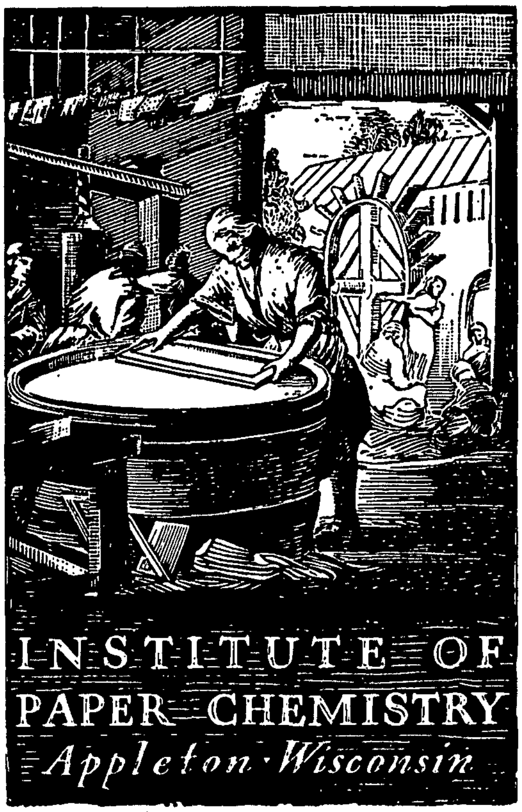

POLYCHLORINATED BIPHENYLS IN PULP AND PAPER MILLS
PART II. DISTRIBUTION AND REMOVAL

Project 3295

Report Two
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

July 22, 1977

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Quantitative studies were undertaken to identify the individual process streams containing polychlorinated biphenyls (PCBs) in four mills _using recycled paper as a source of fiber_. Most of the PCBs were found in the discharge streams from the stock preparation steps (deinking, hydrapulping, washing and screening) where they were sorbed on the fiber fines. Efficient removal of these fines in the mill waste treatment plant reduced the total PCBs in the mill effluent by 97-98%. In most cases efficient removal of fines will be sufficient for a mill to meet present PCB effluent standards of 10 parts per billion. It must be remembered, however, that the PCBs are not destroyed by the clarification process, but are carried in the solids (sludge).

Leaching studies indicate that the sludge has a marked affinity for PCBs. During a period of twelve weeks, only 0.2% of the PCB was found in the water leachate from two columns containing 27 and 97 milligrams of PCB (on dry weight of sludge the PCB level of the two columns was 20 and 82 ppm, respectively).

During the distribution studies in the papermaking process, we encountered PCB losses of up to 160 grams/day across the drier section (between the couch and paper rolls) of the paper machine. These losses were found on machines producing papers from recycled fibers containing 2-10 ppm PCB (oven-dry basis). Vapor traps, installed over the drier rolls and at the roof vents showed that the concentration of the PCBs in the exhaust gases, even before dilution by

atmospheric air, was only 0.03 mg/m^3. The PCB concentration in the final paper product was always under 3 ppm, even when the incoming stock PCB level was 2-10 ppm.

We also studied, to a limited extent, the removal processes which could be used to further reduce the concentration of PCB in waste discharges. Processes such as carbon adsorption, solvent extraction, and incineration, which were under extensive investigation by equipment manufacturers, were deliberately excluded. Gas-sparging or foam separation, centrifugation, and fat absorption systems showed promise as polishing procedures for removing PCB from effluents.

In conclusion, we think that the PCB problem can be solved to meet the present effluent guide lines. We recommend that, first, efforts be made to omit PCB containing papers from the recycle process. Second, if this cannot be done, a good clarification system should be used to remove PCBs from mill wastewaters.

INTRODUCTION

Since the late 1960's polychlorinated biphenyls (PCBs) have been known to be present in paper products and mill effluents. The PCBs are not used in the production of pulp or paper, but enter the system with the wastepaper used as a source of fiber.

A comprehensive literature search (1) during the early phase of this project disclosed very little quantitative information of PCBs in mill effluents. There have been reports (2-4) of PCBs in effluents from mills using wastepaper, but in most cases these were on the final effluent from the mill. No data have been reported either on the individual sources of PCBs from the mill to the waste treatment plant or on the distribution of PCBs within the mill system. Therefore, a quantitative study of the distribution of PCBs within the mill was undertaken with the hope that segregation of streams containing most of the PCBs would lead to:

- treatment of the contaminated streams prior to their dilution by other streams entering the treatment plant,
- reduction or elimination of streams containing components detrimental to the selected "PCB removal process",
- treatment of a stream in recycle-loops (white water, pulp wash water) to remove PCBs, thereby reducing their accumulation in the loop and carry-over into the product,
- the economic justification and use of an advanced treatment technology.

PROCEDURE

Four mills were selected for detailed studies on the concentration and total loading of PCBs in:

1. the individual process discharges to the mill waste treatment plant;
2. the recycling streams <u>within</u> the mill system.

The selection of these mills, from all of the mills in the country utilizing wastepaper as a source of fiber, was based on:

- their representation of the two basic types of stock preparation (hydrapulping and deinking),
- their utilization of bleached and unbleached fiber,
- their production of three distinctive grades of paper product (printing, boxboard and direct "consumer goods").

The descriptions of the four mills given in Table I are arranged according to the types of processes and in decreasing volumes of mill wastewater.

In our first sampling trials, we attempted to monitor PCBs using grab samples. Due to the high variability of the PCB concentrations in the incoming wastepaper, however, we were compelled to use 6-, 8- or 24-hour composites in most of our studies. The values given in Table II indicate the fluctuations over a period of six hours in samples from two hydrapulpers of different capacity at Mill B. These samples were taken from each batch of stock in the hydrapulpers (2000 or 4000 pounds of fiber per batch) just prior to discharge of the stock. The range of PCB was from 49 to 800 parts per billion (ppb) for the six hour period. The 24-hour composite value (141 ppb), however, compared favorably with the "weighted-average" value for the individual samples. When the concentrations of PCB in the individual hydrapulper samples are averaged on the basis of hydrapulper

TABLE I

DESCRIPTION OF MILLS SELECTED FOR POLYCHLORINATED BIPHENYL DISTRIBUTION STUDIES

Mill	Process	Fiber Source	Product	Production ton/day	Bleaching Sequence	Paper Machines	Effluent Treatment Type	Effluent Treatment gpd
A	Deinking	Purchased, pulp & waste-paper	High grade writing & printing	250	C-E-H	3	Primary[a]	4,000,000
B	Deinking	Ledger & envelope	Napkins & placemats	100	H-H	2	Primary & secondary	1,500,000
C	Hydra-pulping	Mixed corrugated clippings	Boxboard	250	None	3	Primary	3,000,000
D	Hydra-pulping	Mixed corrugated clippings	Boxboard	87	None	1	Primary & secondary	700,000

[a]Secondary treatment plant under construction.
[b]Effluents for primary and secondary treatment are combined with effluents from two other mills.

TABLE II

PCB FLUCTUATIONS IN HYDRAPULPERS OF MILL B[a]

Sample Number	PCB (Aroclor 1242), ppb
1	49
2	57
3	122
4	800
5	131
6	60
Composite (24-hours)	141

[a]Hourly grab samples were taken over a six-hour period.

capacity (2000 pounds for batches 2, 4 and 6 and 4000 pounds for batches 1, 3 and 5) the weighted average is 169 ppb. Therefore, even though we found high fluctuations in the PCB values in the incoming wastepaper, composite samples were representative. Unless otherwise specified, composites were prepared for all samples.

Flow data were collected during the entire sampling period and were used with the concentration data to prepare PCB balances. In Mills B and D, the flow data were difficult, and at certain locations impossible, to obtain. In these cases, the data on flow were calculated by an indirect method, i.e. through differences in the solids content of the streams. In cases where three or more streams came together, and the flow and solids data were unattainable, the values used for the balances were careful "guesstimates" by the mill staff, based on their experience.

During the later trials, when the loss of PCB on the driers was being evaluated, the individual samples were taken at one hour intervals. These data were used to establish losses, as well as to show trends in the PCB content of the stock fiber and paper products.

The procedures for the development of traps for obtaining samples of the PCB-containing vapors, the columns used in determining the leachability of the sludge, and the techniques for the removal of PCBs from solutions are discussed in the individual sections of the report.

Analytical methods, detailed in a report by Easty et al (5), were developed during the first part of this study. Increased complexity of the determination, with subsequent increased time required to analyze each sample, reduced the number of samples which could be assayed during the study period. Although the in-depth study was, therefore, somewhat curtailed over that originally proposed, we achieved our objectives.

RESULTS AND DISCUSSION

STREAMS TO THE WASTE TREATMENT PLANT

With the aid of the mill's staff we selected sampling and flow measurement points at each mill. Hourly aliquots of 250 ml or 500 ml were taken manually from the flow lines with glass containers and composited into a single glass container. To the sample bottle, capped with an aluminum-line cap, 15 ml. of 37% formaldehyde was added for each liter of effluent. This was the stabilizing agent suggested for samples containing PCBs (6). The preserved composite samples were used for the determination of solids and PCBs. The data were then used to establish:

- the major sources of PCBs entering the treatment plant,
- the efficiency of the treatment plant for removing PCBs from the effluent stream,
- the distribution of PCBs in the individual process streams.

In two of the mills (Mills C and D), the distribution of the PCBs in the individual process streams included the entire process, i.e. from hydrapulping to the finished product. In Mill A, due to the long and variable holding time in the stock chests, it was difficult to obtain representative samples of the incoming fiber stock. Therefore, the two parts of the process (stock preparation and papermaking) were studied separately. In Mill D only the individual process streams making up the total mill discharge to the treatment plant were evaluated. Difficulties encountered in determining flows from the paper machine discharges (or recycle loops) negated the development of PCB balances for this mill.

The effluents from the stock preparation steps were found to carry the bulk of the PCBs. For example in Mills A, B, C and D (Table III), these flows account for 99%, 99%, 96% and 78% of the total PCB load, respectively. (For details see appendix, Fig. 2-5). The sum of the PCB loadings for the process streams in stock preparation and papermaking areas are in some cases different from the amount of PCBs entering the waste treatment plant. For example, in Table III, the values for Mill A are 824 and 984 grams/day and for Mill B these are 360 and 243 grams/day, respectively. The variabilities have been attributed to at least two major factors:

- analytical variances of ±20%,
- inaccuracies in flow estimates in more complex deinking processes.

On the other hand, the PCB values for Mills C and D, having simpler stock preparation stages, are in better balance, i.e. 175/175 and 23/21 grams/day.

TABLE III

PCBs IN STREAMS DISCHARGED TO THE WASTE TREATMENT PLANT[a]

	Mill A (Deinking)		Mill B (Deinking)		Mill C (Hydrapulping)		Mill D (Hydrapulping)	
Process Step	g/day	%	g/day	%	g/day	%	g/day	%
Stock preparation	813	99	357	99	169	96	18	78
Papermaking	11	1	3	1	6	4	5	22
Total	824	100	360	100	175	100	23	100
Treatment plant								
Influent	984	100	243	100	175	100	21	100
Effluent								
Primary	341	35	8	3	42	24	<1	?[b]
Secondary	None		5	2	None		None	
Sludge	643	65	185	77	93	53	<1	?
Total	984	100	198	82	135	77	<2	?

[a]See appendix, Fig. 2-5 for details.

[b]Mixed with effluents from two other mills for treatment.

Based on influent and effluent PCB values, Mill B, with a two stage primary and secondary treatment system, removed approximately 98% of the PCBs, whereas Mills A and C, with primary treatment alone, removed 65% and 76%. PCB removal from Mill D's waste could not be determined because of (a) very low initial PCB concentrations in the waste, and (b) further dilution due to mixing with wastes from two other mills prior to discharge into a combined treatment plant. Most of the PCB removed in the treatment plants could actually be accounted for in the sludges.

