Monsanto

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August 4, 1978

Office of Toxic Substances (TF-794)
Environmental Protection Agency
401 "M" Street, S.W.
Washington, D. C. 20460

ATTENTION: Ms. Joni T. Repasch

Dear Ms. Repasch:

On June 7,.1978, the EPA published a proposed rule in 43 Federal Register beginning on page 24,802 covering Manufacturing, Processing, Distribution in Commerce, and Use Bans of Polychlorinated Biphenyls (PCB's). This letter sets forth Monsanto Company's comments on the proposed rule. Please include these comments, with the attachment, in the official record of this proceeding.

Our comments are divided into two parts. The first part provides general comments which focus on the EPA's proposed maximum concentration of 50 ppm and the justifiable need for a heat transfer system use authorization. The second part sets forth specific language and recommendations related to these matters, and to certain other matters in specific sections of the proposed rule.

GENERAL COMMENTS

The proposed immediate, mandatory removal from service of heat transfer systems containing fluids whose PCB concentration equals 50 ppm or greater is not justified in view of the lack of any significant risk to health or the environment. To require industry immediately to remove from service and drain all these systems or to replace the systems entirely to meet a 50 ppm concentration level is an arbitrary mandate and will generate a substantial, immediate risk of injury and environmental harm from spillage and result in an abrupt, massive buildup of PCB contaminated fluid without available disposal facilities or time to develop orderly plans to

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carry out the disposal. Furthermore, the EPA cites no evidence in the preamble of any environmental or health hazard to support the proposed reduction in the regulated concentration of PCB's in a PCB mixture under Section 761.2(w) from 500 ppm to 50 ppm, nor does the May, 1978 EPA Support Document/Draft Voluntary Environmental Impact Statement upon which the proposed rules are based support this reduction. Therefore, Monsanto strongly recommends the EPA withdraw this proposed reduction.

Yet even with the withdrawal of the 50 ppm concentration, it is imperative that an authorization be granted for continued use of heat transfer systems containing residual PCB's. The evidence conclusively establishes that the heat transfer system use activity meets the requirements for granting an authorization to allow continued operation, and Monsanto requests the EPA to grant such an authorization. On page 42 of the EPA Support Document, the EPA states that before it grants an authorization for continuation of a non-totally enclosed use activity the following two requirements must be met:

(1) the activity authorized must not pose an unreasonable risk of injury to health or the environment, and

(2) the ban would cause major and extensive economic disruptions.

Regarding the first requirement, an analysis of potential PCB exposure from various sized PCB contaminated heat transfer systems is illustrative of the insignificant risk of injury to health or the environment posed by authorizing continued use of these systems. The highest risk area for leakage in these systems is in the pump seals, but inspection maintenance for pump seals is also emphasized because of user awareness of this risk. A pump seal failure would be rapidly detected by inspectors or automatic monitoring devices and loss of fluid would be unlikely to exceed from 1% to 5% of the total fluid volume in the system.

For example, a 500 gallon system containing 1% volume of PCBs has a total PCB content equal to 60 pounds, and a leak of 5% of the total fluid (which is unlikely) would release only 3 pounds of PCB's. Similarly, a 10,000 gallon system containing a PCB contamination of 500 ppm has a total PCB content of 60 pounds, and a leak of 5% of the total fluid (again unlikely) would release only 3 pounds of PCB's. A leakage of 3 pounds of PCB's is below the EPA's designated harmful quantity for PCB spills into navigable waters (10 pounds) under 40 CFR 118.4 issued pursuant to the Federal

Water Pollution Control Act and, in Monsanto's opinion, does not create a significant risk to health or the environment. Furthermore, the above examples are worst case situations because they assume no spill prevention program (for example, diking) or effluent control program in effect. If such programs were in effect it would be highly unlikely for any amount of PCB's approaching 3 pounds to escape into the environment.

The proposed immediate, mandatory removal of these systems from service also meets the standards for the second requirement for an authorization by resulting in substantial, widespread economic disruption. Since the EPA states in the preamble and the Support Document that it lacks information necessary to evaluate the impact of the ban on the heat transfer system use activity, the following information is presented which is generally consistent with the specific information requests in 43 FR 24810 relative to hydraulic die-casting systems, and which clearly and conclusively demonstrates this economic impact:

1. Number of systems contaminated. It is estimated that when the sale of PCB heat transfer fluids was discontinued in 1972 there were 450 heat transfer systems using this fluid. This estimate is based on (a) the current level of new systems introduction, (b) the ten year period (1962-72) during which PCB heat transfer systems were specified, and (c) the total volume of 20 million pounds of PCBs sold for heat transfer systems from 1962 through 1971 as reported by the 1972 Interdepartmental Task Force on PCBs COM-72-10419 pages 6 and 7.

2. The average liquid volume of the systems. It is estimated that about one-half of all PCB contaminated heat transfer systems have less than a 500 gallon liquid volume. Systems greater than 500 gallon volumes are estimated to average about 2,000 gallons. These estimates are based upon a review of systems filled in 1977 and 1978 and upon the average system size of Monsanto units converted in the 1970-72 period - a typical cross section of the industry pattern.

