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Polychlorinated Biphenyls (PCB's) in Municipal Wastewaters

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These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

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POLYCHLORINATED BIPHENYLS (PCB's) IN MUNICIPAL WASTEWATERS:
An Assessment of the Problem in the Canadian Lower Great Lakes

by

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ABSTRACT

A survey of polychlorinated biphenyls (PCB's) concentrations in the raw wastewaters from 33 municipalities was carried out. In addition, detailed investigations of the fate of PCB's during conventional secondary treatment were performed at the Hamilton Wastewater Treatment Plant. PCB concentrations in raw wastewaters ranged from less than 0.1 to 1.8 ppb, with the industrial areas of Hamilton, Toronto and Windsor exhibiting the highest levels. Only the 1254 and 1260 Aroclors were detected in any of the wastewaters. The primary treatment facilities surveyed removed, on the average, 50% of the PCB load, whereas the secondary plants averaged 66% removal. PCB concentrations in digested sludges ranged from 0.6 to 76.6 ppm (dry weight).

PCB removal during wastewater treatment is largely by accumulation in the primary and/or waste activated sludge streams. There seemed to be little biodegradation. There are indications that multiple-hearth incineration may destroy the PCB's encountered in dewatered sludges. However, more experimental work is necessary to substantiate this observation.

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RÉSUMÉ

La concentration des biphényles polychlorés (BPC) dans les eaux usées non traitées de 33 villes a fait l'objet d'une étude. De plus, une enquête poussée sur le sort de ces composés soumis au traitement secondaire classique s'est poursuivie à la station d'épuration de Hamilton. Leur concentration variait entre moins de 0,1 et 1,8 ppm, les plus forts taux étant enregistrés dans les régions industrielles de Hamilton, Toronto et Windsor. Seuls les Aroclors 1254 et 1260 étaient présents dans toutes les eaux non traitées. En moyenne, les installations de traitement primaire observées ont éliminé 50 p. 100 des BPC et celles de traitement secondaire, 66 p. 100. La teneur en BPC des boues digérées se situait entre 0,6 et 76,6 ppm (poids des boues séchées).

Pendant le traitement des eaux usées, les BPC s'éliminent surtout en s'accumulant dans les dépôts de la décantation primaire ou dans les boues activées résiduaires. Au cours du traitement, la biodégradation a semble peu importante. Il se pourrait, par ailleurs, que l'incinération dans des fours à soles multiples arrive à détruire les BPC présents dans les boues déshydratées. Toutefois, il faudra poursuivre les expériences pour le confirmer.

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CONCLUSIONS

This report includes the results of a polychlorinated biphenyls (PCB's) survey conducted on 33 municipal wastewaters in Ontario. In addition, detailed investigations of the fate of PCB's within a conventional secondary wastewater treatment plant are described. Conclusions arising from these studies are:

(i) PCB's, exclusively the 1254 and 1260 Aroclors, were detected in all municipal wastewaters sampled. Raw wastewater PCB levels ranged from less than 0.1 ppb to a high of 1.8 ppb. The primary treatment plants surveyed averaged 50% PCB removal, whereas the secondary plants averaged 66% PCB removal. It was estimated that the total PCB's receiving water load from the 33 plants was 246 kg/yr or 67 mg/capita/year.

(ii) PCB's are accumulated in the sludge streams of the treatment plants. Digester sludge samples ranged from 0.6 to 76.6 ppm (dry weight).

(iii) Industrial centres such as Toronto, Hamilton and Windsor had the highest PCB concentration in the raw wastewaters and, consequently, high concentrations in the sludges.

(iv) PCB's, particularly the 1254 and 1260 Aroclors, degrade very little, if at all, during conventional secondary wastewater treatment. Removals are largely by physical separation with the primary sludges and accumulation in the activated sludge.

(v) It appeared that PCB's might be destroyed when incinerated in a multiple-hearth incinerator. Further research, however, is necessary to determine the preferred method for disposing of high level PCB sludges.

(vi) With the phasing out of PCB's and limitation to closed cycle uses in recent years, it is unlikely that any special treatment for their removal from municipal

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wastewaters will be required. However, because of their persistence, PCB's will continue to remain in the aquatic environment at detectable levels for some time.

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1 BACKGROUND AND STUDY OBJECTIVES

In 1966, the chemical compounds polychlorinated biphenyls (PCB's) were first discovered in the environment, even though they had been commercially available and used in many applications since the early 1930's (Gustafson, 1970). Since this time, considerable research effort in several countries has been devoted to determining the extent of PCB distribution in the environment, and the toxicity to various species of life. For example, Savage et al (1973) studied the occurrence of PCB's in silage; Veith and Lee (1971) measured PCB concentrations in fish of the Milwaukee River; Carnes et al (1973) analyzed solid wastes for PCB content; Veith (1972) monitored PCB levels in the waters of Green Bay and numerous researchers have studied interrelated influences. A detailed review of the copious PCB-related literature is beyond the scope of this report. However, Gustafson (1970) and Risebrough et al (1968) give detailed summaries of the state of the problem. Two of the more recent papers on the subject are by Hutzinger et al (1974) and Peakall (1975).

PCB's have a high chemical stability and have been used in a number of industrial applications including transformer oils, capacitor dielectrics, hydraulic lubricants, plasticizers, printing inks and surface coatings, to name some. Recent concern about their persistence in the environment has limited usage in the past two or three years to essential applications, such as fire resistant hydraulic transformer and insulating condensers. The report of the Interdepartmental Task Force on PCB's (1972) identified the following sources of PCB pollution: (i) open burning or incineration of municipal and industrial solid wastes; (ii) vaporization of paints, coatings, plastics, etc.; (iii) accidental spills or improper waste disposal; and, (iv) municipal and industrial sewers and sewage sludge disposal. The latter source was considered to be the largest contributor and it was estimated that in 1972, 6,000 tons/year of PCB's were discharged to the environment in this way. Schmidt et al (1971) sampled nine sewage treatment plant outfalls in California and identified the PCB Aroclors 1252, 1254 and 1260 at concentrations ranging from 0.2 to 96 ppb. A more recent study by Dube et al (1974) reported PCB's in Wisconsin treatment plant effluents. They found Aroclor 1254 present at

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levels ranging from less than 0.05 to 2.8 ppb. Furthermore, detailed studies at one secondary treatment plant indicated that PCB removals through the plant were in the order of 70%. It could not be determined from the data whether this removal was by biological decomposition or physical separation by adsorption/entrapment on the primary and waste activated sludges. Oden (1968), in a survey of 100 Swedish treatment plant sludges, found that the median PCB concentration was 1 ppm, with 67% of the samples lying between 0.4 to 2 ppm. Liu and Chawla (1976) have also identified PCB's in the ppm range in sewage samples collected from several Ontario wastewater treatment plants.

