Polychlorinated Biphenyl Concentrations in Sewage and Sludges of some Waste Treatment Plants in Southern Ontario

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INTRODUCTION

Many reports have appeared in the literature in recent years describing the widespread environmental contamination of polychlorinated biphenyls (PCB's). (RISEBROUGH et al., 1968; JENSEN et al, 1969; PEAKALL and LINCER, 1970; VEITH and LEE, 1970; GUSTAFSON, 1970; EDWARDS, 1971.) PCB's occur in most countries of the world in lakes, rivers, sediments, soils, crops, plankton, fish, birds, animals and man. Very little can be done to remove the PCB's already in the environment other than to await the slow chemical and bacteriological degradation processes, but every effort must be taken to minimize further release. In spite of the restrictions imposed on the industrial uses of PCB's in 1971, significant amounts of the chemical are still being discharged into municipal sewer systems. DUBE et al. (1974) report concentrations of 0.05 - 2.8 $\mu g\ \ell^{-1}$PCB's in sewage plant effluents collected at numerous Wisconsin cities. These levels correspond to mass transports of up to 23 kg/yr./city, while SCHMIDT et al., (1971) report mass transports as high as 300 kg/yr. for some waste treatment plant effluents in California. This paper presents the results of a survey of PCB levels in raw sewage at six waste treatment plants (in Hamilton, Dundas, Burlington and Oakville) and of sludge samples from four major urban areas of Southern Ontario. In addition, it is shown that there is a significant uptake of PCB's by crops grown on sludge treated land.

MATERIALS AND METHODS

All solvents used were glass distilled, pesticide grade (Caledon Laboratories Inc.). They were not purified further before use.

Wastewater was collected as single grab samples at the raw sewage inlet pipe from six sewage treatment plants in the Hamilton-Oakville area. All-glass containers were used to insure against adsorption of PCB's onto container walls. The

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samples were stored at a constant temperature of 3°C and were always extracted within 24 hours of collection.

The PCB's were extracted from the raw sewage, sludge and crops as follow. Raw material (200 ml sewage or sludge, 30 g crops), acetonitrile (300 ml) and concentrated sulphuric acid (10 ml) were blended for 30 mins. (Waring Blender equipped with bakelite cap). The mixture was allowed to settle, the supernatant filtered through 1 cm diatomaceous earth (Johns Manville "Celite") into a 2ℓ separatory funnel and any remaining solids blended with 100 ml acetonitrile for a further 30 minutes. The supernatant was filtered through 'celite' and added to the previous sample and the whole process repeated until no solid remained. Sufficient distilled water was added to the combined supernatants to produce a 55:45 water : acetonitrile solution (usually a total of about 600 ml resulted). This solution was then extracted three times with petroleum ether (150 ml : 75 ml : 75 ml respectively); the extract was washed twice with distilled water and dried through ~15 g activated sodium sulphate. Finally the extract was evaporated to 1-2 mls in a rotary evaporator. The PCB's were separated from any other organo-chlorine compounds by passing the reduced extract through a conditioned florisil column and eluting with 225 ml hexane or petroleum ether (CHAU, 1972). The eluate was then evaporated to 1-2 ml and made up to exactly 3 ml by the addition of fresh solvent. Prior to injecting into the G.C. the extract was shaken with 0.5 ml mercury to remove residual sulphur compounds. This step was repeated until the mercury no longer turned black.

When raw sewage contained very little particulate matter, a simpler extraction procedure gave similar results to the one just described. Two hundred millilitres of sewage was partitioned with three 50 ml batches of petroleum ether. The combined organic phases were dried through 15 g Na_2SO_4 and reduced to 3 mls in a rotary evaporator. The extract was then purified on a florisil column, evaporated to exactly 3 mls and treated with mercury as in the previous procedure.

The extracts were analyzed using a gas chromatograph (Varian series) equipped with an electron-capture detector (Ni^{63}). The gas column (1.8 m x 1.5 mm i.d.) was packed with 4% OV-101 and 6% OV-210 on Chromsorb W HP $^{80}/_{100}$ mesh. Nitrogen was used as a carrier gas at 50 ml/min. The injection port, column and detector temperatures were 250°C, 200°C and 300°C respectively.

The PCB's in the samples were identified by comparison with chromatograms of standard Aroclors. Concentrations were determined from the peak height ratios of four major peaks for Aroclor 1254 and three major peaks for Aroclor 1260. The minimum amount of PCB which could be detected with confidence by the GC was 22 pg in 10 $\mu\ell$ injection. Allowing for the increase in concentrations during extraction from the aqueous phase, the limit of detection in the raw sewage was estimated as 0.5 $\mu g\ \ell^{-1}$ with an accuracy of $\pm 0.1\ \mu g\ \ell^{-1}$.