3. The range of liquid volume. Heat transfer systems of greater than 10,000 gallons are unusual. Small experimental pilot plant units may contain 50 gallons.

4. Fluid top-off. Heat transfer fluids are designed to be thermally stable within the recommended temperature range of operation and to operate at low pressure. Accordingly, routine top-off is minimal. Average top-

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off may be higher because of fluid removal from parts of the system when maintenance is performed on other components of the system such as pumps, valves and heaters or in the event a system malfunction causes a thermal degradation of the fluid. Monsanto's experience indicates that some systems may require no top-off for three to five years; other systems may require a top-off of 50% in one year if major maintenance programs requiring drainage are undertaken. However, systems are not routinely drained.

5. Efforts to reduce PCB contamination. We estimate that greater than 90% of the plants operating with PCB heat transfer systems converted to alternative non-PCB fluids in 1970-72. Some of those converting drained and refilled the system with non-PCB fluid; some drained, flushed and refilled; some drained, chemically cleaned and refilled; and other dismantled and discontinued use of liquid systems. We estimate that these efforts have generally resulted in current system PCB levels in the industry ranging from around 100 ppm to several thousand ppm. Recovery from heat transfer systems would generally be expected to be greater than 90%. Note that for the purposes of these comments the term "recovery" is defined as the percentage of total system fluid volume extracted from the system by draining.

6. Servicing fluids to remove PCB's from systems. Following is a review and analysis of the potential success of three methods the EPA has considered for PCB removal:

   (a) Drain and refill. If small systems (500 gallons or less) are drained and refilled with a non-PCB fluid, a 98-99% recovery of dissolved PCB's can be expected. This service method will not, however, remove PCB absorbed by the heat transfer system walls. In the case of systems larger than 500 gallons a 90-99% recovery can be expected depending upon the complexity of the piping layout and heat exchanger design.

   (b) Distillation is of questionable efficiency in separating and removing PCB's from heat transfer fluid due to the similarity in boiling ranges of PCB's and non PCB heat transfer fluids. The boiling ranges for these respective fluids are as follows:

PCB		
	Therminol FR 1	617°F - 690°F
	Therminol FR 2	644°F - 707°F

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Non-PCB	Therminol 55	635°F - 734°F
	Therminol 66	643°F - 668°F

(c) Carbon treatment experiments to remove PCB's are currently being conducted to investigate the carbon treatment removal method, but no data are presently available.

7. Present PCB levels in systems - We estimate the range of PCB concentration levels in heat transfer systems to be from about 100 ppm to about 30,000 ppm.

8. Cost of new systems - The cost of a new system could result in a large dollar expenditure compared to the much lower cost of replacing fluid. Replacing a heat transfer system may well mean totally rehabilitating a plant because these systems are integral parts of the users' plants, and replacement of heat transfer systems is impossible without replacement of reactors, coolers and heat exchangers. Such replacement would usually require a multimillion dollar expenditure. Further, the costs of lost production would be extraordinarily high in terms of lost wages, lost sales and product shortages which could impact a wide area of other manufacturing industries using finished products during the length of time required to replace each system. Thus the immediate, mandatory removal of these systems from service would result in substantial, widespread economic disruption in industries using heat transfer systems and the products produced from processes using such systems.

9. Cost of draining and refilling systems - We estimate the cost of draining and refilling systems would be from $10 million to $30 million, depending upon authorized PCB level, and based upon the model of an average 2,000 gallon system and the estimated 450 systems in the industry. For example, PCB reduction to a concentration level of 500 ppm in a 2,000 gallon system, with a current 1% PCB volume (10,000 ppm) and assuming a 90% fluid recovery, would result in a marginal removal cost of approximately $220 per pound. It is estimated that to reduce from a 500 ppm level to a 50 ppm level would require a marginal removal cost of about $30,000 per pound. Starting with a PCB content in the 2,000 gallon system of 240 pounds, draining the system (90% recovery) would leave 200 gallons of fluid containing 2 gallons of PCB's or 24 pounds. This quantity should, when the system is refilled with 2,000 gallons of flushing fluid, result in a PCB concentration of 1500 ppm. A

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second draining and refilling with flushing fluid should initially drop PCB's to 2.4 pounds or 150 ppm, but this amount would shortly increase as PCB's are released from the surface walls into the fluid. Once a proper concentration has been obtained to assure the concentration remains below 500 ppm, the flushing fluid would be drained and the system refilled with non-PCB heat transfer fluid.