Since there was little information available on the extent of the PCB contributions from municipal wastewaters in the Lower Great Lakes, a study was initiated under the Canada-Ontario Agreement on Great Lakes Water Quality, with the following objectives:

(i) to determine, by selected sampling of Ontario wastewater treatment plants, the concentrations of PCB's in raw and treated wastewaters and in primary, waste activated and digested sludges; and,

(ii) to determine the fate of PCB's within a conventional activated sludge treatment plant.

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2 EXPERIMENTAL PROCEDURES

2.1 Study Sites and Sampling Procedures

Thirty-three wastewater treatment facilities at various locations (Figure 1 and Table 2) in the Lower Great Lakes were selected for PCB sampling. The plants ranged in size from 0.1 mgd (455 m^3/day) to 180 mgd (818,000 m^3/day) and included conventional activated sludge, primary and lagoon wastewater treatment systems. Sampling procedures at a particular plant involved hourly sampling of the influent and effluent and preparation of a flow-proportioned 24-hour composite sample; and sampling of other plant streams (i.e., primary sludge, waste activated sludge, digested sludge, digester supernatant and dewatered sludge cake, where applicable). Influent and effluent samples were collected with Isco automatic samplers. A sample tubing which did not cause PCB contamination was selected for the automatic samplers. Other plant streams were grab sampled twice during the day and a composite sample prepared. It became evident from early results that the PCB's were concentrated in the plant sludge streams; consequently, some of the latter plant sampling involved sludge samples only.

All samples were collected in acetone washed glass bottles. Plant flows were recorded and total solids determinations carried out on all sludge samples.

2.2 Procedure for Detailed Sampling of the Hamilton Wastewater Treatment Plant

A detailed sampling study was conducted at the Hamilton Wastewater Treatment Plant. This plant receives a relatively high loading of PCB's in the raw wastewater (thus facilitating PCB tracing through the plant), it is close to the Wastewater Technology Centre, treats a large volume of wastewater with accurate flow measurement in all major plant streams, and incorporates virtually all facets of conventional wastewater treatment and sludge disposal (including flotation, vacuum filtration and incineration). For these reasons, the Hamilton plant was selected and it was felt that the results would have general application to other plants having similar unit operations and processes. A schematic diagram of the Hamilton Wastewater Treatment Plant is shown in Figure 2. Design data for the individual plant components are summarized in Table 1.

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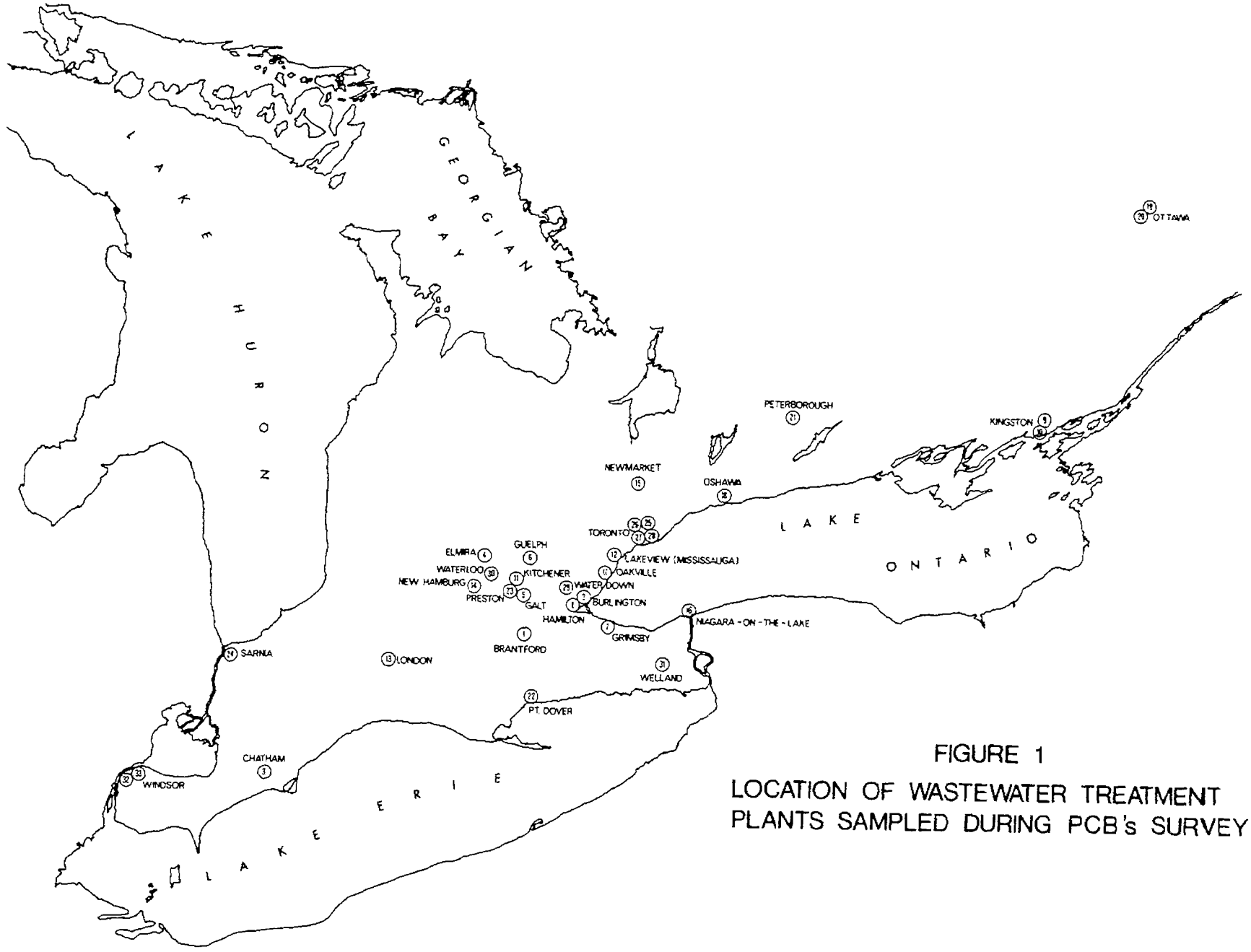