Table IV gives data on the PCB distribution among fibers, fiber fines, ultrafines and liquid phase (filtrate) in pulp slurries from Mills A and C. The data show that most of the PCB is associated with the fine and ultrafine fractions. It is also noticeable that Mill A fines and ultrafines, which are 10% of the solids fraction, contain 80% of the PCBs. Similar correlations can be seen with Mill C data, where 6.1% of the solids contain 83% of the PCBs. A reasonable conclusion based on these data and our earlier observations is that most of the PCB is associated with the fines and ultrafines in most pulp slurries. We believe that this is due to the high surface area available for sorption. The efficient removal of these fines by flocculation and clarification should result in the removal of most of the PCB from the mill effluents.

In many cases, if the discharge limits are not lowered from the presently proposed 10 ppb, the efficient removal of the fines from the mill effluents will be sufficient to meet the standards. It must be remembered, however, that the PCBs are not destroyed by clarification processes, but are removed with the solid phase (the sludge).

TABLE IV

PCB DISTRIBUTION IN PULP SLURRIES

Fraction	Sample from Mill A			Sample from Mill C		
	% Solids	PCB, ng[a]	% PCB in solids	% Solids	PCB, ng[a]	% PCB in solids
Total	100	11.0		100	0.59	
Fiber[b]	90	2.1	19	94	0.09	15
Fines[c]	8	7.7	70	6	0.37	63
Ultrafines[d]	1.8	1.0	10	0.1	0.12	20
Filtrate[e]	0.2	0.2		0.3	0.1	

[a]Nanogram (1×10^{-9} g).
[b]Solids not passing through a 200-mesh screen.
[c]Through 200-mesh, but not through Whatman No. 1 filter paper.
[d]Through Whatman No. 1 filter paper, but not through 0.45 μm filter.
[e]Through 0.45 μm filter.

A study of the flow patterns (appendix, Fig. 2-5) indicates that the stock preparation effluents which carry the bulk of the PCB load, are also high-volume discharges. Therefore, there may be no advantage in giving them <u>separate</u> treatment in primary or secondary systems for the removal of PCBs. Since the stock preparation effluents from the deinking process contain surfactants and other agents that are generally detrimental to the operation of the clarifier, there might be some advantage in removing these streams from the total mill effluent.

Separate treatment of these streams for the removal of PCBs might even warrant the use of more advanced (expensive) technology, if the volumes were low. At the same time, the operation of the mill clarifier might be markedly improved.

STREAMS WITHIN THE PULP AND PAPERMAKING PROCESS

The PCBs entering the pulp and papermaking process are distributed throughout the system (Tables V, VI and appendix, Fig. 6-10). The PCB balance data are somewhat erratic within the process steps (appendix, Fig. 6-10), mainly caused by the aforementioned analytical variances and also in some cases by estimated flow rates. In addition, the representative samples were difficult to obtain in some of the process stream flows. The PCB balances between the sum of the PCBs in the incoming stock and the sum of the PCBs in the paper machine section of the process are quite comparable within each mill system. Mill A, which had flow meters on many of the streams of the paper machine under study, provided excellent balance data (appendix, Fig. 6-7). Mill C, where careful selection of the sampling points and flow measurement capabilities allowed adequate sampling and the collection of flow data, gave very good balances along the individual process steps (appendix, Fig. 8-10). Because Mills B and D did not have reliable flow data and sampling points on the paper machine, the in-process PCB balances of these mills could not be determined.

The significant points from Tables V, VI and Appendix, Fig. 6-10 are that:

- large quantities of PCBs are recycling within the mill white water and broke system (wire pit, recovery pit, couch trim, roll trim). At PCB loading levels of 206-320 grams/day, (Table V, appendix, Fig. 6 and 7) these amount to 25-30% of the incoming PCBs. In the systems with lower "incoming" PCB levels [8-44 grams/day (Table VI, appendix, Fig. 8, 9 and 10)], the recycling load was 5-15%
- difference between the grams of PCB at the couch roll (less the couch trim) and the grams of PCB in the paper roll and roll trim for each

of the studies showed losses across the drier section of the papermaking process. These were positive values in all cases (except for Trial 2 at Mill C in Table VI). These losses ranged from 19-48% for Mill A and 0-12% for Mill C

- the amounts of PCB in the incoming wastepaper used in Mills A and C did not appear to be as variable (on a day-to-day basis), over the two months study period, as for Mill B
- if the limits for PCBs in the paper products are lowered, the installation of a system to reduce the fines in the whitewater and broke streams should reduce the carry-over of PCBs into the paper products.

TABLE V

PCB DISTRIBUTION ON THE PAPER MACHINE AT MILL A[a]

	% of Total PCB	
	Trial 1	Trial 2
In Fiber Slurry to Headbox[b]		
Purchased	4	None
Broke	42	9
Deinked	24	65
Saveall	30	26
From the Paper Machinery[c]		
In couch trim	6	7
In roll trim	4	2
In product	71	43
Unaccounted for	19	48

[a] See appendix, Fig. 6-7 for details.
[b] PCB/day to headbox = 188 g in Trial 1 and 279 g in Trial 2.
[c] PCB/day from paper machine = 196 g in Trial 1 and 321 g in Trial 2.

TABLE VI

PCB DISTRIBUTION ON A PAPER MACHINE AT MILL C[a]

	% of Total PCB		
	Trial 1	Trial 2	Trial 3
At Headbox[b]	100	100	100
Distribution on Paper Machine			
Sewered[c]	17	11	37
Recycled[d]	4	3	12
Couch and product trim[e]	3	4	2
Product	68	82	37
Unaccounted for	8	0	12

[a]See appendix, Figures 8-10 for details.

[b]Grams PCB/day Trial 1 = 235; Trial 2 = 8.0 and Trial 3 = 49.

[c]Excess white water after screening.

[d]Recycled white water and screenings.

[e]Recycled as broke.

LOSSES OF PCB DURING DRYING

In our earliest work (5), we noted losses of PCBs from aqueous solutions, fibers, and fiber suspensions (the latter to a lesser extent) which were exposed to the atmosphere. Because of the unexpected losses on the paper machine, a study was set up to determine the potential losses from fibers during drying. These studies concentrated on determining PCB levels in:

- the fibers of handsheets which had been spiked with Aroclor 1242 and dried under controlled conditions in the laboratory,
- the fibers from the couch and paper rolls of the three paper machines at Mill A, and
- the vented vapors from the drier section of the machine at Mill A.

Handsheet Studies

Heavy (2.4 g) and tissue-weight (0.6 g) handsheets were prepared from PCB-free softwood kraft pulp which had been beaten to 485 Canadian Standard Freeness and spiked with Aroclor 1242 at a level of approximately 10 ppm (dry fiber). An eight point experimental program was used to demonstrate that PCBs were being lost to the air. These points were:

	A	B	C	D
Heavy (H)	2 samples	1 sample	2 samples	1 sample
Tissue (I)	1 sample	2 samples	1 sample	2 samples

The sheets were analyzed:

A. wet prior to the addition of Aroclor 1242

B. wet after the addition of Aroclor 1242,

C. dry after the addition of Aroclor 1242 and being dried for 2 hours at 20°C in the laboratory

D. dry after the addition of Aroclor 1242 and being dried at 109°C.

In the first trial (Table VII and for details see appendix, Table XX) the handsheets were prepared <u>immediately</u> after the addition of the Aroclor and a brief mixing. The PCB content of these samples was about 2.2 ppm for the "heavy" and 1.1 ppm for the "tissue" weight sheets. The last "heavy" sheet, made approximately 2 hours after the first sheet of the set, showed a concentration of 4.2 ppm. This 91% increase in the PCB content was postulated to have been caused by the increased contact time between the PCB (Aroclor 1242) solution and the fibers.

We therefore conducted a second trial in which the pulp slurry was mixed slowly with the Aroclor solution (at 10 ppm on oven-dry fiber) overnight, under refrigeration, in a closed vessel. This resulted in a PCB level of 5.3 ppm in the fiber.

TABLE VII

LOSS OF AROCLOR 1242 DURING THE DRYING OF HANDSHEETS IN THE LABORATORY[a]

	% Loss of Aroclor 1242	
	Trial 1	Trial 2
Heavy weight sheets (204 g/sheet)		
Analyzed wet	0[b]	0[b]
Air (20°C for 3 hours)	0	0
Drum (109°C to 5% moisture)	60	53
Tissue weight sheets (0.6 g/sheet)		
Analyzed wet	0[c]	0[c]
Air (20°C for 3 hours)	0	0
Drum (109°C to 5% moisture)	66	87

[a]See appendix, Table XX for details.

[b]PCB control (100%) level in Trial 1 = 2.2 ppm; Trial 2 = 5.3 ppm.

[c]PCB control (100% level in Trial 1 = 1.13 ppm; Trial 2 = 5.3 ppm.

Heavy filter papers were used as blotters on both sides of the handsheets during pressing and drying. Immediately after the sheet was formed and the excess water had been drawn off, a blotter was placed on top of the handsheet and the handsheet was removed from the mold. A second blotter was placed under the handsheet and the sandwich was pressed at 50 pounds per square inch (3.5 kg/cm^2) for 5 minutes. The samples were placed on the drum with the blotters, as a sandwich, and dried at 109°C to a 5% moisture level. Each set of handsheets and each <u>pair</u> of blotters (from each of the handsheets) was wrapped separately in aluminum foil and analyzed for PCB within 24 hours of preparation.

The data from these two tests can be summarized:

1. The transfer of PCBs from the aqueous to solid phases increased with contact time over a 2 to 18 hour period.

2. A short period of air drying (20°C for 2 hours) did not appear to reduce the amount of PCB retained by the paper.

3. Drum drying at 109°C, however, markedly reduced (by 53-88%) the PCB concentration in the paper. The loss was slightly less from the heavier handsheets than from the tissue-weight sheets.

4. The blotters sorbed some of the PCB (2-15%) that was pressed out of the handsheets (Table VIII and appendix, Table XXI) and the blotters from the handsheets which had been drum dried showed that 22-31% of the PCB had been transferred to the blotters by volatilization. These "aqueous" and "volatile" PCB transfers would parallel the PCB transfer experienced in the felts and vapors from the driers of the paper machines (unaccounted for losses in the Distribution Study).

<u>Mill Studies</u>

Since the data from the handsheets confirmed our earlier findings, that PCBs can escape from fibers and aqueous phases during drying or exposure to the atmosphere, further field studies of these losses were carried out on three paper machines at Mill A.

In the first part of this study, five <u>sets</u> of samples were taken from the dryer section of the three paper machines. These samples were taken over a period of one month during normal operations at the mill. Each <u>set</u> included samples of:

TABLE VIII

PCB IN BLOTTERS DURING HANDSHEET STUDY IN THE LABORATORY[a]

Blotters from	% PCB in Blotters			
	Trial 1[b]		Trial 2[c]	
	Heavy	Tissue	Heavy	Tissue
Handsheets analyzed, wet	11	15	6	3
	15	22	2	3
Handsheets analyzed, air-dry	13	7	3	2
	7		4	
Handsheets analyzed, drum-dry	31	7	14	4
	22			4

[a]See appendix, Table XXI for details.

[b]Based on a PCB concentration of 2.2 ppm in heavy and 1.1 ppm in tissue weight handsheets.

[c]Based on a PCB concentration of 5.3 ppm for both heavy and tissue weight handsheets.

- wet pulp from the couch roll (trim),
- starch being used for paper sizing, and
- dry paper from the final roll.

All of these data are presented in terms of oven dry (o.d.) fiber or solids.

Two of the five sets (taken during January 1977) gave data indicating losses of PCB of 32%, averaging 40 grams lost per day in the drier section (Table IX and appendix Table XXII).

The other sets were difficult to analyze. These contained high concentrations of interfering materials resulting in distorted gas chromatograms (5) for Aroclors 1242 and 1254 (Table X). The interferences precluded the development of accurate PCB balances in these three instances. The source of interfering materials was not determined, although they may have been caused by the high kraft fiber content of the grade of paper being produced (Table X).