The direct cost estimates of flushing and draining, excluding costs associated with lost production and resulting disruption of supply to consumers, are as follows:

(a)	Flushing fluid - 2x2,000 gallons at $2.00 per gallon	$8,000
(b)	New fill of non-PCB heat transfer fluid - 2,000 gallons at $8.00 per gallon	$16,000
(c)	Disposal of initial drained fluid and 2 flushing fluid changes - 6,000 gallons at $2.26 per gallon	$16,000
(d)	Labor and overhead - 4 men 10 to 15 days	$12,000
	Total	$52,000

This estimate assumes that only two flushings are required and that draining and flushing proportionately reduces PCB concentration level without a major breakdown of the system involving gasket replacement or rewelding which could easily double or triple costs. Based upon this estimate, the cost of removal of 235 pounds would give a marginal removal cost of $220 per pound to achieve a residual level below 500 ppm. To achieve a level of 50 ppm it is likely that at least two further drain and flush procedures and chemical cleaning would be required. At $50,000 per procedure, the final 1.6 pound removal would carry a marginal removal cost of at least $30,000 per pound.

The above information relative to environmental and health injury and economic impact is clear evidence which meets the two requirements necessary to support the grant of a use authorization for heat transfer systems containing residual PCB's. Accordingly, Monsanto recommends the proposed rules be revised to authorize for a period of 5 years the continued use and servicing of all 500 gallon capacity or less heat transfer systems used and serviced in a manner other than a totally enclosed manner to the extent these systems contain 1% or less by volume of PCB's, provided users attain this 1%

PCB volume within one year after the effective date of the rule. For systems with greater than 500 gallon capacity, Monsanto recommends the EPA authorize for 5 years continued use and servicing of these systems in a manner other than a totally enclosed manner to the extent they contain a PCB concentration of 500 ppm or less, provided users attain this 500 ppm PCB concentration within 2 years after the effective date of the rule. These transition time periods would permit an orderly reduction of PCB levels during which disposal of fluids by incineration could be planned, thereby avoiding spillage and buildup of PCB contaminated fluid inventories awaiting disposal. Please note that proposed language for this use authorization is set forth as new Section 761.31(h) on pages 10-11 of these comments.

Specific Suggested Changes in the Proposed Rules

Sec. 761.2(w) "PCB mixture." In addition to the proposed arbitrary 50 ppm concentration, the definition includes any material, no matter how dilute in PCB concentration, if the material is contaminated by a substance containing a PCB concentration of 50 ppm or greater. For example, if a gallon of heat exchange fluid containing 500 ppm PCB were diluted to 1,000 gallons with a non-PCB flushing fluid (final concentration 0.5 ppm PCB), the resulting flushing fluid when drained would still be arbitrarily considered a PCB mixture. We recommend the definition be changed to read:

> (w) "PCB Mixture" means any combination of chemical substances which contains 500 ppm (0.050 percent on a dry weight basis) or greater of a PCB chemical substance. This definition includes, but is not limited to, dielectric fluid and contaminated solvents, oils, waste oils, heat transfer fluids, other chemicals, rags, soil, paints, debris, sludge, slurries, dredge spoils, and materials contaminated as a result of spills.

Sec. 761.2(bb) "Manufacture 'for Commercial Purposes.'" We recommend for clarification the addition of the following subsection to the definition, which is consistent with the discussion by the EPA set forth in column 1, 43 FR 24805:

> (3) As the desired product. Inadvertent manufacture as a by-product in the manufacture of another chemical is not "manufactured for commercial purposes."

Sec. 761.2(cc) "PCB Sealant, Coating, or Dust Control Agent." This term is defined based on the state of the

analytical art. In complex mixtures such as waste oils, analysis for PCB is not sensitive because of background interference. We recommend that a concentration level be set related to the toxicological properties of PCB's and the demonstrated injury risk associated with human and environmental exposure. Such a concentration would, among other things, avoid a moving target definition depending upon the sophistication of the analytical equipment used.

Sec. 761.2(dd) "Process 'for Commercial Purposes.'" We recommend the addition of the following subsection to the definition. This is consistent with the discussion in column 1, 43 FR 24805 and our proposed modification of section 761.2(bb).

> (3) for means other than PCB removal. Processing which removes PCB from the material to be used for commercial purposes does not constitute "processing for commercial purposes."

Sec. 761.2(ff) "Significant Exposure." This term is defined based on the state of the analytical art. We believe that significant exposure should be, as discussed above relative to Section 761.2(cc), a specific concentration related to the toxicological properties of PCB's and to injury risk associated with human or environmental exposure. We recommend, consistent with the 1977 American Conference of Governmental and Industrial Hygenists publication of Threshold Limit Values for Chemical Substances in the Workplace, that this section be amended to read as follows:

> (ff) "Significant Human Exposure" means any exposure of humans to PCB chemical substances or PCB mixtures in excess of 0.5 mg/cu. meter TWA for a 40 hour week by an applicable analytical method.

Sec. 761.1(gg) "Small Quantities for Research and Development." The definition of this term is unjustified and arbitrary. No data are presented in the preamble by the EPA that use in research has posed any measurable risk of injury to health or harm to the environment. Monsanto has no evidence of any adverse effect of PCB's in laboratory use. We suggest as an alternative replacing section 761.2(ff) with the following wording taken in part from the TOSCA Inventory Reporting Regulations, 42 FR 64576, section 710.2(y):

> (gg) "Small Quantities for Research and Development" means any quantity of PCB chemical substance or PCB mixture manufactured or processed only for purposes of scientific experimentation or analysis of chemical

> research on, or analysis of, PCB's, including research or analysis for the development of a product that (1) are no greater than reasonably necessary for such purposes, and (2) are used by, or directly under the supervision of, a technically qualified individual(s).