FIGURE 1

LOCATION OF WASTEWATER TREATMENT PLANTS SAMPLED DURING PCB's SURVEY

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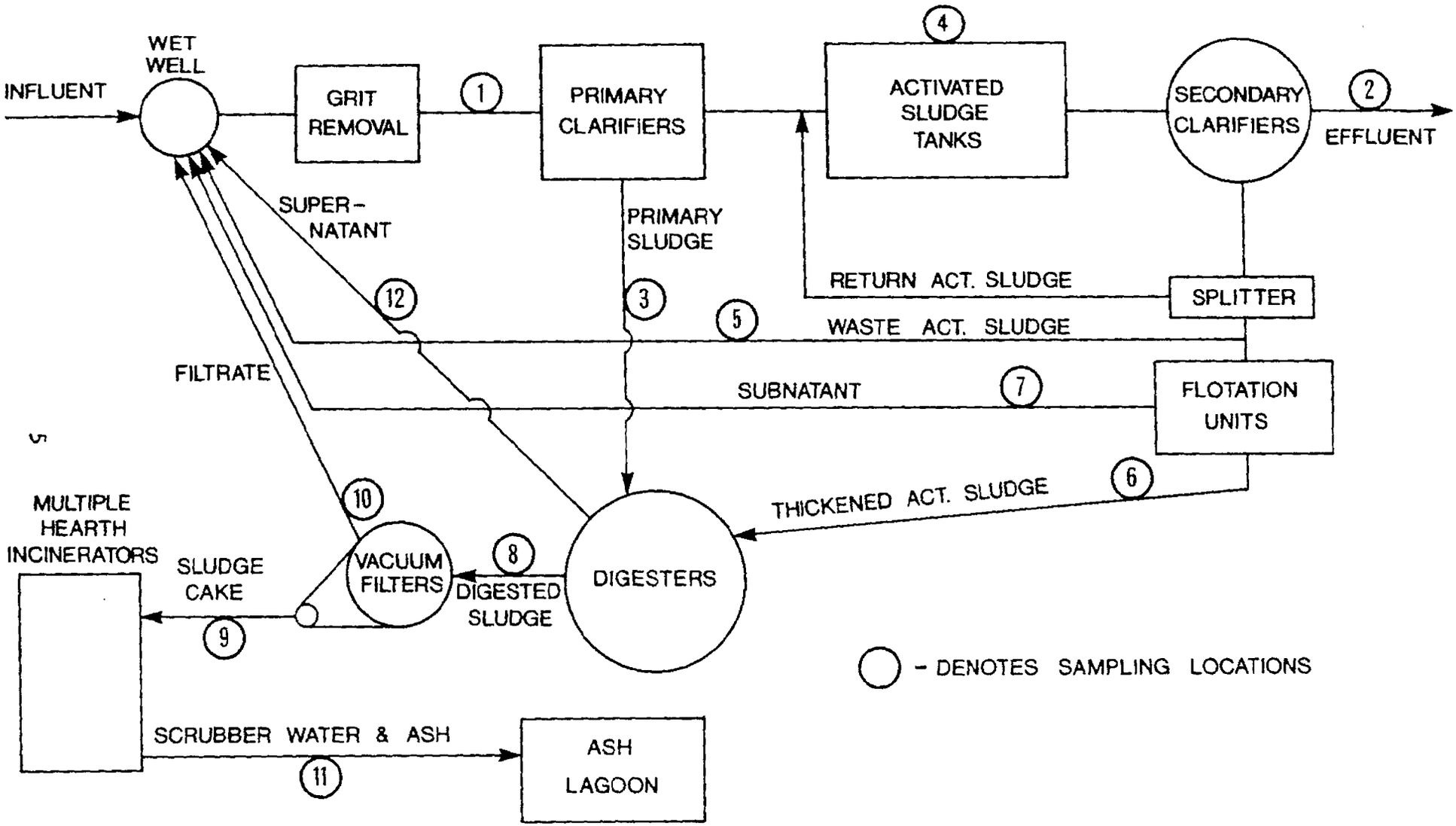

FIGURE 2. SCHEMATIC DIAGRAM OF THE HAMILTON WASTEWATER TREATMENT PLANT

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TABLE 1. DESIGN DATA FOR THE HAMILTON WASTEWATER TREATMENT PLANT [DESIGN FLOW = 60 mgd (273,000 m^3/day)]

COMPONENT	DETAILS
Main Pumping Station	- 78 ft (23.7m) deep x 40 ft (12.2m) dia. - 5 pumps
Degritter Facilities	- 4 bar screens - 4 -35 ft (10.7m) dia. degritters
Primary Clarifiers	- 8 tanks Retention Time 2.2 hrs Overflow Rate - 740 gpd/ft^2 (36.2 m^3/day·m^2)
Aeration System	- 8 tanks with mechanical aeration Retention Time - 6 hrs
Secondary Clarifiers	- 8 tanks Retention Time - 2.9 hrs Overflow Rate - 520 gpd/ft^2 (25.4 m^3/day·m^2)
Flotation of Waste Activated Sludge	- 4 units Total Surface Area - 1,600 ft^2 (148.6 m^2)
Digesters	- 4 primary, 4 secondary Total Volume - 14 MG (63,588 m^3) Retention Time - 40 days
Vacuum Filtration	- 4 Filters Total Area - 2,000 ft^2 (185.8 m^2)
Incinerators	- 2 Multiple Hearth Units

The PCB balance sampling was initiated on February 11 and continued until February 19, 1974. No samples were collected on February 16 and 17. The sampling locations are shown in Figure 2. Automatic samplers were set up to take hourly samples at locations 1 (influent) and 2 (effluent). Since it is very difficult to sample the raw sewage line at the Hamilton plant, the effluent from the wet well was sampled. This stream contains not only raw sewage but waste activated sludge, digester supernatant, flotation subnatant and vacuum filtrate which have been cycled back to the wet well. Corrections were made in subsequent calculations for the waste loading from the additional sources. Four flow proportioned composite samples were prepared from the hourly influent and effluent

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samples for the periods 03 to 08, 09 to 14, 15 to 20, and 21 to 02 hours. Samples of primary sludge (location 3) were collected from each of the eight primary clarifiers at six-hour intervals and combined into one daily composite. Twice daily samples were collected for the mixed liquor (4), waste activated sludge (5), thickened waste activated sludge (6), and flotation unit subnatant (7). Digested sludge (8), filter cake (9), vacuum filter filtrate (10) and incinerator scrubber water stream (11) were sampled twice during each daily eight-hour sludge dewatering period. Digester supernatant (12) was sampled only when it was discharged to the wet well. The flow quantities of the various plant streams were recorded daily.

2.3 Analytical Procedures

A detailed description of the procedures used for PCB analysis is presented in the Appendix to this report. In brief, the procedures consisted of extraction, clean-up and chromatographic separation steps and are similar to, or modifications of, methods previously developed by Chau (1972). Other analyses performed during the project were in accordance with Standard Methods (APHA et al, 1971).

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3 RESULTS AND DISCUSSION

3.1 PCB's Survey Results

The data collected during the wastewater treatment plant survey is presented in Table 2. The fact that PCB's were detected in all samples verifies the ubiquitous nature of polychlorinated biphenyls. PCB's were removed to various degrees through the treatment plants. The average removals for primary and secondary treatment plants were 50% and 66%, respectively.

Only Aroclors 1254 and 1260 were detected in the wastewater and sludge samples. Thus, these same Aroclors must be the predominant PCB's used in industrial applications. At most treatment plants there appeared to be a mixture of the two Aroclors. Some samples demonstrated chromatograms which closely resembled one Aroclor or the other. For example, the samples from the Hamilton and Windsor Little River plants contained only 1260, whereas in the samples from New Hamburg, Preston and Windsor West plants, Aroclor 1254 predominated. Other investigators have found that Aroclors 1254 and 1260 are predominant in wastewaters, although Dube et al (1974) identified Aroclor 1248 in a Wisconsin wastewater and Schmidt et al (1971) found Aroclor 1242 in some California wastewaters.