RESULTS AND DISCUSSION

Monitoring sewage for trace organic compounds is frequently achieved by collecting and analysing 24-hour composite samples, rather than single-grab samples (SHANNON, 1973). Although this allows total loadings to be calculated, short-term fluctuations within a 24-hour period remain undetected. These fluctuations and corresponding maximum concentrations can be very important parameters when considering design criteria for treatment systems. Earlier experiments in this laboratory indicated that the concentration of PCB's at the Hamilton Sewage Treatment plant was highest between 11:00 a.m. and 6:00 p.m. (coinciding with the peak industrial hours). Therefore, it was decided to collect all the samples for this survey as single-grab samples within these hours.

Six sewage treatment plants in the Hamilton-Oakville area were included in the survey. These were selected to cover a cross-section of wastewaters from domestic/heavy industrial, through domestic/light industrial, to strictly domestic. Hamilton Sewage Treatment plant received a large contribution of heavy industrial effluent and hence this plant was studied in most detail (36 samples collected over a period of 35 weeks). Of the other plants, Dundas, Oakville West and Burlington Skyway had some light industrial effluent while Oakville East and Burlington Elizabeth Gardens were strictly domestic. All the plants had conventional primary and activated sludge treatment.

The concentrations of PCB's in sewage samples collected from Hamilton are presented in Table 1. The thirty-six samples range from a minimum of 1.5 $\mu g\ \ell^{-1}$ to a maximum of 27.3 $\mu g\ \ell^{-1}$ with a mean of 10.8 $\mu g\ \ell^{-1}$ and a standard deviation of 6.2. This is significantly higher than results for raw sewage from several U.S. cities (DUBE et al., 1974) and is even higher than previously reported data from Hamilton (SHANNON, 1973). If it is assumed that the average concentration of 10.8 $\mu g\ \ell^{-1}$ flows for 8 hrs/day and that the concentration during the remaining 16 hours is zero, the annual plant loading (based on a daily flow of 236 x 10^6 ℓ/day) is 310 kg PCB/year. This is a significant amount and is based on very conservative assumptions. It is disturbing to see that the concentration of PCB in the samples collected in 1976, nearly two years after the main sampling program, was comparable to that in the earlier samples. It had been hoped that the concentrations would gradually decrease after the 1971 restrictions were implemented, but from these results, such a trend

TABLE 1

PCB CONCENTRATIONS IN HAMILTON RAW SEWAGE

Date	Concentration of Aroclor 1254, $\mu g\ \ell^{-1}$	Concentration of Aroclor 1260, $\mu g\ \ell^{-1}$	Total Aroclor Concentration, $\mu g\ \ell^{-1}$
4/3/74			6.3
6/3/74			10.9
12/3/74			8.9
21/3/74			15.2
25/3/74			20.7
8/4/74			11.9
17/4/74			8.2
24/4/74			9.2
7/5/74	9.8	17.5	27.3
9/5/74	4.3	10.7	15.0
13/5/74	0.8	0.7	1.5
14/5/74	0.8	0.7	1.5
15/5/74	0.8	0.7	1.5
16/5/74	1.8	1.9	3.7
17/5/74	5.5	2.7	8.2
7/6/74			5.6
11/6/74	5.0	6.5	11.5
18/6/74	8.1	9.9	18.0
21/6/74	7.4	5.2	12.6
26/6/74	5.9	3.9	9.8
2/7/74	5.0	4.6	9.6
8/7/74	10.2	4.2	14.4
12/7/74	4.6	3.4	8.0
17/7/74	6.6	6.5	13.1
19/7/74	15.5	9.8	25.3
21/8/74	3.8	0.9	4.7
28/8/74	9.0	4.6	13.6
10/9/74	14.6	4.4	19.0
11/9/74	6.9	1.8	8.7
17/9/74	6.8	0.9	7.7
24/9/74	2.2	0.6	2.8
1/10/74	4.9	1.2	6.1
9/10/74	8.2	4.8	13.0
16/10/74	6.1	3.7	9.8
17/10/74	4.6	1.5	6.1
28/10/74	13.7	7.1	20.8
4/2/76	5.6	3.4	9.0
Mean	6.4	4.4	10.8

is not apparent. Table 1 also gives the breakdown of the total PCB concentration into the contributions from the individual commercial Aroclors. Aroclor 1254 and Aroclor 1260 were the only two identified and these were present in about equal portions.

Table 2 lists the Aroclor concentrations for the five other treatment plants included in the study. As expected, the concentrations are much less than those for Hamilton with only three of the plants recording values >2.9 μg ℓ^{-1}. These three, Dundas, Oakville-West and Burlington Skyway treat mixed domestic/light industrial effluents compared to purely domestic sewage at Burlington Elizabeth Gardens and Oakville-East (both of which reported <1.6 μg ℓ^{-1}).