It would also seem appropriate to include as new section 761.2(kk) the definition of "Technically Qualified Individual" based upon section 710.2(aa) of the TOSCA Inventory Reporting Regulations.

Sec. 761.2(hh) "Totally Enclosed Manner." This term is defined with reference to section 761.2(ff) and, consistent with our recommended changes above to that section, we suggest section 761.2(hh) be changed to read:

> (hh) "Totally Enclosed Manner" means any manner that will ensure any exposure of human beings or the environment to PCB chemical substances will be insignificant.

Sec. 761.2(jj) "Applicable Analytical Method." We propose the following new definition of this term:

> (jj) "Applicable Analytical Method" means a method (other than the perchlorination procedure) which distinguishes PCB Chemical Substance as defined in section 761.2(t) from all other materials.

The basis for exclusion of the perchlorination procedure is discussed more fully in the attached letter dated March 15, 1976 from J. Coleman Weber of Monsanto to Dr. I. E. Wallen of the EPA.

Section 761(kk) "Technically Qualified Individual." We proposed a new definition for this term with the following wording taken from Section 710.2(aa) of the TOSCA Inventory Reporting Regulations, 42 FR 64576:

> (aa) "Technically Qualified Individual" means a person (1) who because of his education, training, or experience, or a combination of these factors, is capable of appreciating the health and environmental risks associated with the chemical substance which is used under his supervision, (2) who is responsible for enforcing appropriated methods of conducting scientific experimentation, analysis, or chemical research in order to minimize such risks, and (3) who is responsible for the safety assessments and clearances related to the procurement, storage, use, and disposal of the chemical substance as may be appropriate or required

within the scope of conducting the research and development activity. The responsibilities in clause (3) of this paragraph may be delegated to another indiviudal, or other individuals, as long as each meets the criteria in clause (1) of this paragraph.

Section 761.31(f) Hydraulic die casting systems-use. The same considerations that support a use authorization for hydraulic die casting systems apply to other industrial hydraulic systems as well. Therefore, we recommend that all references in this section to the words "hydraulic die-casting system" be changed to "industrial hydraulic system."

Section 761.31(h) Heat transfer systems - use. We recommend this new use authorization as follows:

(h) Heat Transfer Sytems - Use. Heat transfer systems containing PCB mixtures may be used and serviced in a manner other than a totally enclosed manner until five years after the effective date of this rule subject to the following conditions:

(1) One year after the effective date of this rule no heat transfer systems of 500 gallon capacity or less may contain fluid whose PCB mixture volume is greater than 1%.

(2) Two years after the effective date of this rule no heat transfer systems of greater than 500 gallon capacity may contain fluid whose concentration of PCB mixture exceeds 500 ppm.

(3) Ninety days after the effective date of this rule each person who owns a heat transfer system containing residual PCB's above the authorized levels shall report to EPA, and retain records of, the number of such systems he owns, the volume capacity of each such system, and the PCB volume or concentration, as appropriate, of the fluid contained in such systems. This report shall be sent to the Pesticides and Toxic Substances Enforcement Division (EN-342), Environmental Protection AGency, 401 M Street S.W., Washington, D. C. 20460. Each person who owns such a system shall also keep a current record of the dates of each draining or refilling and the measured PCB concentration or volume, as appropriate, of the fluid in the refilled systems on those dates for each system. If any such system is

sold, the transaction and the parties thereto shall be reported to EPA by the Seller. At its discretion, EPA may require the submission of a copy of a person's current record.

(4) Each report submitted to EPA under paragraph (h)(3) of this section shall contain the certification found in §761.31(b)(2).

(5) Each person who owns a heat transfer system containing residual PCB's above the authorized levels shall develop and implement a plan for the control of PCB exposures and contamination in accordance with Annex VII.

Your favorable consideration of the above comments is respectfully requested.

Sincerely,

W. R. Corey
Director, TOSCA Administration

ACM GC8074

March 15, 1976

Dr. E. E. Wallen
Environmental Protection Agency
Office of Toxic Substances
401 M Street S.W.
Washington, DC 20460

Dear Dr. Wallen:

Monsanto has a concern over the validity of the perchlorination technique used by EPA and others to measure and/or confirm polychlorinated biphenyls in environmental materials.

In our investigation of the perchlorination method, we have found that such chemicals as biphenyl, alkylated biphenyl, and many other substituted biphenyls, interfere with the perchlorination technique. It also appears that various petroleum components may interfere. If these chemicals were present in environmental materials that were being tested for PCB's using the perchlorination method, erroneously high PCB concentrations would be reported.