High PCB's concentrations in the sludge samples indicate that the removal mechanism is physical (i.e., solid liquid separation by settling). This finding is consistent with the low water solubility of PCB's. The concentration factors (i.e., ratio of influent concentration to primary sludge concentration) ranged from a low of 17.5:1 for the Windsor Little River plant to a high of 1,900:1 for the Toronto Highland Creek plant. The average concentration factor for all plants was 400:1. Dube et al (1974) reported similar concentration factor values for several Wisconsin wastewater treatment plants. Digested sludges contained relatively high PCB levels with the samples from Hamilton being by far the highest at 76.6 ppm (dry weight). All other digester sludges averaged 3.2 ppm. It was not unexpected to find that the various dewatered sludge cakes contained elevated PCB concentrations, with Hamilton again being the highest at 69.8 ppm. Estimates were made of the amounts of PCB's being:

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TABLE 2. POLYCHLORINATED BIPHENYLS (PCB's) IN WASTEWATERS AND SLUDGES FROM SELECTED ONTARIO MUNICIPALITIES (1974)

	LOCATION (see Figure 1)	AVG. FLOW (MIGD)	TREATMENT[3] PROCESS	INFLUENT	EFFLUENT	PRIMARY SLUDGE	WASTE ACTIVATED SLUDGE	MIXED LIQUOR	PRIMARY DIGESTER	SECONDARY DIGESTER	SUPER-NATANT	SLUDGE[3] CAKES	AROCLORS
1	Brantford	10.2	CAS	-	-	71 (1.7)[4]	16	5	87 (2.4)	-	-	-	1254 & 1260
2	Burlington	8.0	EA	1.5	<0.1[5]	-	105	-	-	-	-	-	1254 & 1260
3	Chatham	4.5	CAS	0.5	<0.1	57 (1.5)	-	-	69 (2.0)	-	-	-	1254
4	Elmira[1]	0.5	CAS	0.2	0.2	2900 (38.4)	27	16	-	-	-	-	1254 & 1260
5	Galt	5.5	CAS	-	-	100 (1.5)	13	5	61 (2.4)	-	-	-	1254 & 1260
6	Guelph	7.5	CAS	-	-	230 (3.7)	-	-	740 (6.3)	230 (3.9)	-	-	1254 & 1260
7	Grimsby	0.2	L	0.1	<0.1	-	-	-	-	-	-	-	1254
8	Hamilton	52.0	CAS	1.8	0.3	647 (11.3)	113	-		6700 (76.6)	850	13600 (69.8)	1260
9	Kingston City	11.9	P	0.3	0.2	114 (2.9)	-	-	630 (6.8)	-	120		1254 & 1260
10	Kingston TWP	0.9	CAS	-	-	23 -	17	-	-	-	7	1900 (6.1)	1254 & 1260
11	Kitchener	12.0	CAS	0.9	0.2	32 (2.2)	29	15	180 (4.1)	332	-	-	1254 & 1260
12	Lakeview	16.0	CAS	-	-	140 (3.6)	19	-	880 (10.6)	-	-	-	1254 & 1260
13	London Greenway	8.3	CAS	0.2	<0.1	74 (2.2)	13	15	-	-	-	-	1254 & 1260
14	New Hamburg	0.2	L	0.4	<0.1	-	-	-	-	-	-	-	1254
15	Newmarket	1.6	CAS+PR	0.4	<0.1	13 (0.4)	23	5	59 (0.6)	-	1	-	1254 & 1260
16	Niag.-On-The-Lake[2]	0.5	L	0.4	<0.1	-	-	-	-	-	-	-	1254 & 1260
17	Oakville	6.0	CAS	0.2	<0.1	112 (2.3)	55	8	101 (4.8)	100 (5.7)	6	-	1254 & 1260
18	Oshawa	9.0	P	<0.1	<0.1	83 (1.4)	-	-	103 (1.6)	106 (1.2)	54	-	1254 & 1260
19	Ottawa-Greens Corners	65.0	P	0.3	<0.1	60 (1.6)	-	-	53 (3.1)	23 (2.5)	31	150 (2.7)	1254 & 1260
20	Ottawa - Watt Cr.	6.8	CAS	-	-	140 (4.1)	9	-	140 (5.3)	240 (5.5)	78	-	1254 & 1260
21	Peterborough	9.0	CAS	1.0	<0.1	115 (2.5)	24	-	92 (4.6)	-	-	-	1254 & 1260
22	Port Dover	0.4	P	0.9	0.3	-	-	-	170 (2.7)	-	-	-	1254 & 1260
23	Preston	2.4	CAS	-	-	61 (1.3)	-	3	-	-	-	-	1254
24	Sarnia	7.0	P	0.3	0.2	87 (2.4)	-	-	792 (4.9)	53 (2.5)	11	-	1254 & 1260
25	Toronto - Main	180.0	CAS	0.5	0.4	33 -	-	7	123 (1.5)	133 (3.0)	3	-	1254 & 1260
26	Toronto - Humber	63.0	CAS	0.6	0.4	22 -	-	-	113 (1.4)	240 (3.0)	-	-	1254 & 1260
27	Toronto - Highland	19.0	CAS	<0.1	<0.1	190 -	23	15	363 (4.5)	263 (3.3)	433	-	1254 & 1260
28	Toronto - North	9.0	CAS+PR	<0.1	<0.1	76 (2.0)	-	3	67 (2.3)	80 (2.7)	60	-	1254 & 1260
29	Waterdown	0.1	CAS	<0.1	<0.1	5	-	-	37 (0.4)	-	-	-	1254 & 1260
30	Waterloo	6.7	CAS	0.2	<0.1	11	-	5	52 (0.6)	53 (0.6)	3	-	1254 & 1260
31	Welland	7.1	P	0.1	<0.1	43 (0.9)	-	-	38 (2.9)	105 (2.6)	-	-	1254 & 1260
32	Windsor - West	24.0	P+PR	1.7	0.9	2500 (20.8)	-	-	-	-	-	3500 (11.8)	1254
33	Windsor - Little River	4.0	CAS	0.4	<0.1	7 -	-	-	48 (0.6)	-	-	-	1260