TABLE IX

LOSS OF PCBs ACROSS THE DRIER OF PAPER MACHINES AT MILL A[a]

Machine No.		Basis Weight[b]	PCB Loss[c] g/hr	PCB Loss[c] %
3[d]		37	1.4	32
4[e]	I	50	1.8	28
	II		1.7	30
	III		2.2	36
	IV		2.4	41
	V		1.7	26
		Average	1.96	32

[a]See appendix, Table XXII for details.

[b]In lb/500 sheets (64 x 96 cm)(25 x 38 in).

[c]Calculated as difference between PCB (dry basis) on couch and paper rolls (couch + starch size = 100%).

[d]Single 5-hour composites sampled.

[e]Hourly samples I-V, analyzed individually.

TABLE X

STOCK SOURCE DURING PCB LOSS STUDIES AT MILL A
POSSIBLE EFFECT ON GAS CHROMATOGRAMS

Trial	Bookstock, %	Broke, %	% in Total (In "Virgin" Portion) Softwood	Kraft	Groundwood	Unknown[a]	G.C. Pattern
1	40	20	14(35)	0	0	26(65)	Good
2	25	30	0	36(80)	9(20)	0	Distorted
3	20	40	0	26(65)	0	14(35)	Distorted
4	30	40	0	30(100)	0	0	Distorted
5	35	30	0	14(40)	0	21(60)	Good

[a]Unspecified.

Calculations show that 40 grams of PCB per day that are supposedly carried with the vent gases from the drier are equivalent to 7 ppb going to the atmosphere. These values are based on an average air flow of 130,000 cu ft/min (CFM) from the entire paper machine.

The second part of the study at Mill A was an attempt to trap the PCBs from the drier vent gas while the mill was producing a grade of paper which, based on our experience, was known to have high levels of PCB contamination. We needed to confirm that the PCB losses were to the air and not entirely by transfer to the drier felts or to some other media.

A vapor trap (Fig. 1) was placed over the ninth roll of the drier, at a point which the mill staff thought would correspond to a 109°C temperature. This is the temperature at which we had found 60-80% loss of PCB from handsheets in the laboratory.

The vapors from the drier were passed through a packed column (8 mm. solid glass beads) containing ethylene glycol as a primary absorbent. A drying tube, containing powdered cellulose (Whatman standard grade) and attached to the outlet of the packed column, acted as a secondary trap. This system had been developed in our laboratories and had been shown to trap 97-101% of the PCB air-sparged from an aqueous solution of Aroclor 1242 (Table XI and appendix Table XXIII).

The PCB content of the couch roll fiber (Table XII and appendix, Table XXIV) averaged 3060 ppb (range 1865-5790), the starch contained 310 ppb, and the paper fiber averaged 1300 ppb (range 830-1570 ppb). The PCBs in the starch sample did not originate in the commercial starch used to prepare the sizing. It could have been leached onto the starch when the excess sizing was

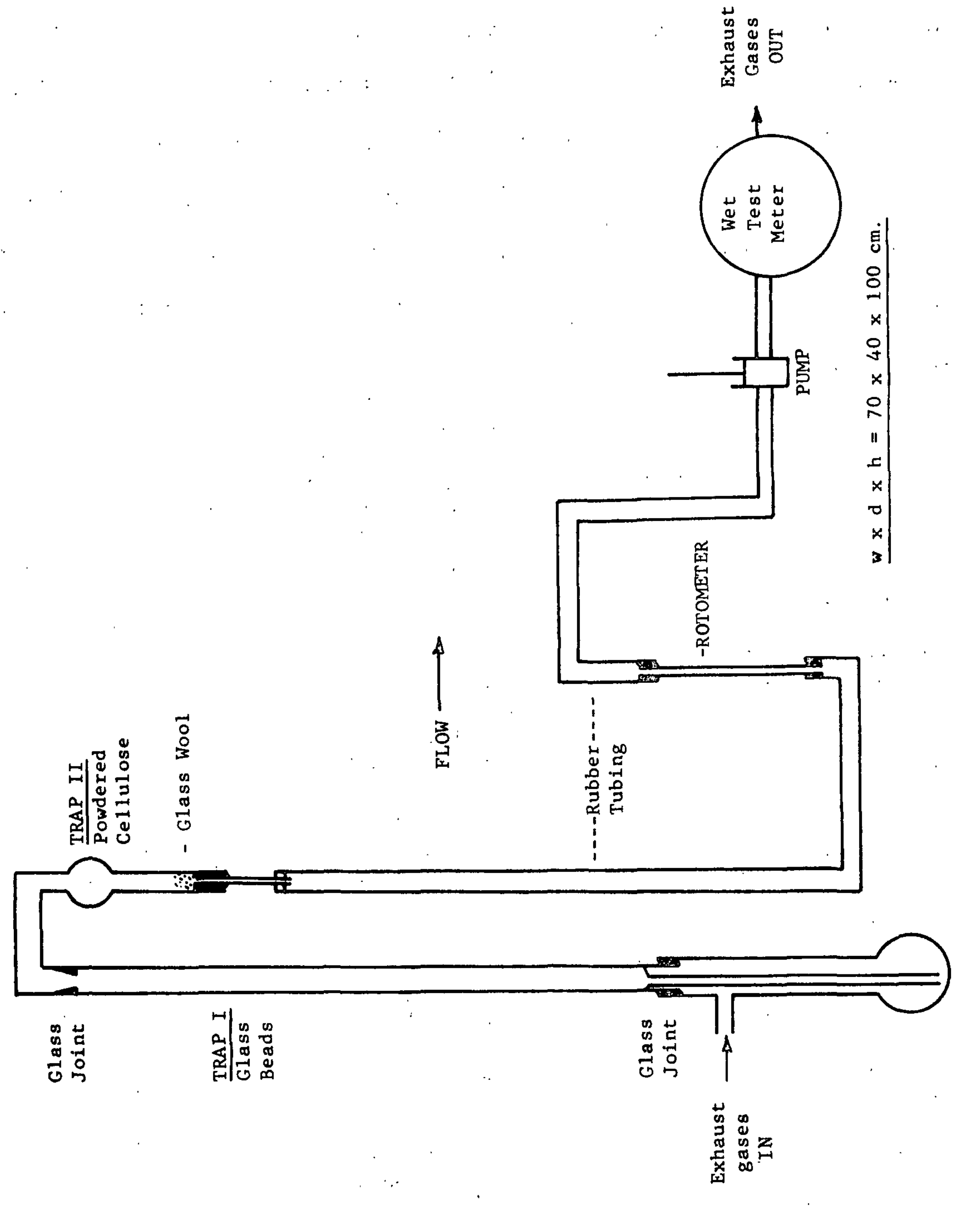

Fig. 1. Diagram of Trap for Determination of PCBs in Exhaust Gases from Dryers.

rinsed from the sheet and recycled to the starch storage tank, or it could have been in the steam used to cook the starch through direct steam injection. Boiler blow-down samples nearly always showed evidence of small amounts of Aroclor 1254, the source of which is unknown. The average loss of PCB in the drier section was 52% of that coming off of the couch roll (6.1 grams/hour or 146 grams per day). The trap recovered 4.5 micrograms of Aroclor 1242 in 150 liters of vapor, for an equivalent of 6.5 grams/hour (based on an air flow of 130,000 cubic feet/minute in the paper machine system). Because of the position of the trap, i.e., over an expected area of high PCB release, the "true" discharge from the vent system could not be determined.

TABLE XI

DETECTION OF PCBs IN AIR OR VAPORS WITH VARIOUS TRAPPING METHODS

Test Solution	Type of Trap	% PCB Recovered
Water with Aroclor 1242, sparged	Dry ice bath	2
Mill effluent, sparged	Petroleum ether	33
Water with Aroclor 1242, sparged	Deactivated[b] Florisil	28
Water with Aroclor 1242, sparged	Deactivated[b] Florisil	61
Water with Aroclor 1242, sparged	Powdered cellulose	78
Water with Aroclor 1242, sparged	Ethylene glycol	101
Water with Aroclor 1242, sparged	Ethylene glycol + powdered cellulose	97 0.5
Water with Aroclor 1242, sparged	Ethyene glycol	97

[a]See appendix, Table XXIII for details.
[b]With 3% (w/w) moisture.

A second vapor-trap trial was set up to establish PCB loss into the atmosphere (Table XIII). Samples were taken from the couch, starch and paper areas of the machine over a five hour period. Two vents, which were readily accessible on the roof of the mill, were fitted with ethylene glycol traps. The first trap (No. 1) was over the wet-end of the drier and the second (No. 2) was near the middle of the drier. Samples of fiber were taken from the couch and paper rolls every fifty minutes during the five hour test, and the starch and trap samples were composited for the entire test period (5 hours).

The gas chromatograms of the first samples of couch and paper fiber were distorted and were very difficult to quantify (Table XII and appendix, Table XXIV). The chromatograms for the sixth set of each (C-6 and P-6), were quite good for the couch and "fair" for the paper. According to Easty (8), the early peaks for the latter were reduced somewhat in height, as might be expected if volatilization had occurred.

Quantification using peak heights yielded values which may be somewhat high (5-20%) if the early peaks are lower than the usual Aroclor 1242 pattern. This would cause the real PCB values of the paper samples, with missing early peaks, to be lower then indicated. The true PCB losses would therefore, be slightly higher than indicated by our data.

Samples of the ethylene glycol from the roof traps showed good chromatographic patterns that also had significant reductions in the early peaks (usual for Aroclor 1242). This was surprising, because one would expect volatilized

PCBs to be enriched in the early (more volatile) peaks. While there was a question as to the fate of the light PCB fractions (early peaks) that seemed to be lost from the paper as it went through the drier and was not trapped in the roof traps, the loss of PCB to the atmosphere was confirmed. Both Aroclor 1242 and 1254 type polychlorinated biphenyl compounds were being discharged at the rate of 164 grams per day and 4 grams per day, respectively. These would result in airborne levels of 0.03 mg/m^3 for Aroclor 1242 and 0.001 mg/m^3 for Aroclor 1254.

TABLE XII

LOSS OF PCBs DURING THE DRYING OF PAPER AT MILL A - FIRST TRIAL[a]

Sample[b]	PCB loss g/day	PCB loss %[c]
1	346	72
2	130	51
3	64	36
4	83	54
5	85	44

Trap captured 158 g/day

[a] See appendix, Table XXIV for details.

[b] Hourly samples of couch and paper fiber, 5-hour composites for starch trap.

[c] Based on couch + starch size as 100%.

Additional work would be required to pinpoint the fate of the earlier peaks (more volatile PCBs).

TABLE XIII

LOSS AND CAPTURE OF PCB DURING THE DRYING OF FIBERS AT MILL A[a]

Sample[b]	Trial 1 g/day	Trial 1 %	Trial 2 g/day	Trial 2 %
Paper Machine Loss[c]				
1	347	72	44	29
2	131	51	41	32
3	65	36	49	38
4	84	54	62	46
5	86	44	55	42
6	--	--	64	47
7	--	--	134	35
Average	146	52	64	38
Captured				
Over drier roll	158	56		
On mill roof				
Trap 1			60	
Trap 2			50	

[a]See appendix, Tables XXIV and XXV for details.
[b]Individual samples for couch, starch and paper - traps were composites.
[c]Calculated as difference between PCB (dry basis) in couch and paper roll samples (couch + starch size = 100%).

LEACHING OF POLYCHLORINATED BIPHENYLS FROM SLUDGE

PCBs have been shown to have a marked affinity for pulp fines. The sorbed PCBs are difficult to remove completely by solvent extraction (5). The removal of the fines by clarification has been postulated as one method for reducing the concentration of PCBs in mill effluents. It should be recognized that the PCBs are not destroyed in the clarification process but are removed with the sludges. Sludges are used as landfill or as soil additives and if the PCBs were leachable, they would pollute the environment.