A recent article in the Journal of the AOAC (Vol.58, No.3, 1975) points out two other limitations of the perchlorination procedure:

1. High and variable reagent blanks, which cause erroneously high findings.

2. Formation of bromononachlorobiphenyl, which causes low recoveries.

A copy of the article is attached.

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Since these limitations can lead to significant errors in determining trace levels of PCB's in environmental samples, we suggest that EPA carefully review the validity of the perchlorination technique. Results that have been obtained using this technique may not be valid.

If any other information is needed, please let us know.

Sincerely,

J. Coleman Weber
Manager, Product Acceptability

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cc: Dr. A. C. Trakowski
Environmental Protection Agency

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Limitation on the Use of Antimony Pentachloride for Perchlorination of Polychlorinated Biphenyls

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Division of Chemistry and Physics, Food and Drug Administration, Washington, DC 20204

Two contaminants are present in commercially available antimony pentachloride ($SbCl_5$) used to perchlorinate polychlorinated biphenyls (PCBs) to decachlorobiphenyl (DCB). DCB is found in the $SbCl_5$ perchlorination reaction blank in which no PCBs were added. Bromononachlorobiphenyl (BNCB) is found after use of $SbCl_5$ to perchlorinate PCBs. Levels of DCB found in the $SbCl_5$ reaction blanks from various distributors ranged from 8 to 972 ng DCB/ml $SbCl_5$. The relationship of the formation of BNCB to amounts of various PCB Aroclors perchlorinated is examined.

Polychlorinated biphenyl (PCBs) residues are extracted, cleaned up, and detected by methods similar to those used for organochlorine pesticides. PCB residues are quantitatively determined by comparing the gas-liquid chromatographic (GLC) response of the multicomponent residue and commercial PCBs (Aroclor®) or a mixture of Aroclors producing a GLC response pattern similar to that of the residue (1). This approach is limited because the multicomponent PCB residue may not have the same proportional composition as the Aroclor or Aroclors used as the quantitation reference. Residues can be composed of mixtures of chlorobiphenyl components from more than 1 Aroclor. Metabolic and other environmental factors complicate the description of the PCB residue composition.

There has been considerable work to develop methods to convert the multicomponent PCBs to a single derivative on which to base the residue determination. Procedures have been reported to catalytically dechlorinate PCBs with hydrogen over palladium or platinum to biphenyl, cyclohexylbenzene, and bicyclohexyl (2, 3). A principal disadvantage with that procedure is that the hydrocarbon product is determined with a GLC flame ionization detector, resulting in low sensitivity. Attempts have been made to convert PCBs to the fully chlorinated decachlorobiphenyl (DCB) (3–5). Armour (6) reported optimum conditions for perchlorinating PCBs with antimony pentachloride ($SbCl_5$). The method provides a qualitativ confirmatory procedure for PCB determination The GLC electron capture detector response enhanced because total PCBs are manifested as single peak for DCB. In measuring the sing peak for DCB the analyst is not faced wi analytical judgments such as baseline correctio method of integration, or discrimination betwee PCBs and non-PCB components. However, it necessary to be aware that the various Aroclo give rise to different equivalents of DCB and that the nonchlorinated biphenyl (also use as a fungicide) is perchlorinated by $SbCl_5$ DCB. Nonetheless, using the perchlorinatio derivatization can reinforce the residue val determined by measuring a multicompone PCB residue.

During attempts to apply the perchlorinatio derivatization in determining low residue leve of PCB and make use of the increased electro capture response to DCB, 2 contaminants wer indicated which led to erratic recoveries of DC

Experimental

Reagents and Apparatus

(a) *Antimony pentachloride.*—Hooker Chemic Niagara Falls, NY 14302 (received in glass bo with lead-lined cap); Matheson Coleman & B (MCB), Norwood, OH 45212 (reagent grad B&A (Allied Chemical), Morristown, NJ 07 (reagent grade, 99%); Research Organic-Inorgan Chemical (ROC-RIC), Belleville, NJ 07 (99.99%); and J. T. Baker Chemical, Phillipsbu NJ 08865 (Baker Analyzed Reagent).

(b) *Gas chromatograph.*—Searle-Analytic (D Plaines, IL 60068) Model 5360 with 6' × 4 mm glass column containing 1% OV-101 on 80–1 mesh Chromosorb W (HP). Operating conditions column flow, 60 ml nitrogen/min; column, 202°C detector, 202°C; injector, 225°C; pin-cup dete electron capture detector with titanium ^3H f detector voltage (constant dc) adjusted to ca one-half full scale recorder deflection for 0.7 DCB when full scale deflection is 1×10^{-9} amp

(c) *Mass spectrometer.*—Varian MAT (25 Roc 22, Springfield, NJ 07081) CH5-DF mass spectrom eter (MS) coupled to Varian Aerograph 2740 g

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chromatograph via all-glass system using Watson-Biemann 2-stage separator. GLC operating conditions: 6' × 4 mm id glass column containing 3% OV-1 on 80–100 mesh Chromosorb W (HP); column flow, 60 ml helium min; column 240°C. MS operating conditions: electron energy, 70 ev; emission current, 300 μa; multiplier voltage, 2.2 kv.