1-2 Samples contained considerable pesticide residues

3 Sludge cakes were from vacuum filters or sludge disposal lagoons

CAS = Conventional Activated Sludge

EA = Extended Aeration

L = Stabilization Pond

P = Primary

4 Figures in parenthesis are dry weight concentration in ppm

5 0.1 ppb = Limit of Detectability

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(i) received at wastewater treatment plants; and (ii) discharged to the receiving water, for the 33 survey sites. Calculations for 26 treatment plant analyses of influent and effluent PCB loadings per year are summarized in Table 3. The total PCB loading being received at the treatment plants was 564 kg/yr (1,243 lb/yr), whereas the amount being discharged to the receiving waters was approximated as 246 kg/yr (542 lb/yr). The 26 plants had a sewered population totalling 3.66 million people. Therefore, the per capita PCB contributions for influents and effluents were 154 and 67 mg/cap/yr, respectively. The larger and more heavily industrialized municipalities of Toronto, Hamilton, Ottawa and Windsor, accounting for 82% of the population, also accounted for 91% of the total PCB's load going to waste treatment facilities. The wastewater and sludge concentration data in Table 2 verify the industrial influence factor. For example, strictly domestic municipalities such as Waterdown, Newmarket and Grimsby had low PCB levels in influents, effluents and sludges. The PCB's in these domestic wastewaters perhaps originated from storm water or household material that contain low amounts of PCB's. Some grab samples collected from the Guelph storm sewer system verified that PCB's are present in storm water discharges (i.e., average PCB content of the Guelph samples was 0.12 ppb). Veith and Lee (1970) found trace amounts of PCB's in some dishwasher detergents, aluminum foil and packaging materials.

Based on the estimates made in Table 3, it appears that about 44% of the total PCB load received at treatment plants is eventually discharged to the receiving stream. The other 56% is probably accumulated in the sludges (there may be some slight biodegradation). This presents a potential sludge disposal problem which will be discussed in more detail later. The Monsanto Company, sole producer and supplier of PCB's in North America, has restricted the sale of PCB's to essential closed cycle uses in the past five years. As a result, the PCB loadings in wastewaters are likely to decrease in the future. However, the persistence of the material makes it a problem, particularly in land disposal of sludges.

3.2 Fate of PCB's Within a Secondary Treatment Plant

A detailed seven day sampling program was carried out on various process streams of the Hamilton Wastewater Treatment Plant. The sampling

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TABLE 3. ESTIMATED INFLUENT AND EFFLUENT PCB's LOADINGS FOR SELECTED ONTARIO MUNICIPALITIES

LOCATION	LOADING (kg/yr)[1&2] INFLUENT	LOADING (kg/yr)[1&2] EFFLUENT	SEWERED[3] POPULATION
2. Burlington	19.9	<1.3 (0.65)[4]	67,000
3. Chatham	3.3	<0.7 (0.35)	32,000
4. Elmira	0.2	0.2	4,800
7. Grimsby	0.03	<0.03 (.015)	1,720
8. Hamilton	154.1	25.8	318,000
9. Kingston City	5.9	3.9	70,000
11. Kitchener	17.9	4.0	111,000
13. London - Greenway	2.7	<1.4 (0.70)	110,000
14. New Hamburg	0.1	<0.03 (0.015)	3,000
15. Newmarket	1.1	<0.3 (0.15)	15,000
16. Niagara-on-the-Lake	0.3	<0.1 (0.05)	3,500
17. Oakville	2.0	<1.0 (0.5)	25,000
18. Oshawa	<1.0 (0.5)	<1.0 (0.5)	87,000
19. Ottawa - Greens Corners	32.3	<10.7 (5.35)	358,000
21. Peterborough	14.9	<1.5 (0.75)	57,000
22. Port Dover	0.6	0.2	2,500
24. Sarnia	3.5	2.3	58,000
25. Toronto - Main	165.9	119.2	1,250,000
26. Toronto - Humber	62.6	41.7	540,000
27. Toronto Highland	<3.1 (1.55)	<3.1 (1.55)	200,000
28. Toronto North	<1.5 (0.75)	<1.5 (0.75)	170,000
29. Waterdown	<0.02 (0.01)	<0.02 (0.01)	2,140
30. Waterloo	2.2	<1.1 (0.55)	40,000
31. Welland	1.2	<1.2 (0.60)	35,000
32. Windsor - West	67.5	35.8	100,000
33. Windsor - Little River	2.7	<0.7 (0.35)	60,000
TOTAL	563.7	246.2	3,660,360

1 Calculations Based on Flows and Concentration Data in Table 2

2 To Convert kg to lbs Multiply by 2.205

3 Water and Pollution Control Directory 1973-74

4 Assumed Concentration was 50% of Detectability Limit

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procedures were described in Section 2.2. The results of the study at the Hamilton plant are summarized in Figure 3. Averages and standard deviations for PCB levels measured at each sampling location are presented. In addition, the PCB mass transported via each stream has been calculated from flow and concentration data. Because the sampling period was relatively short and no attempt was made to account for storage changes in the various units, the results presented in Figure 3 should not be interpreted in a mass balance sense. However, the data demonstrate the relative fate of PCB's within a conventional secondary treatment system. Average flow and total solids data are summarized in Tables 4 and 5, respectively.

Based on the seven day influent and effluent loading, the treatment plant removed 87% of the PCB material received. Of the total influent loading of 3.92 kg (including digester supernatant, vacuum filtrate and flotation subnatant), 31% or 1.21 kg was removed in the primary sludge and transported to the digesters via the thickened waste activated sludge. Waste activated sludge returned to the wet well recycled 1.93 kg. Approximately 45% or 1.77 kg could not be accounted for. The reasons for this are probably: (1) accumulation within the system; (2) sampling which was not sufficiently sensitive to pick up some large PCB fluctuations or biological decomposition. Analysis of heavy metal (Cr, Zn, Ni, Cu and Pb) data collected at the Hamilton Wastewater Treatment Plant during the period of the PCB survey showed that, within the system, the heavy metal accumulation pattern was similar to that of the PCB's. This suggests that the plant was not at steady state and the PCB loss probably cannot be attributed to degradation.

Lack of steady state operation is also apparent in the digestion system. Here, during the seven day period 1.74 kg of PCB's were added, 13.6 kg were withdrawn for sludge dewatering and supernatant return. Over an extended time period, the PCB input/output to the digesters should balance. The amount of PCB's stored in the four digesters was calculated to be 212 kg (469 lb). This represents a large reservoir of PCB's, equivalent to 450 days of PCB influent loading.

