984. Analysis of hazardous waste by fused silica capillary gas chromatography/mass spectrometry. Anal. Chem., 56: 237–240.

Tobin, P., 1986. Known and potential sources of hexachlorobenzene. In: C.R. Morris and J.R.P. Cabral (Eds.), Hexachlorohenzene: Proceedings of an International Symposium, IARC Scientific Publications 77. International Agency for Research on Cancer, Lyon, pp. 3–11.

Topp, E., I. Scheunert and F. Korte, 1989. Kinetics of uptake of ^{14}C-labeled chlorinated benzenes from soil by plants. Ecotoxicol. Environ. Safety, 17: 157–166.

Veith, G.D., D.J. Call and L.T. Brooke, 1983. Structure-toxicity relationships for the fathead minnow, *Pimephales promelas*: narcotic industrial chemicals. Can. J. Fish. Aquat. Sci., 40: 743–748.

Wadden, R.A. and L.R. Berrafato-Triemer, 1989. Mechanisms of atmospheric release of chlorobenzene and toluene from a storage lagoon under ambient conditions. Environ. Sci Technol., 23: 1492–1499.

Wang, M.-J. and K.C. Jones, 1991. Analysis of chlorobenzenes in sewage sludge by capillary gas chromatography. Chemosphere, 23: 677–691.

Wang, M.-J. and P.-Z. Lang, 1990. Transportation and fate of twenty organic pollutants in the Second Songhua River (Shaokou-Songhuajiangcun reach). China Environ. Sci., 10 (4): 241–249.

Wang, M.-J., P.-Z. Lang, F.-S. Long, Y.-Z. Ding and X. Yuan, 1990. Investigation of organic pollutants in the fishes in the mid-reach of the Second Songhua River. China Environ. Sci., 10: 81–88.

Wild, S.R., S.P. McGrath and K.C. Jones, 1990a. The polynuclear aromatic hydrocarbon (PAH) content of archived sewage sludges. Chemosphere, 20: 703–716.

Wild, S.R., K.S. Waterhouse, S.P. McGrath and K.C. Jones, 1990b. Organic contaminants in an agricultural soil with a known history of sewage sludge amendments: polynuclear aromatic hydrocarbons. Environ. Sci. Technol., 24: 1706–1711.

Williams, D.T., G.L. Lebel and E. Junkins, 1988. Organohalogen residues in human adipose autopsy samples from six Ontario municipalities. J. Assoc. Off. Anal. Chem., 71: 410–414.

Wong, P.T.S., Y.K. Chau, J.S. Rhamey and M. Docker, 1984. Relationship between water solubility of chlorobenzenes and their effects on a freshwater green alga. Chemosphere, 13: 991–996.