Results and Discussion

A peak identical to that of DCB was found in the reaction blank for the Armour perchlorination procedure (6) with the described GLC operating conditions. The identification of DCB was confirmed by GLC-MS of a hexane extract of a hydrolyzed sample of $SbCl_5$ which had not been subjected to the perchlorination procedure. Various quantities (0.2–2.0 ml) of $SbCl_5$ from the 5 commercial sources were examined to determine the presence of DCB. $SbCl_5$ alone was carried through the perchlorination reaction (6) except that no $CHCl_3$ was present with $SbCl_5$ in the reaction vessel. DCB was determined by GLC. Table 1 lists the amounts of DCB found.

After perchlorinating PCBs with $SbCl_5$, a secondary peak with a GLC retention time relative to DCB of 1.31 was observed similar to that reported by Huckins *et al.* (7). This later eluting peak is seen in Fig. 1, the chromatogram from the 0.2 ml $SbCl_5$ (Hooker Chemical) perchlorination of 0.50 μg Aroclor 1221. This peak was found when $SbCl_5$ from each supplier was used. The peak was determined by GLC-MS to be due to bromononachlorobiphenyl (BNCB). BNCB was assumed to be a competing product with DCB arising from a small amount of $SbCl_4Br$ in $SbCl_5$, so parameters relating to possible limitations of the perchlorination procedure were studied. Various quantities (0.5–10 μg) of Aroclors 1221, 1242, 1254, and 1260 in $CHCl_3$ were perchlorinated. Recoveries of DCB and estimates of the relative amounts of BNCB formed are given in Table 2. Calculation of the relative

Table 1. DCB (ng/ml) formed from various amounts of $SbCl_5$

Supplier	$SbCl_5$, ml 0.2	1.0	2.0	Av.
Hooker Chemical	37	46	47	43
MCB	35	42	38	38
B&A	960	1042	913	972
ROC-RIC	12	13	12	12
J.T. Baker	9	7	7	8

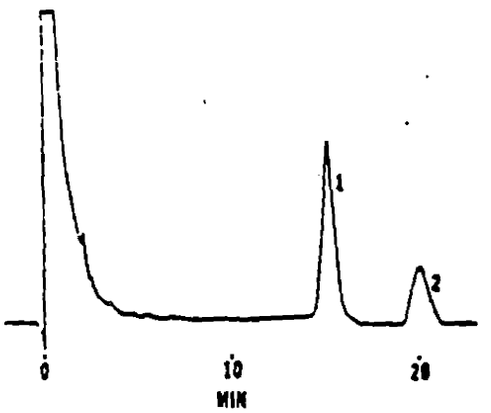

FIG. 1—Electron capture GLC curve from the 0.2 ml $SbCl_5$ (Hooker Chemical) perchlorination of 0.50 μg Aroclor 1221: 0.31 ng equivalent Aroclor 1221 injected. Peak 1 represents 0.81 ng DCB. Peak 2 represents 0.28 ng BNCB.

amounts of BNCB product formed was based on comparison of the electron capture GLC peak height of BNCB with that of a DCB reference.

The amount of DCB determined in the reaction blank was directly proportional to the amount of $SbCl_5$ used (Table 1). This indicates $SbCl_5$ was the source of the DCB and that contamination from other possible sources during the perchlorination was negligible. The procedure for perchlorinating PCBs specifies the use of 0.2 ml $SbCl_5$. $SbCl_5$ producing 5–972 ng $SbCl_5$/ml in the reaction blank would add 0.5–65 ppb. based on a 3 g sample.

DCB produced in the reaction blank was assumed to come from PCB contamination of $SbCl_5$. In an effort to locate the origin of this contamination, $SbCl_5$ bottle closures were investigated. GLC analysis of hexane, in which the plastic caps were soaked for 4 days, did not reveal PCBs. Hooker Chemical, the sole domestic source of $SbCl_5$, supplied $SbCl_5$ in glass bottles with lead-lined caps. This bulk supplier of $SbCl_5$ indicated that the production of chlorine in carbon anode half-cells with linseed oil or other organic binders forms certain organic compounds: however, the destructive oxidative environment in the electrolytic cells would make the production of PCB unlikely as a result of this pathway. On the other hand, antimony metal is commonly obtained as a metallurgical by-product by carbon reduction of its oxide; therefore,

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Table 2. DCB and BNCB from perchlorination of various Aroclors with 0.2 ml $SbCl_5$[a]

Aroclor	Amt, μg	DCB recd, %	BNCB[b] recd, %	DCB + BNCB[b] combined rec, %
1260	10	86	0	86
1254	10	84	0	84
1242	10	88	4	92
1221	10	67	16	83
1260	4	81	0	81
1254	4	83	0	83
1242	4	78	8	86
1221	4	70	18	88
1260	0.5	89	2	91
1254	0.5	78	6	84
1242	0.5	72	10	82
1221	0.5	60	19	79

[a] Hooker Chemical $SbCl_5$.
[b] Quantity calculated by comparison of electron capture GLC response to BNCB vs. response to DCB reference standard.

it is conceivable that PCBs could be associated with the antimony metal employed in the $SbCl_5$ process. No heat transfer systems containing PCBs are used in either the chlorine or $SbCl_5$ production facilities, and $SbCl_5$ does not come into contact with plastics in the manufacturing operation or in shipping containers (Hooker Chemical and Plastics Corp., 1974, private communication).