Therefore four 10 x 120 cm (4 x 48 inch) glass columns were set up in the laboratory to determine the amount of PCB which would be leached from sludges containing high (82 ppm) and low (20 ppm) concentrations of PCB. Two of the columns, used as controls, were filled with sludge and flooded with water but not percolated during the twelve weeks of the test period. The other two were percolated with distilled water at average rates of 125 and 1100 ml per day. To minimize PCB losses during sampling, the column tips went to the bottom of small-mouth sample bottles containing 50 ml of hexane.

The concentration of PCB in the leachate from the two percolated columns ranged from 0.5-4 ppb, with an average concentration of 1.5 and 2.5 ppb for the high and low PCB sludges, respectively (Table XIV and appendix, Table XXVI for details). This amounted to 0.2% (146 micrograms) of the high PCB (82 ppm) containing sludge, which had been leached at an average rate of 1100 ml per day (97 liters total volume). The low PCB (20 ppm) sludge leached at a rate of 125 m/day (10 liters total volume), lost only 0.1% (25 micrograms) of the PCB.

At the end of the test, all four columns were drained and the final drained fluid and sludges were analyzed for PCBs. The PCB losses based on sludge data were 13% (13 milligrams) for the high and 22% (7 milligrams) for the low PCB sludge columns (Table XIV). The control columns for the two sets showed a gain of 3 milligrams for the high PCB column and a loss of 3 milligrams for the low PCB column. These values are negligible and fall within the analytical variance for PCB determinations.

TABLE XIV

LEACHING OF PCB FROM CLARIFIER SLUDGES FROM MILL B[a]

	Sludge PCB			Leachate		
Column	Initial, mg[c]	Final, mg[c]	Change, %	Volume, liter	Av. PCB, ppb	Leached %
1. Control[b]	88	91	+3	--	--	--
2. Leached	97	84	-13	97	1.5	0.2
3. Leached	31	24	-22	10	2.5	0.1
4. Control[b]	27	24	-11	--	--	--

[a]See appendix, Table XXVI for details.
[b]Control — wet sludge flooded with distilled water during test period.
[c]Milligrams based on dry weight of sludge in columns.

More simulated and actual field studies would be required to further answer the PCB-sludge stability question.

PROCESS FOR THE REMOVAL OF PCBs FROM MILL EFFLUENTS

The efficient operation of a waste treatment plant's primary clarifier should markedly reduce the PCB concentration in effluent streams from mills utilizing recycled paper as a source of fiber. The present aqueous discharge limit of 10 ppb can, in many cases, be met with primary treatment processes alone or with a combined primary-secondary treatment system. If, however, the limits were to be reset to lower values (1-5 ppb), other processes might be required to polish the effluents.

In our investigation of adjunctive processes, we deliberately omitted those systems currently under study by equipment manufacturers: carbon adsorption, solvent extraction and incineration. We investigated other potentially valuable processes such as: gas-sparging, foam separation, centrifugation, and fat absorption.

Gas-sparging and Foam Separation

Two systems were used in these studies:

- a 2.5 x 107 cm (1 x 42 inch) glass column with a fine disc
- a 5 x 120 cm (2 x 48 inch) glass column with a coarse disc

and each was used with either air or nitrogen as the sparging (or foam forming) gas.

The gas, from compressed air or nitrogen cylinders, was fed to the base of the column through a mercury pressure-relief chamber and a rotometer. The exhaust gas, from the top of the column, was passed through one or more traps for the capture of the entrained PCBs. At the end of each trial period, the original effluent, the treated effluent and the content of all of the traps were analyzed for PCBs.

The data show that air sparging can be used to remove 98% of the PCBs from an aqueous solution with an initial concentration of 158 ppb or 81% of the remaining PCBs from a 4.2 ppb treatment plant effluent (Table XV and appendix, Table XXVII). Due to difficulties encountered during the development of efficient PCB traps, detailed in the earlier section of this report, the PCB balances in the first trials were very poor. Later we were able to trap all, or almost all (97-101%), of the PCBs swept from the column in the gas phase.

By modifying the top of the column to permit the separation of the foam from the top of the aqueous phase, we developed a foam-separation process. The foam was separated from the exhaust gas, and the gas was passed through secondary traps to remove entrained PCBs.

TABLE XV

GAS SPARGING OF 2 LITERS OF SOLUTION IN 5 x 120 CM COLUMN AT 20°C[a]
TO REMOVE PCB

Sample	Gas	Hrs	Trap	% PCB[b] Removed	Recovered
Aroclor 1242[c]	Air	4	-20°C bath	98	0
" "	Air	1	-30°C bath	25	8
" "	Air	2	Petr. ether	17	7
Decker[d]	N_2	2	-30°C bath	25	4
Screen[d]	Air	6	Petr. ether	71	71
Treatment plant effl.[c]	Air	2	Ethylene glycol	81	79

[a]See appendix, Table XXVII for details.

[b]Based on micrograms in initial sample as 100%.

[d]Samples from Mill B.

[c]Pure solution of Aroclor 1242 in water.

Reductions of 52-86% of the PCBs were obtained from effluents containing high concentrations of PCB (Table XVI and appendix, Table XXVIII). At the same time, the PCBs were concentrated in the foam, for example, a ten-fold increase in Run 18 (Table XXVIII a 7-fold in Run 22, and 19-fold in Run 24. The volume of the foam was very small in proportion to the volume of material in process, in most cases being about 100 ml (5%) for a 2000 ml charge. In some cases where the foam was "wet" because of either high gas rates or the presence of detergents in the effluents, the foam volume was 12-15% of the process volume.

Gas rates and the addition of detergents are process variables which could be used to optimize the process. Rates on the order of 15-30 liters of gas per hour for the large (5 x 120 cm) column appeared adequate. The addition of a detergent (Triton X-100) did not appear to enhance and, in fact, it was detrimental to the removal of PCBs, as was TECHMANGAN, an oxidative catalyst manufactured by Tennessee Eastman (Table XVIIA and appendix, Table XXIX for details).

TABLE XVI

FOAM SEPARATION FOR THE REMOVAL OF PCB FROM EFFLUENTS[a]

Run No.	Effluent	Gas Type	Gas Hr.	Type of Trap	% PCB[b] Removed	% PCB[b] Recovered
18	Treatment plant effl.	Air	6	Petr. ether	78	33
20	Screen No. 1	Air	3	None	35	24
21	Screen No. 1	N_2	5	None	36	42
22	Screen No. 1	Air	3	Hexane	86	57
24	Treatment plant	Air	1.5	Florisil	55	18 18
25	Screen No. 1	Air	2	Hexane	52	38

[a]See appendix, Table XXVIII for details.
[b]Based on micrograms of PCB in initial samples = 100%.

Air sparging or foam separation might be developed into a valuable polishing process for the removal of PCBs and suspended solids (Table XVIIB and appendix, Table XXX). The transfer of the solids to the foam after the removal from the effluent amounted to 93% of the suspended solids, with the concentration of these solids in small volumes (55 ml) of foam (Run 18, Table XVIIB). Final effluents with less than 2-4 ppb of PCB and low suspended solids could be obtained by treating primary or secondary treatment plant effluents by foam separation, if more conventional processes are not adequate. With the development of efficient traps, the PCBs contained in the exhaust gas could be removed and the gas discharged contamination free.

TABLE XVI A

REMOVAL OF PCB FROM MILL A SCREEN EFFLUENTS[a]
WITH AND WITHOUT ADDITIVES

Run No.	Additives	% PCB[b] Removed	Recovered
Small column - 400 ml (air-sparged)			
16	None	71	71
17	TECHMANGAM[c], 300 ppm	54	88
Large column - 2000 ml (foam separation)			
18	None	78	33
19	0.05% Triton[d] X-100	--	40
20	0.01% Triton[d] X-100	38	34
21	0.01% Triton[d] X-100 + TECHMANGAM, 300 ppm	36	42

[a]See appendix, Table XXIX for details.
[b]Based on PCB in Initial sample as 100%.
[c]TECHMANGAM - Manganese sulfate (product of Tennessee Eastman).
[d]Triton X-100, a wetting agent and detergent (product of Rohm & Haas).

While both gas-sparging and foam separation might be potential treatments for effluents with low (less than 10 ppb) concentrations of PCBs, they have not been optimized. Detailed studies are needed to check a number of process variables.

TABLE XVIIB

CHANGES IN EFFLUENT NONFILTERABLE SOLIDS FOLLOWING FOAM SEPARATION[a]

Run No.	Additives	Nonfilterable solids, mg/liter Influent	Effluent	Foam
18	None	2,725	200	92,500
20	0.01% Triton[b] X-100	2,800 2,800	1,360 1,360	7,300 7,300
21	0.01% Triton[b] X-100 + TECHMNA-GAM[c], 300 ppm	2,760	1,434	7,800
22	None	3,010	1,432	21,040
23	None	296	175	4,440
24	None	42	36	640
25	None	11,090	7,170	23,400

[a]See appendix, Table XXX for details.

[b]Triton X-100, a wetting agent and detergent (product of Rohm & Haas).

[c]TECHMANGAM, manganese sulfate (product of Tennessee Eastman).

Centrifuging

A Westphalia laboratory centrifuge was used to carry out several studies on the removal of PCBs from effluents by removing suspended solids. Two basic bowl designs were used:

a. The nozzle bowl which separated the solids from the aqueous phase in a continuous process. The solids are discharged through the outer wall of the rotating bowl by means of nozzles (0.4 mm) and the lighter fluid portion discharged from a port near the top-center of the bowl. Adjustment of the rate of feed to the bowl determined the separation ratio (v/v) between the two streams. In our studies, most of the work with the nozzle bowl was at a 50/50 separation, approximately 500 ml in each stream.

b. A solid bowl which separated the solids from the liquid phase on a batch basis. The solids were collected as a paste inside the bowl and the liquid was discharged from the center top of the bowl. The rate of feed to the bowl determined the degree of solids removal for each stream being processed. Optimum removal, by very slow feed rates, was practiced throughout our studies.

The suspended solids and PCBs were removed from the effluents through centrifugation (Table XVIII). With either the nozzle or solid bowl, the PCBs and suspended solids were transferred from the liquid to the solid phase, the basic difference between the two systems being the degree of concentration achieved in the solid phase. With the nozzle bowl, the PCBs and suspended solids from one liter of effluent were in 500 ml of a suspension (as "solids"), while with the solid bowl, they were concentrated in a low volume (15-25 ml) of paste-like material.

Except for the treatment plant effluent sample, which was processed through the solid bowl, the removal of PCBs/suspended solids by centrifugation was no better than that achieved by the efficient operation of a clarifier. From our studies, it would appear that while centrifuging might have some potential as a polishing process, the high energy consumption for a high volume waste stream would probably rule out consideration of the process on a basis of poor economics.

Fat Adsorption

The use of fats as PCB sorbents was based on the fact that chlorinated hydrocarbons and many other organic compounds are more soluble in fats and oils than in water. Polychlorinated biphenyls can be bio-accumulated in the fatty tissues of organisms by extraction from water or from materials in the organisms' food chain.

TABLE XVIII

CENTRIFUGATION OF EFFLUENT SAMPLES FROM MILL B TO REMOVE PCB[a]

	Whole Effluent		Liquid[b]		Solids[c]	
	PCB, μg	SS[d], mg	PCB, μg	SS[d], mg	PCB, μg	SS[d]
With Nozzle Bowl:						mg/l
Decker	30	6222	10.5	324	14.4	10910
Screen #1	502	2758	138	78	320	5940
Treatment plant effl.	19.5	177	7.8	92	10.7	227
With Solid Bowl:						%
Decker	40	5424	8.2	229	3.6	9.5
Screen #1	638	3207	192	106	349	7.6
Treatment plant effl.	9.6	231	0.46	18	8.1	8.6

[a]Concentrations are reported for 1 liter of sample.
[b]"Light weight" portion of separated effluent.
[c]"Heavier" portion of separated effluent (contains most of suspended solids), for Nozzle bowl = 50% of volume; for Solid bowl = paste from bowl.
[d]Suspended solids.