Essentially all of the PCB's remained in the sludge solids throughout the flotation thickening of the waste activated sludge (i.e., 0.0006 kg (0.0013 lb) in the subnatant and 0.53 kg (1.17 lb) in the

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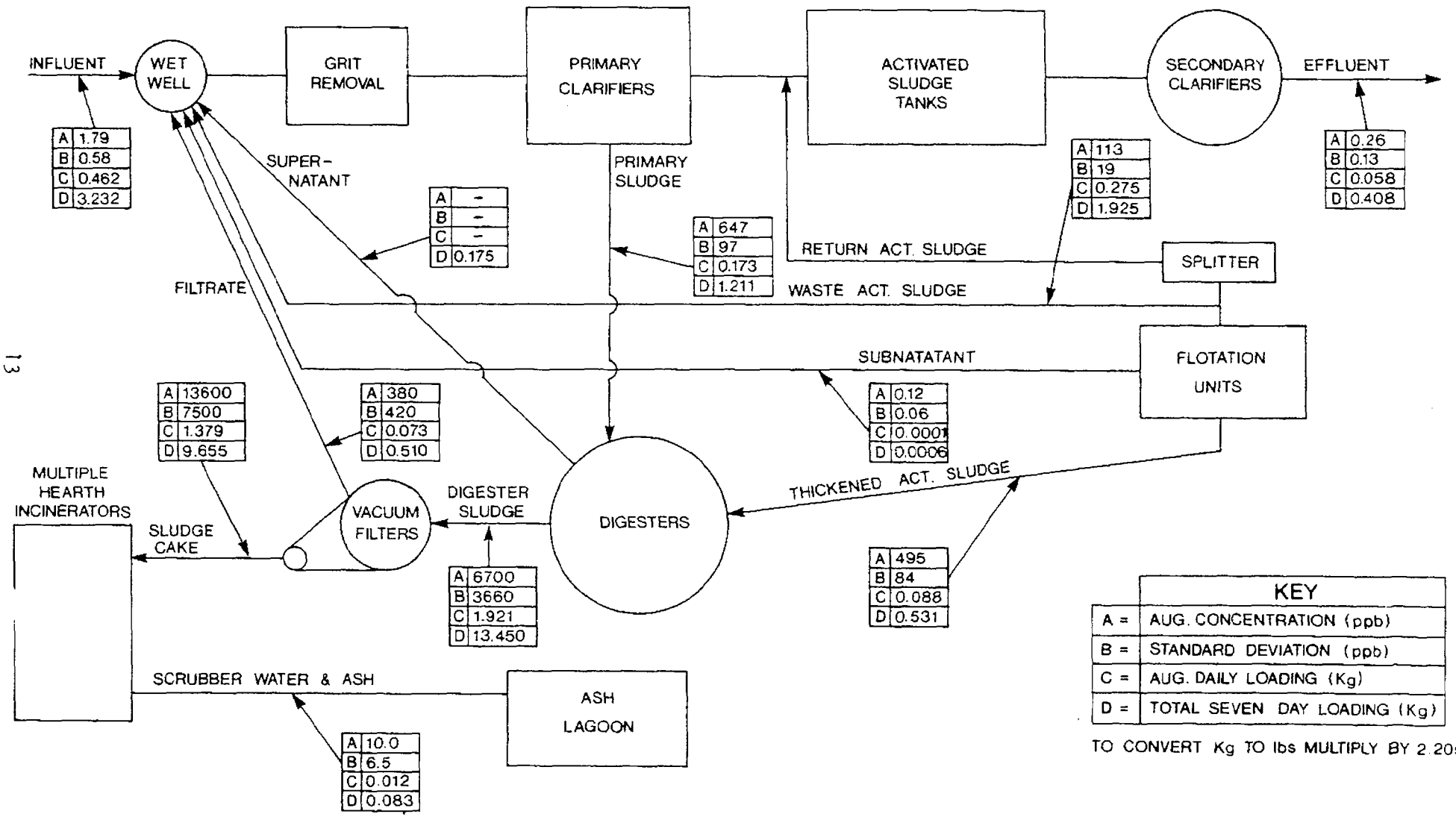

FIGURE 3. PCB's TRANSPORT WITHIN THE HAMILTON WASTEWATER TREATMENT PLANT

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TABLE 4. FLOWS FOR VARIOUS PLANT STREAMS DURING PCB's SAMPLING

STREAM	FLOW (mgd)			
	AVERAGE		STANDARD DEVIATION	
Influent & Effluent	56.0	(2629)[1]	6.6	(3.10)
Primary Sludge	0.0595	(3.12)	0.0115	(0.61)
Waste Activated Sludge	0.4813	(25.3)	0.1168	(6.14)
Thickened Sludge	0.0382	(2.01)	0.0105	(0.55)
Digester Supernatant	0.0184 one day only	(0.97)		
Flotation Subnatant	0.1148	(6.04)	0.0529	(2.78)
Digester Sludge to Vacuum Filters	0.0627	(3.30)	0.0079	(0.42)
Sludge Cake	119.2 Tons		31.6 Tons	
Vacuum Filtrate	0.0393	(2.06)	0.0055	(0.29)
Incinerator Scrubber Water	0.252	(13.26)	0.053	(2.79)

[1]Values - Parenthesis are l/sec

TABLE 5. TOTAL SOLIDS CONCENTRATIONS OF PLANT STREAMS DURING PCB's SAMPLING

STREAM	TOTAL SOLIDS (%)	
	AVERAGE	STANDARD DEVIATION
Primary Sludge	5.75	0.44
Waste Activated Sludge	1.53	0.10
Thickened Sludge	5.64	0.85
Mixed Liquor	3240 mg/l	585 mg/l
Digested Sludge	8.69	2.02
Sludge Cake	19.50	1.16
Vacuum Filtrate	3475 mg/l	1250 mg/l
Supernatant	2.18 (one day only)	-
Incinerator Scrubber Water	1210 mg/l	290 mg/l

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thickened sludge). Losses to the filtrate in the vacuum dewatering of the digested sludges were relatively high at 0.51 kg (1.12 lb). This was consistent with high solids content of the filtrate (i.e., 3,475 mg/l in Table 5). About 25% of the PCB load applied to the vacuum filter as digested sludge could not be accounted for the in the sludge cake plus filtrate. It is suspected that this discrepancy was most likely due to insensitive sampling procedures. In this regard, note in Figure 3 the large standard deviations of the PCB concentration in the digested sludge, sludge cake and filtrate samples.

Ninety-nine percent of the PCB load applied to the multiple-hearth incinerators was lost during incineration (i.e., 9.66 kg fed in the sludge cake and 0.08 kg remaining in the scrubber water and ash). Two loss mechanisms were possible: (i) combustion and destruction of the PCB's; or, (ii) volatilization and transport to the atmosphere. It has been reported (Anon, 1973) that a multiple-hearth furnace operating at 815 to 925°C (1,500 to 1,700°F) and an exhaust temperature of 590°C (1,100°F) is capable of 99.9% destruction of PCB residuals in sewage sludge. Lowering exhaust temperatures to 425°C (800°F) results in a slightly lower destruction of PCB's to 94%. Since the Hamilton incinerators were generally operated between 815 to 925°C with exhaust temperatures of 370 to 425°C, it is possible that the PCB losses were due to combustion. However, the fact that PCB's were detected in the scrubber water suggested some material was being volatilized. It is suggested that further research should be undertaken on this aspect of PCB's in sewage treatment plants, with appropriate analyses of the stack gases.

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APPENDIX

METHODS FOR PCB ANALYSIS IN WASTEWATERS AND SLUDGES

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APPENDIX

METHODS FOR PCB ANALYSIS IN WASTEWATERS AND SLUDGES

A.1 Method 1

This method is used for samples having a high proportion of solids, such as sludges, supernatants, and mixed liquors. For samples with a low solid content, see Method 2.