Two parameters (various quantities and various Aroclors) were studied in relationship to the production of BNCB as a competing product of DCB during the perchlorination of PCBs. BNCB was calculated by comparison of the electron capture GLC response to BNCB vs. the response to DCB. Several factors are considered: (*1*) In this reaction bromination is kinetically favored over chlorination. With perchlorination of lower amounts of PCBs the relative yield of BNCB to DCB is greater because the brominating agent is the limiting quantity in contaminated $SbCl_5$. (*2*) Bromination occurs to a larger degree for a given quantity of the less chlorinated PCBs such as Aroclors 1221 and 1242 rather than for 1254 and 1260. This likely is due to a greater number of reactive sites and less steric hindrance. (*3*) In the range of PCBs perchlorinated (0.5–10 μg) in the above study, it is likely that with lower amounts of PCBs and/or less chlorinated Aroclors the decrease in DCB recovery is principally due to the increase in BNCB formed.

One of the major advantages of perchlorination in determining minute quantities of PCBs is the inherent increase in effective GLC detector response. Contaminated $SbCl_5$, as described here, would preclude its use in many of these cases.

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Analytical Chemistry
Method 73-9
Job No. 1048006

DETERMINATION OF POLYCHLORINATED BIPHENYLS IN THERMINOL 66 BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

SCOPE

This procedure is intended for the determination of polychlorinated biphenyls (PCBs) in Therminol 66.

PRINCIPLE

The procedure is based on the fact that PCBs give a characteristic fingerprint chromatogram when analyzed by EC/GC. The Therminol 66, per se, does not interfere with the measurement but may contain some impurities with electron capture activity. This procedure measures electron capture impurities eluting at the same retention time as PCBs. If absolute confirmation is desired, GC/Mass Spectrometry techniques must be used.

REAGENTS AND EQUIPMENT

1. Hexane - Fisher - "Nanograde", Cat. No. H-300.
2. Usual laboratory glassware.
3. Hewlett-Packard 5750 Research Chromatograph equipped with a ^{63}Ni electron capture detector (pulse - 50 μ sec.).

GAS CHROMATOGRAPHIC CONDITIONS

Column: 2m X 1/4" 4% XE-60 on 80/100 Chromosorb W, H.P.

Temperatures:	Flow Rates:
Injection Port - 190°C	Purge - 10% Argon/Methane 120 ml/min.
Column - 170°C	Carrier - Helium - 60 ml/min.
Detector - 300°C	

PROCEDURE

1. Prepare a calibration curve by injection 2, 4, 6 and 8 μl of a PCB (Aroclor 1242) solution in hexane containing about 0.5 ng/μl. Plot Ng of standard vs the area of the PCB peaks on linear graph paper.
2. Weigh 0.2g of sample to the nearest milligram into a 25 ml volumetric flask, dissolve and dilute to volume with nanograde hexane.
3. Inject a suitable size aliquot of this solution into the chromatograph (~5 μl). To insure accurate data, the sample chromatogram must fall within the range of the calibration standards. Measure the area of the PCB peaks and read the nanograms from the calibration curve.

CALCULATIONS

$$\text{ppm PCBs (as Aroclor 1242)} = \frac{(\text{Nanograms from Curve})(\text{Volume of sol'n, in ml})}{(\text{Injection Volume, in } \mu\text{l})(\text{Sample wt., in gm})}$$

$$= \frac{(\text{Nanograms})(25)}{(\text{Injection Volume})(0.2)}$$

RECOVERY EXPERIMENTS

A typical lot of Therminol 66 was analyzed by the above procedure and a chromatogram which was not typical of PCBs was obtained. Measurement of the area where PCBs would elute gave a value of 17.1 ppm.

This sample was spiked with 25, 50 and 75 ppm PCBs (Aroclor 1242) and the following data obtained.

Therminol 66 + 25 ppm Aroclor 1242	35 - 17* = 18
Duplicate	43 - 17 = 26
Therminol 66 + 50 ppm Aroclor 1242	59 - 14 = 45
Duplicate	64 - 14 = 50
Therminol 66 + 75 ppm Aroclor 1242	78 - 7 = 71

*Background from PCB free Therminol 66

In practice, there will be no way to correct the background interference from the impurities in the Therminol 66 and so numbers below 50 ppm will probably be biased on the high side.

Samples which give chromatograms not typical of PCBs should be reported as none detected, less than the calculated value.

db

Monsanto Industrial Chemicals Co.
Applied Sciences
St. Louis, Mo.