Two quick laboratory trials were made to determine the potential of fat absorption for the removal of PCBs from mill effluents. The feed for the first was a sample of screening stage effluent containing high suspended solids

(3000 mg/l) and PCBs (1393 ppb). The feed for the second was a treatment plant effluent, low in both suspended solids (75 mg/l) and PCBs (15 ppb).

The fat (melted lard) was deposited on solid glass (8 mm) beads in a 2.5 x 91 cm (1 x 36 inch) column and allowed to cool until semi-solid. One liter of the effluent, at 20°C, was slowly (10 ml/min) passed through the column. At the end of the run, the column was drained and the absorbed PCBs were removed with the lard by washing the column with small portions of petroleum ether.

Both feeds (screening and treatment plant effuents), treated effluent, and the column extract were analyzed for PCBs.

The first column, in which solids had deposited on the top beads, was emptied, the beads were washed with water, and the solids were analyzed for PCBs. Lard was removed from both samples with acetonitrile (6), which preferentially extracts the PCBs from oils and greases and then they were cleaned with Florisil and assayed quantitatively by gas chromatography.

In the two lard absorption trials we were able to remove 68% and 47% of the PCBs from a screen and a treatment plant effluent (Table XIX). The recovery of the PCBs from the lard in these two trials was 55% and 23%, respectively. In the test with the screen effluent, which contained a relatively high concentration of suspended solids, a large part of the PCBs (64% of the recovered) were removed with the fibers filtered out on the beads at the top of the column. The poor recovery of the PCBs removed from the treatment plant effluent, where suspended solids concentrations were low and fibers were not removed by the beads, could not be explained.

TABLE XIX

TREATMENT WITH LARD TO REMOVE PCBs FROM EFFLUENTS OF MILL B[a]

	PCB, μg	% PCB Removed	% PCB Recovered
Sidehill Screen No. 1 effluent treated with lard:			
Feed	1390		
Treated effluent	450	68	
Solids from top of column	490		35
Fat from column	270		20
Treatment plant effluent treated with lard:			
Feed	15		
Treated effluent	8	47	
Fat from column	3.5		23

[a]The samples were passed through a column 0.5 x 91 cm packed with 1 g of fat.

CONCLUSIONS

The following conclusions are drawn from this study:

1. Polychlorinated biphenyls (PCBs) coming into the mill system in fiber stock (recycled paper) at concentrations of 3-20 parts per million (ppm) - 200 to 1500 grams per day - were reduced to 1-3 ppm in the final product. This was an 80-94% removal from the incoming fiber.
2. The bulk of the PCBs were lost during stock preparation (hydrapulping, deinking, screening and washing) and with aqueous discharges from the paper machine (white water). Smaller losses occurred by volatilization in the driers.
3. The PCBs volatized during drying accounted for 6-18% of the total PCB losses. The concentration of PCBs in the exhaust gas from the driers was about 0.03 mg/m^3.
4. Most of the PCBs are sorbed on the fiber fines and the removal of these fines from the mill discharges could result in significant reductions (95-98%) of the PCBs in the effluent. This alone should permit a mill to meet present discharge limits. Removal of fines from the recycling white water could also reduce the carry-over of PCBs into the final product.
5. The removal of PCB during primary and secondary (biological) treatments resulted in its transfer from the aqueous to the solid phase (sludge). The marked affinity between PCBs and fiber fines prevented leaching (less than 0.2%) of the PCBs from sludge under laboratory conditions during a three months study.

6. Several methods were studied as possible polishing processes for further reducing the PCB concentration of the effluents. Gas sparging or foam separation, centrifugation, and fat absorption showed some promise, but time did not permit optimization or economic feasibility study of any of these processes.

ACKNOWLEDGMENTS

The cooperation of mill and Institute personnel who arranged for the sampling and analyses of the myriad of samples taken during this study is greatly appreciated.

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THE INSTITUTE OF PAPER CHEMISTRY

George A. Dubey
George A. Dubey
Research Associate
Division of Industrial
& Environmental Systems

Approved by:

Hardev S. Dugal
Hardev S. Dugal
Director
Division of Industrial
& Environmental Systems

APPENDIX

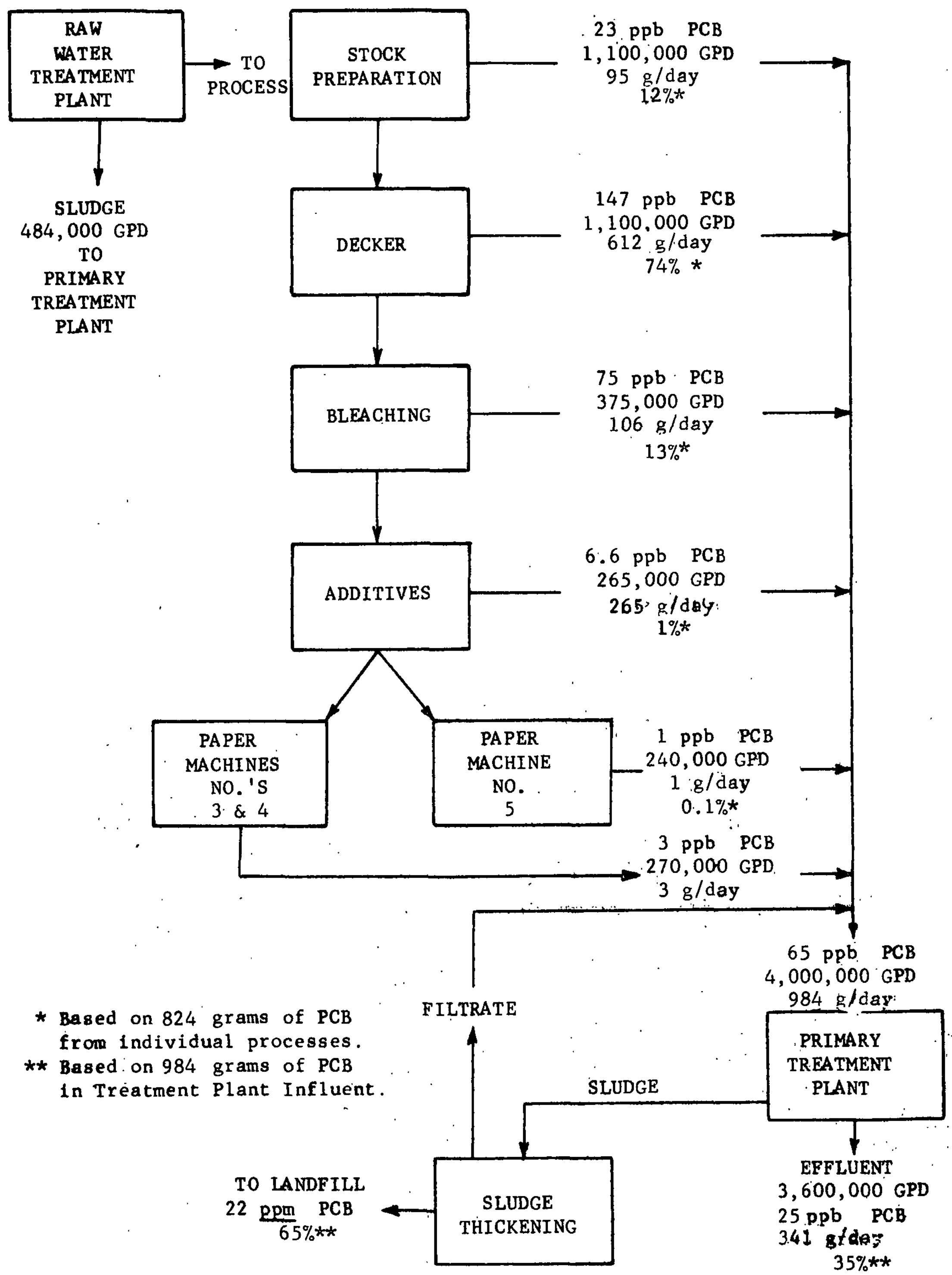

Fig. 2. Occurrence of PCB in Mill A Process Streams Discharged to the Treatment Plant

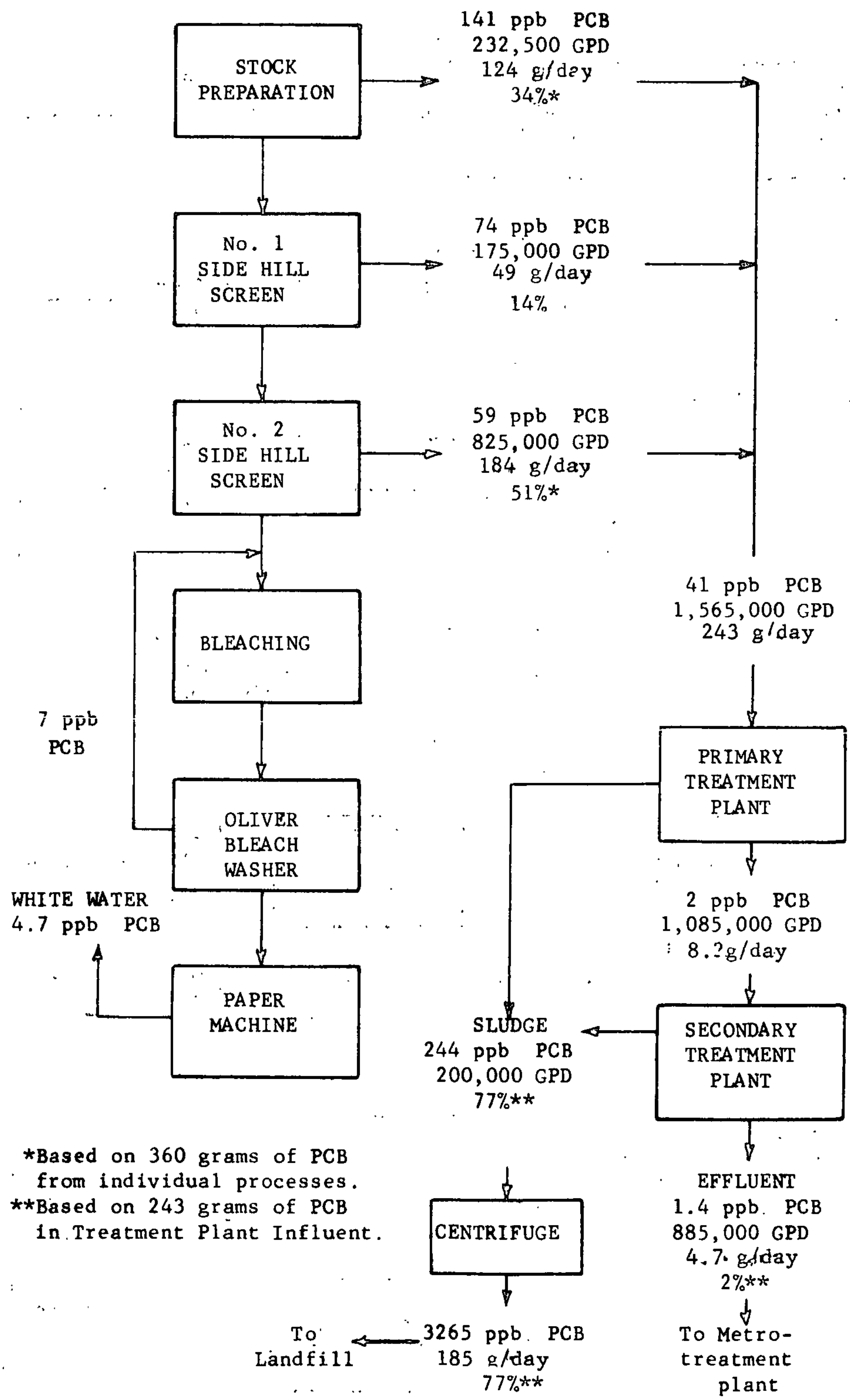

Fig. 3. Occurrence of PCB in Mill B Process Streams Discharged to the Treatment Plant