Most of the PCB's entering a sewage treatment plant become dissolved in or adsorbed on the suspended particulate matter and hence are removed with the sludge during the primary and secondary treatment stages (CHOI et al. 1974; LAWRENCE and TOSINE 1976). This has the fortuitous result that the secondary effluents are relatively free of PCB's. SHANNON (1973) found concentrations in secondary effluents at Hamilton to be <0.1 μg ℓ^{-1} while DUBE et al. (1974) reported <0.3 μg ℓ^{-1} for most of the eleven Wisconsin cities considered in their survey. The PCB concentrations in undigested sludge collected from Sewage Treatment Plants in four large urban areas (Hamilton, Kitchener, Newmarket and North Toronto) are presented in Table 3. The values of between 92 and 348 μg ℓ^{-1} clearly indicate the ultimate fate of PCB's in treatment plants. The Newmarket, North Toronto and Kitchener sludges had been conditioned with Ca, Fe and Al salts, respectively, but this would not have affected the total PCB content. Digestion of the sludge acts as a further concentration process and values as high as 2,085 μg ℓ^{-1} have been reported for digested sludge from Hamilton (SHANNON 1973). It is interesting to note that the ratio of Aroclor 1254:Aroclor 1260 is of the order of 1:1.4 for Hamilton sludge and sewage but about 4.2:1 for the sludge from the other three cities. This presumably is a reflection of the type of Aroclors being used in the different areas.

Table 3 also shows the PCB levels in corn and grass grown on land treated with the Newmarket, North Toronto and Kitchener sludges. The Kitchener and North Toronto sludges were applied at the rate of 800 kg of total Nitrogen per Hectare while the Newmarket sludge was applied at twice that amount. In each case, it was the leaves of the plants which were analyzed. Although these values are comparable with the concentrations in the sludges applied, it is apparent that plants do not biomagnify PCB's to the same extent as fish, birds or animals. The ratio of Aroclor 1254:1260 for both corn and grass is about 2.3:1. This is lower than the 4.2:1 for the sludges applied indicating that the crops preferentially take up Aroclor 1260.

TABLE 2

PCB CONCENTRATIONS IN RAW SEWAGE FROM FIVE SOUTHERN ONTARIO CITIES

City	Concentration of Aroclor 1254, $\mu g\ \ell^{-1}$	Concentration of Aroclor 1260, $\mu g\ \ell^{-1}$	Total Aroclor Concentration, $\mu g\ \ell^{-1}$
Dundas	3.6	0.8	4.4
	0.7	0.5	1.2
Burlington Skyway	1.8	1.1	2.9
Burlington Elizabeth Gardens	0.6	<0.5	0.6
Oakville West	1.9	2.4	4.3
	0.7	<0.5	0.7
Oakville East	1.1	<0.5	1.6
	0.6	<0.5	0.6

TABLE 3

PCB CONCENTRATIONS IN SLUDGES AND SLUDGE TREATED CROPS

Concentration $\mu g\ \ell^{-1}$	Hamilton	Newmarket	Kitchener	North Toronto
Aroclor 1254 in Sludge	81	74	111	118
Aroclor 1260 in Sludge	111	18	26	26
Total Aroclor in Sludge	192	92	137	144
Aroclor 1254 in Corn		37	29	54
Aroclor 1260 in Corn		13	16	27
Total Aroclor in Corn		50	45	81
Aroclor 1254 in Grass		108	84	47
Aroclor 1260 in Grass		120	36	24
Total Aroclor in Grass		128	120	71

The results of this study indicate that raw sewage at four of the six sewage treatment plants contained greater than 2 μg ℓ^{-1} PCB and that Hamilton averaged 10.8 μg ℓ^{-1} with a maximum of 27.3 μg ℓ^{-1}. Based on a conservative estimate, the mass transport of PCB's at Hamilton is approximately 300 kg/yr. Aroclors 1254 and 1260 were identified as the predominant contaminants.

The concentration of PCB's in the sludges of four major urban areas of Southern Ontario was of the order of 100 - 200 μg ℓ^{-1}. This demonstrates the fate of PCB's in a sewage treatment plant and the need for strict control on sludge disposal. High temperature incineration (≈1100 C) is one of the best disposal methods for PCB laden sludge, but this is only practiced at a few of the larger treatment plants. Recently LIU (1976) has reported the isolation of a PCB degrading bacterium. Under laboratory conditions this bacterium can rapidly degrade various commercial PCB's, ranging from the low chlorinated Aroclor 1221 to the higher chlorinated Aroclor 1254. This could prove to be a very valuable degradation technique for a variety of effluents and sludges.

Disposal of sludges containing PCB's by spreading on agricultural land should not be continued since our results indicate significant uptake of PCB's by crops grown on sludge treated land.

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