(i) Samples are well shaken before extraction to ensure homogeneity. Amounts of sample used for extraction are as follows:

-- sludge cakes	25 g
-- digester and raw sludges	50 ml
-- supernatants and mixed liquors	150 ml

(ii) Samples are mixed with 300 ml acetonitrile and 10 ml conc. H_2SO_4 in a Waring blender with a Bakelite top and blended at the highest possible speed without spilling for one-half hour.

(iii) Samples are allowed to settle. Liquid is decanted off, and remaining solid is mixed with 100 ml more acetonitrile and blended for one-half hour more. This step is repeated once more.

(iv) After decantation of the liquid phase, the solid phase is filtered through a 1/2" layer of Celite that has been prewashed with acetone and then washed with acetonitrile.

(v) All filtered and decanted liquids are combined and distilled deionized water is added to make a 50:50 water acetonitrile solution.

(vi) This solution is partitioned with petroleum ether in a separatory funnel (two-litre) three times with 150 ml, 90 ml and 60 ml of petroleum ether, respectively.

(vii) Aqueous layer is discarded and petroleum ether layers are combined and shaken with 200 ml distilled water in the separatory funnel to ensure complete removal of acetonitrile from the petroleum ether solution.

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(viii) The water layer is discarded and the petroleum ether layer is dried by filtering through a 2" layer of anhydrous Na_2SO_4 (See equipment list). Rinse the layer with approximately 25 to 50 ml petroleum ether. All flasks are washed with petroleum ether and the washings are added to the filtered solution through the Na_2SO_4 filter.

(ix) The petroleum ether solution is evaporated to approximately 2 ml on a Rotavap, on a water bath not exceeding 40°C to avoid possible loss of PCB's.

(x) A liquid chromatographic separation column is set up as follows:

- the column used is a 20 mm x 400 mm Pyrex column with a fritted glass disc and a Teflon stopcock at the bottom. A 1/2" layer of anhydrous Na_2SO_4 is placed on the bottom of the column; 30 g of activated Florisil[2] (see equipment list) are wet-packed in hexane above the Na_2SO_4 layer, and then another 1/2" layer of anhydrous Na_2SO_4 is placed on the Florisil layer. The column is washed with 200 ml of hexane and the liquid drawn off to the upper level of the Na_2SO_4. A clean receiving flask (500 ml round-bottom) is placed under the top of the column. For further details regarding the preparation of a chromatographic column see Chau (1972).

(xi) Quantitively transfer the petroleum ether extract to the column. Allow the extract to sink just to the surface of the Na_2SO_4 layer by opening the stopcock. Wash the flask with 3 ml hexane and transfer the washings to the column. Allow the liquid to sink down as before. Repeat twice with 3 ml hexane. Elute the column with 200 ml hexane, catching the eluate in a clean 500 ml round-bottom flask. Elution rate should be about 5 ml/min. For further details regarding elution on a Florisil column consult Chau (1972).

(xii) Evaporate the eluate to 2 ml on the Rotavap. Dilute the eluate to 10.0 ml in benzene in a graduated centrifuge tube or a volumetric flask. Use the extra 8 ml of benzene to rinse the elute flask after transferring the eluate to the graduated centrifuge

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tube.

(xiii) Transfer 2 ml of the benzene solution to a clean, dry centrifuge tube, and add 0.05 ml of mercury (triple-distilled). Stopper the tube tightly with a glass stopper and shake vigorously. If the mercury turns into a black solid (Hg S), then transfer the solution to a new clean, dry centrifuge tube, add another drop of mercury and repeat. Repeat this procedure until no change in the mercury is seen. This procedure removes sulphur residues from the solution as they may cause a large interference on the gas chromatograph.

(xiv) Inject a suitable volume of the mercury-treated solution onto the gas chromatograph. The column and column conditions are the same as for organo-chlorine pesticide analysis (Chau, 1972). Standards used are Aroclor 1254 and Aroclor 1260 (both 300 pg/µl). Further dilutions of the samples to achieve on-scale readings on the chromatograph are often necessary, especially for the digester and filtered sludges. Calculation of the concentration of PCB's in the sample is described in the following.

A.1.1 Calculation of PCB Concentrations

(a) Aroclor 1254 : The last three peaks corresponding to the retention time of DDD and DDT are used for calculation. Additional peaks are used if the results calculated from each of these peaks are too diverse. All results are averaged for reporting (four very small peaks appear after these peaks on the chromatograph, but are too small to be useful). A chromatogram for 1254 is shown in Figure A.1. Using peak (3) for the arbitrary relative retention time of 1.00, the other two peaks used for analysis appear at relative retention times of 0.72 and 0.84, respectively.

(b) Aroclor 1260 : A chromatogram for 1260 is also presented in Figure A.1. The peaks used for analysis (called, 3, 4, 5, 6, 7, and 8) appear at these retention times:

peak (3)	:	1.0	peak (5)	:	1.10
peak (4)	:	0.84	peak (6)	:	1.30

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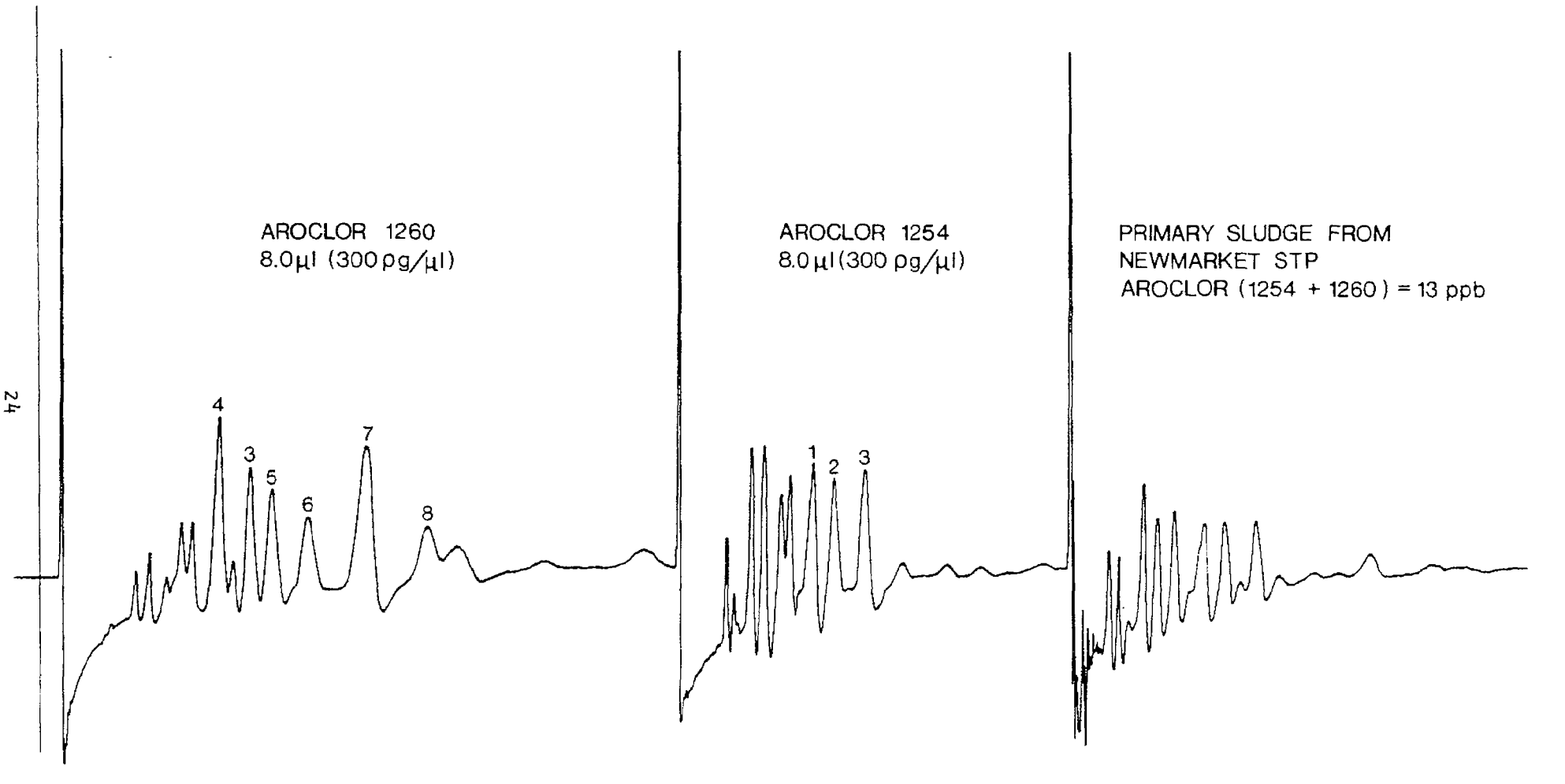

FIGURE A-1 CHROMATOGRAMS FOR AROCLORS 1254 AND 1260 AND A SEWAGE SLUDGE SAMPLE

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peak (7) : 1.60 peak (8) : 1.93

(c) The formula used for calculating the concentration of PCB's in the individual GC peaks is:

$$\text{PCB (ppb)} = \frac{(\text{h sam})}{(\text{h std})} \times \frac{(\text{v std})}{(\text{v sam})} \times \frac{(\text{conc std})}{(\text{w samp})} \times (\text{V}) \times (\text{dilution factor})$$

where: h sam = peak height of the sample

h std = peak height of the standard

v std = injection volume of the standard

v sam = injection volume of the sample

conc std = concentration of the standard

w sam = weight of the sample used for extraction in g or volume of the sample used for extraction in ml

V = volume of sample extract in ml (before mercury treatment)

dilution factor = amount of dilution used for sample after mercury treatments in order to achieve on-scale readings.

(d) The PCB concentration is reported as total Aroclor 1254 and 1260 In the case of Aroclor 1260 predominant, the peaks unique to 1260 are used and reported as such. The lowest level that can be calculated is 0.1 ppb of PCB.

A.2 Method 2

This method is used for samples having a low proportion of solids, such as influents, effluents, subnatants, incinerator washes and filtrates.

(i) Samples are well shaken before extraction to ensure homogeneity. The amount of sample used for the extraction is 400 ml.

(ii) Samples are mixed with 30 ml hexane in a Florence flask (500 ml) and stirred for one hour at high speed with a magnetic stirrer (Teflon coated).

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(iii) Samples are allowed to settle. Then they are poured into a 1-litre separatory funnel and 150 ml petroleum ether is added. The samples are well shaken and allowed to settle. The aqueous layer is repartitioned with 90 ml petroleum ether. The petroleum ether extracts are combined and filtered through a 2" layer of anhydrous Na_2SO_4 to remove water and break up the emulsion. Rinse the Na_2SO_4 well with petroleum ether and add the rinsing to the petroleum ether extracts.

(iv) Follow Method 1 from step (ix) onwards, except that the evaporated eluate from the Florisil column should be diluted to 3.0 ml in benzene instead of 10.0 ml.

A.3 Equipment Required for PCB Analysis

1 gas chromatograph, set up for organo-chlorine pesticide analysis
1 Rotovap and water bath
1 Waring blender and Bakelite top
1 magnetic stirrer
1 10 µl injection needle

A.3.1 Glassware

1 2-litre beaker
1 2-litre Erlenmeyer flask
1 2-litre separatory funnel
1 1-litre separatory funnel
1 Allihn funnel
1 500 ml Florence flask
2 round-bottom 500 ml flasks
1 20 x 400 chromatographic column (Teflon stopcock and fritted glass disc)
2 500 ml graduated cylinders
1 100 ml graduated cylinder
1 10 ml graduated cylinder
15 ml graduated centrifuge tubes
2 10 ml volumetric flasks
4 Pyrex wash bottles
disposable Pasteur pipettes

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Note: Glassware must be washed with soap and hot water, dried and rinsed with washing acetone, pesticide grade acetone and the solvent that will be used in the extraction glassware.

The injection needle must be rinsed at least ten times with benzene between each injection, and periodically should be thoroughly washed with acetone, hexane and benzene.

The glassware listed above is all that is necessary for analysis of a single PCB sewage sample. For routine analysis of a large number of samples, more equipment will be needed. Samples are normally analysed in pairs, in a staggered procedure, so that at any point in the analysis, the analyst is actually working on 8 to 12 samples at different stages of analysis.

A.3.2 Solvents and Chemicals

Note: All solvents must be pesticide grade, except for washing acetone. All glassware must be rinsed with pesticide grade solvents of suitable polarity before use.

- washing acetone (technical grade)
- acetone
- hexane
- petroleum ether
- benzene
- acetonitrile
- methylene chloride
- celite (Johns-Manville)
- anhydrous[1] Na_2SO_4
- Florisil[2]
- concentrated H_2SO_4
- distilled deionized water
- triple-distilled mercury
- Aroclor 1254 (Monsanto Company)
- Aroclor 1260 (Monsanto Company)

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Anhydrous[1] Na_2SO_4: Commercial anhydrous Na_2SO_4 must be treated in the following way before use:

(a) Rinse 500 ml of commercial anhydrous Na_2SO_4 with 900 ml acetone, then 600 ml methylene chloride, then 300 ml hexane, under vacuum.

(b) Dry in a 125°C oven at least overnight. Store in a desiccator.

Florisil[2]: Commercial Florisil must be treated in the following way before use:

-- Place a 2" layer of Florisil in an open 2-litre wide-mouth jar and dry in a 125°C oven for 26 hours. Store in a desiccator, covered.

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