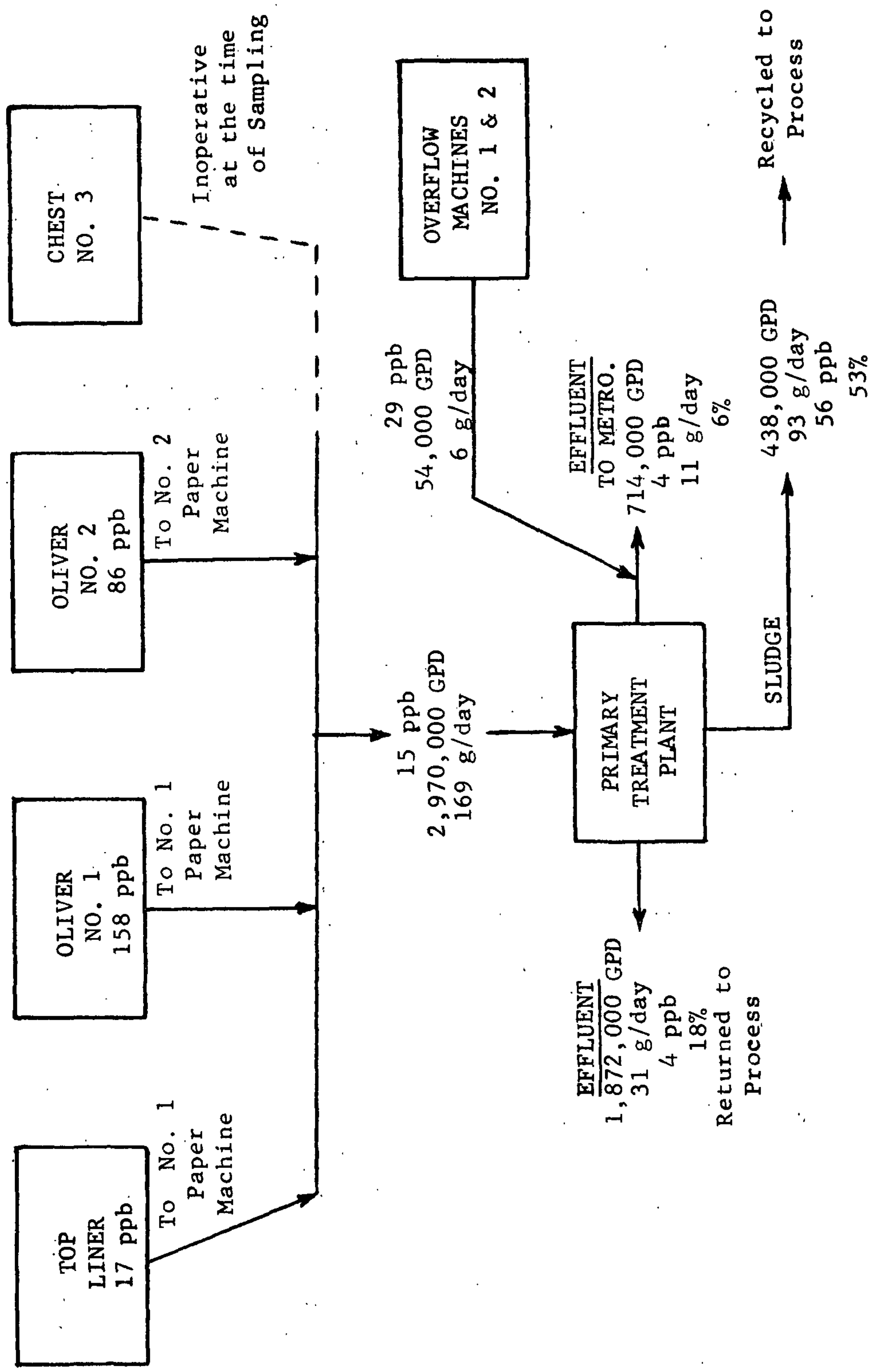

Fig. 4. Distribution of PCB in Process Streams Discharged to the Waste Treatment Plant of Mill C

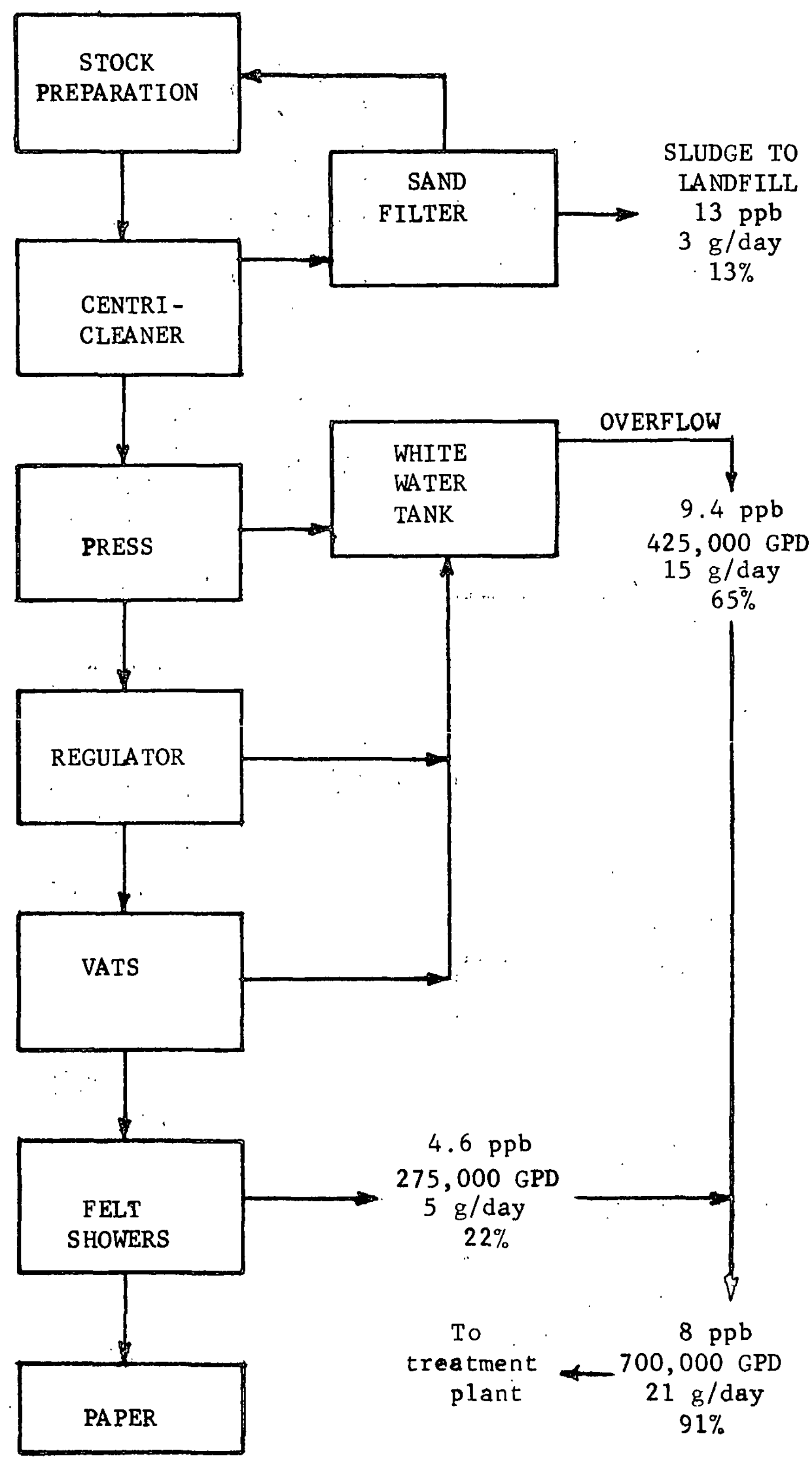

Fig. 5. Distribution of PCB in Mill D's Process Streams Discharged to the Treatment Plant

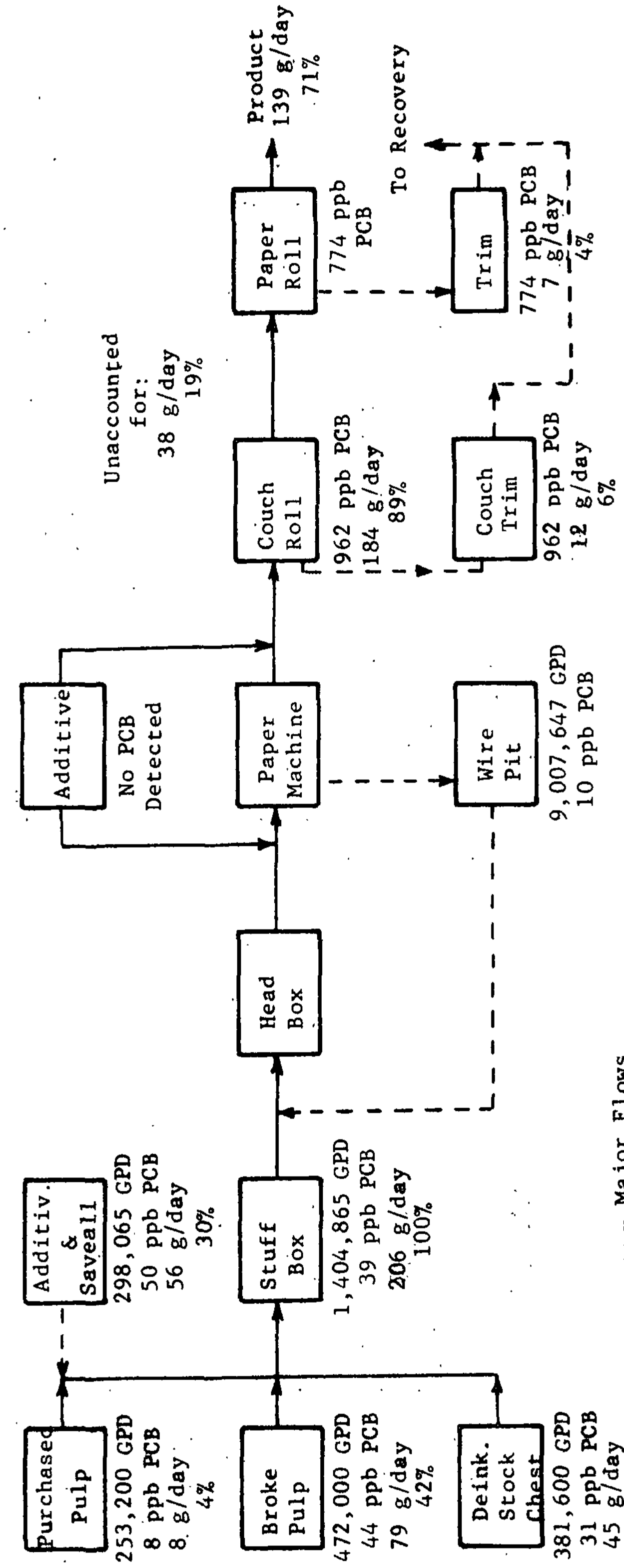

Fig. 6. Polychlorined Biphenyl (Aroclor 1242) in Individual Process Streams of Mill A (First Trial)

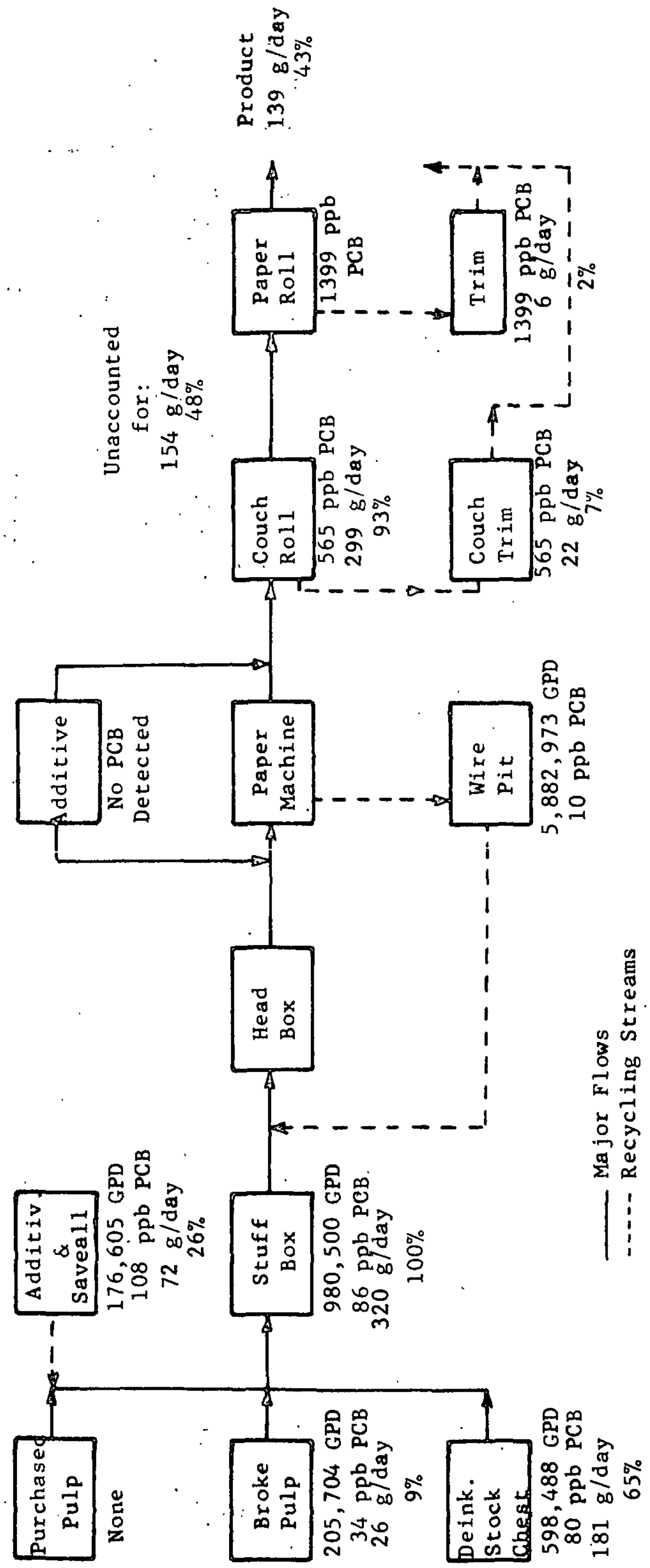

Fig. 7. Polychlorinated Biphenyl (Aroclor 1242) in Individual Process Streams of Mill A (Second Trial)

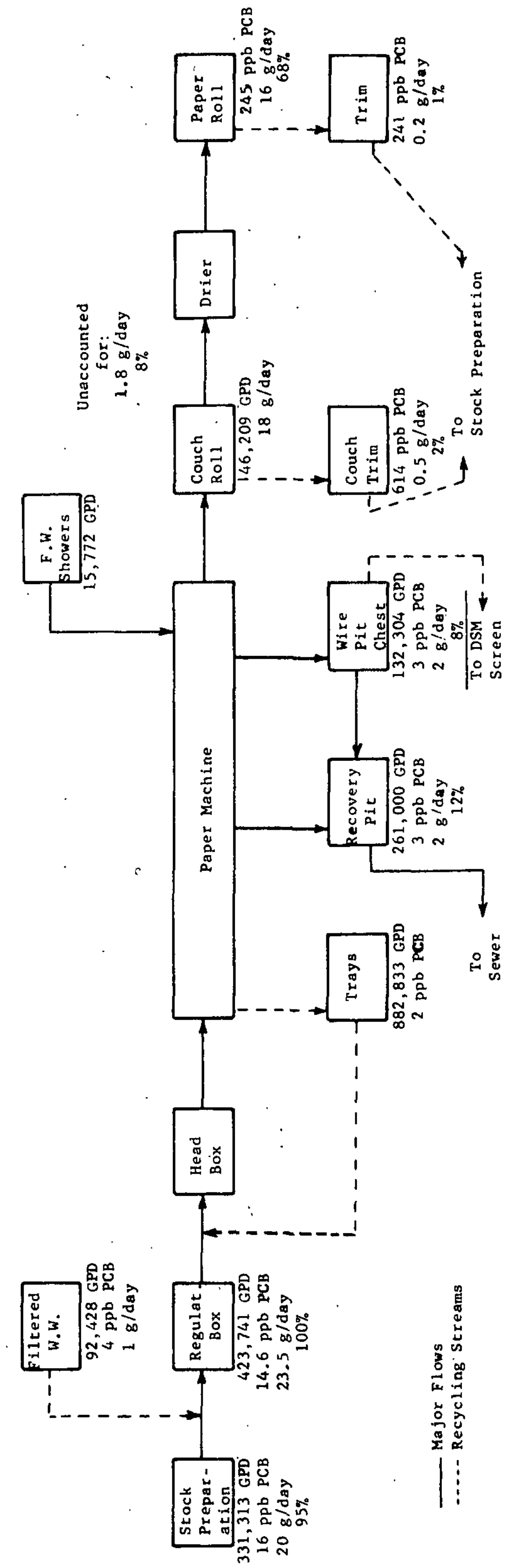

Fig. 8. Polychlorinated Biphenyl (Aroclor 1242) in Individual Process Streams of Mill C (First Trial)

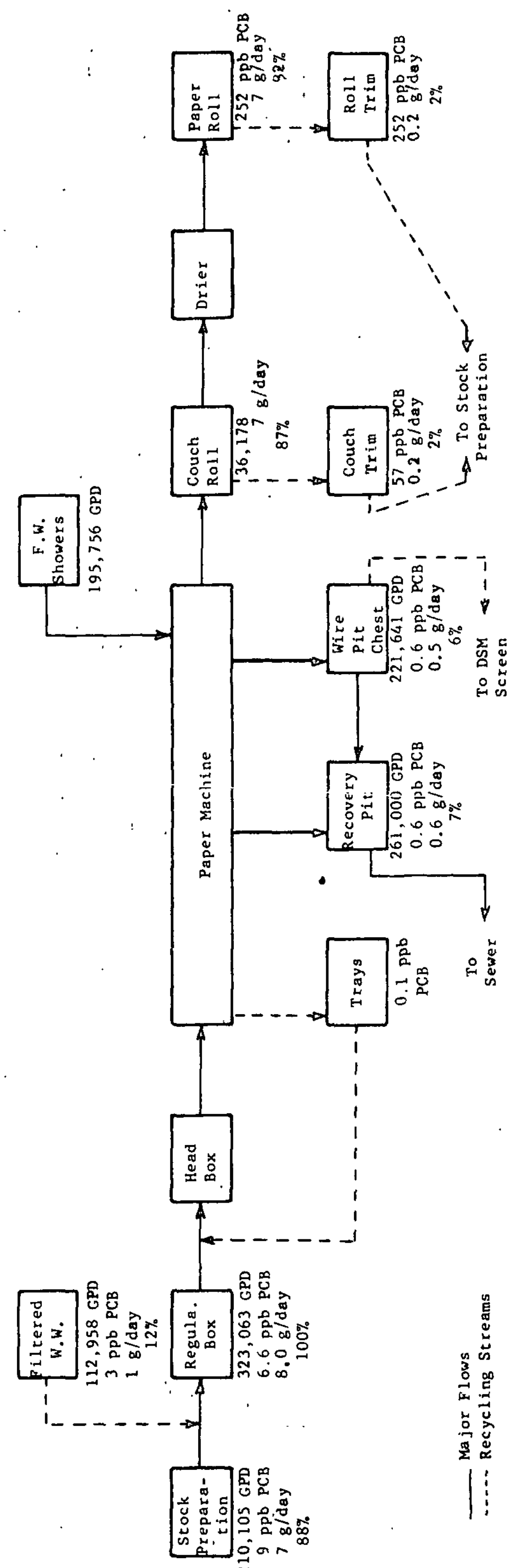

Fig. 9. Polychlorinated Biphenyl (Aroclor 1242) in Individual Process Streams - Mill C (Second Trial)

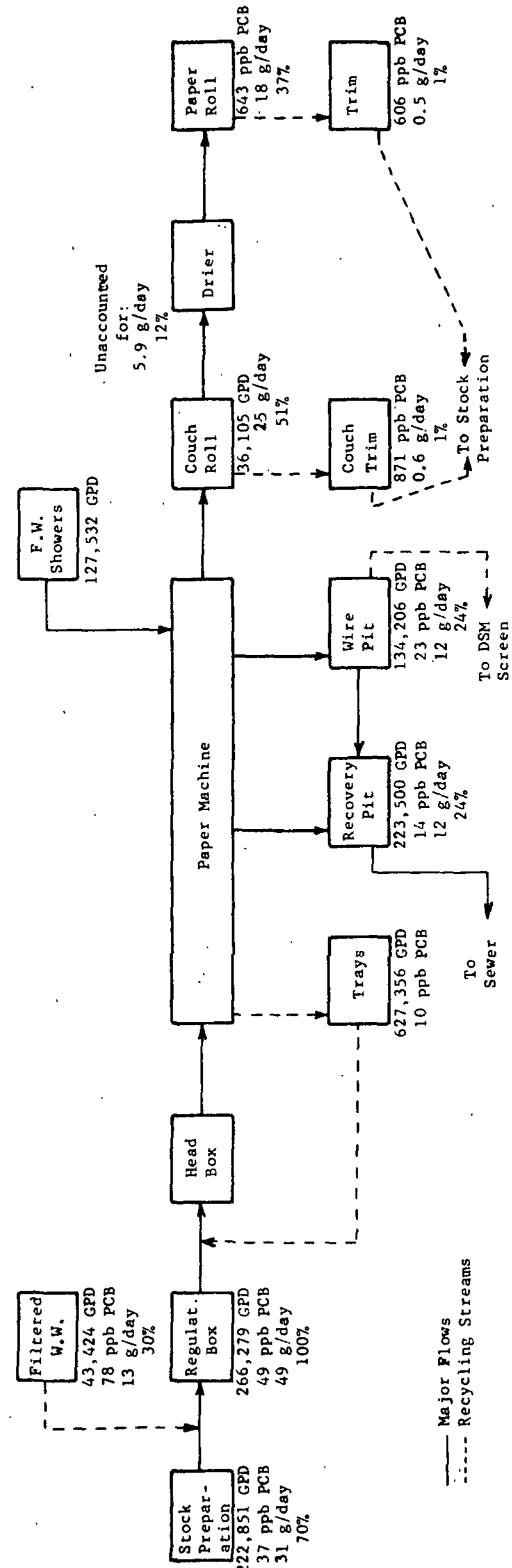

Fig. 10. Polychlorinated Biphenyl (Aroclor 1242) in Individual Process Streams - Mill C (Third Trial)

TABLE XX

LOSS OF AROCLOR 1242 DURING DRYING OF HANDSHEETS IN LABORATORY

Relative[a] Weight	Spiked	Dried	Solids, %	PCB in Trial 1[b] As Rec'd., ppm	Oven dried, ppm	Loss, %[d]	Solids, %	PCB in Trial 2[c] As Rec'd., ppm	Oven dried, ppm	Loss, %[e]
Heavy	No	No	40.2	0	0					
"	"	"	39.6	0	0		Not done			
Tissue	"	"	50.6	0	0					
Heavy	Yes	"	43.2	0.94	2.18		40.4	2.7	6.7	
Tissue	"	"	57.8	0.48	0.83		44.1	2.3	5.2	
"	"	"	51.3	0.64	1.25		44.4	2.4	5.4	
Heavy	"	Air[f]	95.8	2.2	2.30		95.7	8.7	9.1	
"	"	"	95.4	1.9	1.99		95.8	4.9	5.1	
Tissue	"	"	94.4	1.25	1.32		95.8	5.2	5.4	
Heavy	"	Steam[g]	95.7	0.82	0.86	60	98.2	2.5	2.5	53
Tissue	"	"	95.9	0.36	0.38	66	96.5	0.73	0.76	86
"	"	"	95.8	0.34	0.35	69	96.8	0.62	0.64	88
Heavy	"	No	40.9	1.7	4.16		41.4	3.8	9.2	

[a] Heavy = 2.4 grams/sheet; tissue = 0.6 grams/sheet.
[b] Pulp spiked, mixed and handsheets prepared immediately.
[c] Pulp spiked, mixed, allowed to mix overnight and sheets made the following day.
[d] Based on the average of 2.16 and 1.13 ppb for "heavy" and "tissue" weight sheets.
[e] Based on the average of 5.3 ppm for all sheets.
[f] Air dried in the laboratory at 20°C for 3 hours.
[g] Dried on pulp lab steam heated drums (109°C).

TABLE XXI

PCB IN BLOTTERS FROM HANDSHEET PREPARATION IN THE LABORATORY

Blotters[a]	From Handsheets with PCB, ppm	Blotter PCB ppm	Blotter PCB %[b]
Trial No. 1:			
From heavy weight sheets			
Analyzed wet	2.18	0.24	11
" "	4.16	0.32	15
Analyzed air-dry	2.30	0.28	13
" "	1.99	0.16	7
Analyzed steam-dry	0.86	0.67	31 top
		0.48	22 bottom
From tissue weight sheets			
Analyzed wet	0.83	0.17	15
" "	1.25	0.25	22
Analyzed air-dry	1.32	0.08	7
Analyzed steam-dry	0.86	0.08	7
Trial No. 2:			
From heavy weight sheets			
Analyzed wet	6.7	0.32	6
" "	9.2	0.10	2
Analyzed air-dry	9.1	0.14	3
" "	5.1	0.19	4
Analyzed steam-dry	2.5	0.76	14
From tissue weight sheets			
Analyzed wet	5.2	0.14	3
" "	5.4	0.14	3
Analyzed air-dry	5.4	0.12	2
Analyzed steam-dry	0.76	0.19	4
" "	0.64	0.19	4

[a] Blotters (PCB free) heavy weight filter paper between which the handsheets were placed for press and steam drying. Blotters for the handsheets which were analyzed "wet" or "air-dry" were analyzed "wet".

[b] Percentage based on average PCB of 2.16, 1.13 and 5.3 ppm for heavy, light weights in Trial No. 1 and all sheets for Trial No. 2.

TABLE XXII

LOSS OF PCB ACROSS THE DRIER SECTION OF PAPER MACHINES AT MILL A

Machine No.	Sample From	Basis Weight[a]	Production, lb/hr	Aroclor 1242		PCB Loss[b]	
				ppb (o.d.)	g/hr	g/hr	%
3[c]	Couch trim	37	7274	1304	4.30		
	Starch size		385	0	0.0		
	Paper roll		7660	843	2.93	1.37	31.9
4	Couch -1[d]	50	9078	1562	6.43		
	-2		9108	1380	5.70		
	-3		9068	1483	6.10		
	-4		9088	1384	5.70		
	-5		8979	1516	6.17		
	Starch size[c]		426	12	0.002		
	Paper roll-1[d]		9504	1080	4.66	1.77	27.5
	-2		9534	917	3.96	1.74	30.5
	-3		9494	910	3.92	2.18	35.7
	-4		9514	818	3.53	2.35	41.2
	-5		9405	1057	4.51	1.66	26.0
					Average =	1.96	32.4

[a]Pounds, 500 sheets (25" x 38").

[b]Calculated as the difference between the PCB (dry basis) in couch and paper roll (couch = 100%).

[c]Composite samples (5 hours).

[d]Hourly samples, analyzed separately.

TABLE XXIII

DETECTION OF PCBs IN AIR OR VAPORS WITH VARIOUS TRAPPING METHODS

Test Solution	Type of Trap	Concentration, ppb Initial	Concentration, ppb Final	Trapped, mg	Recovered, %
Water with Aroclor 1242, sparged	Dry ice bath	158	3	1	2
Mill effluent, sparged	Petroleum ether	15	4	2	33
Water with Aroclor 1242, sparged	Deactivated Florisil[a]	126	38	135	28
Water with Aroclor 1242, sparged	Deactivated Florisil[a]	29	13	54	61
Water with Aroclor 1242, sparged	Powdered cellulose	22	15	29	78
Water with Aroclor 1242, sparged	Ethylene glycol	24	15	52	101
Water with Aroclor 1242, sparged	Ethylene glycol +	18	6	61	97
	Powdered cellulose			0.3	0.5
Water with Aroclor 1242, sparged	Ethylene glycol	2.1	0.4	3.3+	97+

[a]With 3%(w/w) moisture.

TABLE XXIV

LOSS OF PCBs DURING DRYING OF PAPER AT MILL A OF FIRST TRIAL

	Aroclor 1242			
	In Sample		Loss	
Sample[a]	ppb (o.d.)	g/day	g/day	%[b]
Couch-1	5790	480		
-2	3130	255		
-3	2160	177		
-4	1865	154		
-5	2340	191		
Starch size	310	0.8		
Paper-1	1575	134	346	72
-2	1490	125	130	51
-3	1335	113	64	36
-4	830	71	83	54
-5	1270	107	85	44
		Average	146	52

Trap over drier roll — 4.5 micrograms/150 liters equivalent to 158 g/day PCB[c]

[a]Hourly samples, except for starch size (5-hr composite).
[b]Based on couch fiber + starch size as 100%.
[c]Based on 130,000 CFM (368×10^4 liters/minute) air flow.

TABLE XXV

LOSS OF PCBs DURING DRYING OF PAPER AS MILL A, SECOND TRIAL

	Aroclor 1242			
	In sample		Loss	
Sample[a]	ppb (o.d.)	g/day	g/day	%[b]
Couch-0	1395	116		
-1	1110	93		
-2	1130	94		
-3	1240	102		
-4	1170	97		
-5	1225	102		
-6	4190	346		
Starch size	47162	34		
Paper-1	1270	106	44	29
-2	1020	86	41	32
-3	940	79	49	38
-4	880	74	62	46
-5	920	76	55	42
-6	860	72	64	47
-7	2960	246	134	35

Trap 1 4.5 micrograms/133 liters = 179 grams/day

Average = 164 grams/day[c]

Trap 2 3.7 micrograms/130 liters = 150 grams/day

[a]Sampled every 50 minutes for couch and paper (Starch and Traps Composites).
[b]Based on Couch fiber + Starch Size as 100%.
[c]Based on 130,000 CFM (368 x 10^4 liters/minute) air flow.

TABLE XXVI

LEACHING OF PCB FROM PRIMARY CLARIFIER
SLUDGE FROM MILL B

Column	Column 1 Control[a]	Column 2 Leached	Column 3 Leached	Column 4 Control[a]
Original, ppm (o.d.)	68	82	21	20
" , mg[b]	88	97	31	27
Final, ppm (o.d.)	59	72	20	19
" , mg[b]	91	84	24	24
Change, %	+3	-13	-22	-11
Effluent, liters	--	97	--	10
Range, ppb	--	0.5-4.4	0.8-3.9	--
Average, ppb	--	1.5	2.5	--
Final, ppb[c]	27	4.0	2.3	2.5
Leached, %[d]	--	0.2	0.1	--

[a] Control—wet sludge flooded with water during test period.
[b] Mg of PCB based on dry weight of sludge in the column.
[c] Concentration of PCB in water drained from the column at the end of the test period.
[d] Based on total micrograms of PCB leached from columns (in effluents sampled weekly).

TABLE XXVII

GAS SPARGING OF 2 LITERS OF SOLUTION IN A 5 x 120 CM COLUMN AT 20°C TO REMOVE PCB

Sample Treated	Gas			Trap	Quantity of PCB[a]			%[b]	
	Type	Liter/hr	Hr		Initial	Final	Removed	Removed	Recovered
Aroclor 1242[c]	Air	31	4	-20°C	63(158)	1(27)	62	98	0
" "	Air	34	1	-30°C	20(50)	15(39)	5	25	8
" "	Air	34	2	Petr. ether	18(46)	15(38)	3	17	7
Decker[d]	N_2	32	2	-30°C	12(30)	9(23)	33	25	4
Screen No. 1 centrifuged[d]	Air	15	6	Petr. ether 0°C	5.9(15)	1.7(4)	4.2	71	71
Treatment plant effl.[c]	Air	36	2	Ethylene glycol	4.2(2.1)	0.8(0.4)	3.4	81	79

[a] Micrograms (ppb).
[b] Based on micrograms in Initial as 100%.
[c] Pure solution of Aroclor 1242 in water.
[d] Samples from Mill B.

TABLE XXVIII

FOAM SEPARATION FOR THE REMOVAL OF PCB FROM EFFLUENTS

Run No.	Effluent	Gas Type	Gas L/H[a]	Gas hr	Trap	PCB, μg Initial	PCB, μg Final	PCB, μg Removed	PCB, μg Foam	PCB, μg Trap	%[b] Removed	%[b] Recovered
18	Treatment plant effl.	Air	31	6	Petrol. ether	25(12)	5.4(3)	19.6	7(127)	1.3	78	33
20	Screen No. 1	Air	10	3	None	17(8)	11(6)	6	5.7(24)	--	35	34
21	Screen No. 1	N_2	10	5	None	15(8)	9.6(6)	5.4	6.3(27)	--	36	42
22	Screen No. 1	Air	30	3	Hexane	966(483)	130(70)	836	545(3636)	6	86	57
24	Treatment plant effl.	Air	25	1.5	Florisil	3.8(1.9)	1.7(0.9)	2.1	0.7(36)	Trace	55	18
25	Screen No. 1	Air	34	2	Hexane	60(30)	29(18)	31	21(60)	1.9	52	38

[a] Liters of gas per hour.
[b] Based on micrograms in initial = 100%.

TABLE XXIX

REMOVAL OF PCB FROM MILL A SCREEN EFFLUENT BY AIR-SPARGING AND FOAM SEPARATION, WITH AND WITHOUT ADDITIVES

Run No.	Additives	PCB, ppb		PCB, mg			PCB, %	
		Initial	Effluent	Initial	Effluent	Trap(s)	Removed	Recovered
Small Column - 400 ml (air sparged):								
16	None	15	4	5.9	1.7	4.2	71	71
17	TECHMANGAM[b], 300 ppm	12	6	4.8	2.2	4.2	54	88
Large Column - 2000 ml (form separation):								
18	None	12	3	25	5.4	8.3	78	33
19	0.05% Triton[c] X-100	9	--	14	--	5.6	--	40
20	0.01% Triton[c] X-100	8	6	17	10.6	5.7	38	34
21	0.01% Triton[c] X-100 + TECH-MANGAM[b], 300 ppm	8	6	15	9.6	6.3	36	42

[a]Removal and recovery based on micrograms of PCB initially in column.
[b]TECHMANGAM - Manganese Sulfate (Product of Tennessee Eastman) - oxidation catalyst.
[c]Triton X-100, a wetting agent and detergent (Product of Rohm & Haas).

TABLE XXX

CHANGES IN EFFLUENT NON-FILTERABLE SOLIDS (NFS)
FOLLOWING FOAM SEPARATION

Run No.	Additives	Influent ml	Influent NFS, mg/l	Effluent ml	Effluent NFS, mg/l	Foam ml	Foam NFS, mg/l
18	None	2000	2725	1945	200	55	92500
20	0.01% Triton X-100[a]	2000	2800	1760	1360	240	7300
21	0.01% Triton X-100 + 300 ppm TECHMAN-GAM[b]	2000	2760	1680	1434	315	7800
22	None	2000	3010	1850	1432	150	21040
23	None	2000	296	1920	175	55	4440
24	None	2000	42	1975	36	20	640
25	None	2000	11090	1630	7170	135	23400

[a]Triton X-100, a wetting agent and detergent (a product of Rohm & Haas).
[b]TECHMANGAM, manganese sulfate-oxidation catalyst (a product of Tennessee Eastman).