10/73 - O. Hicks, E. S. Tucker

Analytical Chemistry
Method 73-8
Job No. 1048006

DETERMINATION OF POLYCHLORINATED BIPHENYLS IN THERMINOL 55 BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

SCOPE

This procedure is intended for the determination of polychlorinated biphenyls (PCBs) in Therminol 55.

PRINCIPLE

The procedure is based on the fact that PCBs give a characteristic fingerprint chromatogram when analyzed by EC/GC. The Therminol 55 does not interfere with the measurement. This method measures electron capture active materials eluting at the same retention time as PCBs. If absolute confirmation is desired, GC/Mass Spectrometry techniques must be used.

REAGENTS AND EQUIPMENT

1. Hexane - Fisher - "Nanograde", Cat. No. H300.
2. Usual laboratory glassware.
3. Hewlett Packard 5750 Research Chromatograph equipped with a ^{63}Ni electron capture detector (pulse - 50 μ sec.).

GAS CHROMATOGRAPHIC CONDITIONS

Column: 2M X 1/4" 4% XE-60 on 80/100 Chromosorb W, H.P.

Temperatures: Injection Port - 190°
Column - 170°
Detector - 300°

Flow Rates:
Purge 10% Argon/Methane - 120 ml/min.
Carrier - Helium - 60 ml/min.

PROCEDURE

1. Prepare a calibration curve by injecting 2, 4, 6, and 8 μl of a PCB (Aroclor 1242) solution in hexane containing about 1 ng/μl. Plot ng of standard vs the area of the PCB peaks on linear graph paper.
2. Weigh 0.2g of sample to the nearest milligram into a 10 ml volumetric flask, dissolve and dilute to volume with nanograde hexane.
3. Inject a suitable size aliquot of this solution into the chromatograph (~5μl). To insure accurate data, the sample chromatogram must fall within the range of the calibration standards. Measure the area of the PCB peaks and read the nanograms from the calibration curve.

CALCULATIONS

$$\text{ppm PCBs (as Aroclor 1242)} = \frac{(\text{Nanograms from curve})(\text{Volume of sol'n, in ml})}{(\text{Injection volume, in } \mu\text{l})(\text{Sample weight, in gm})}$$

$$= \frac{(\text{Nanograms})(10)}{(\text{Injection volume})(0.2)}$$

RECOVERY

0.2g Samples of Therminol 55 were spiked in duplicate with 25, 50 and 75 ppm of Aroclor 1242 and 93.4 ± 5.3% recovery was obtained.

db

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St. Louis, Mo.

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ANALYTICAL TEST METHODS

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Burning Waste Chlorinated Hydrocarbons in a Cement Kiln

Technology Development Report EPS 4-WP-77-2
Water Pollution Control Directorate
March 1977

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ACP CCOCET

BURNING WASTE CHLORINATED HYDROCARBONS IN A CEMENT KILN

by

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Petroleum and Industrial Organic Chemicals Division
Water Pollution Control Directorate
Environmental Protection Service
FISHERIES AND ENVIRONMENT CANADA

Report No. EPS 4-WP-77-2
March 1977

ADM CCECCE

REVIEW NOTICE

This report has been reviewed by the Water Pollution Control Directorate, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

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ABSTRACT

An experimental program was carried out in 1975/76 at the St. Lawrence Cement Co., Mississauga, Ontario in which waste chlorinated hydrocarbons, containing up to about 46 weight percent chlorine, were burned in a rotary cement kiln. The chlorinated hydrocarbons were burned in three distinct phases of increasing difficulty of combustion. Materials burned included mixtures of ethylene dichloride, chlorotoluene and up to approximately 50 percent polychlorinated biphenyls (PCB).

These materials were destroyed in the cement kiln with at least 99.98 percent efficiency in all cases. Emissions of high molecular weight chlorinated hydrocarbons were not detected. Three light chlorinated hydrocarbons, dichloromethane, chloroform and carbon tetrachloride, were found in the emissions in the part per billion or lower range. The quantity of precipitator dust requiring disposal, as well as emissions of particulate matter, increased during the test.

The chlorine input from the chlorinated hydrocarbon waste was up to about 0.8 weight percent relative to clinker and this effectively reduced the alkali concentration of the clinker in direct stoichiometric proportion. A reduction in fossil fuels used while burning chlorinated hydrocarbons was noted.

RÉSUMÉ

Au cours d'une série d'expériences réalisées en 1975-1976 à la St. Lawrence Cement Co., à Mississauga (Ontario), on a brûlé, dans un four rotatif à ciment, des hydrocarbures contenant au poids jusqu'à 46 p. 100 de chlore lié. La combustion s'est faite en trois phases de difficulté croissante. Les substances consumées comprenaient des mélanges de dichlorure d'éthylène et de chlorotoluène ainsi que d'autres atteignant près de 50 p. 100 de biphényles polychlorés (BPC).

Dans tous les cas, la combustion a eu un rendement d'au moins 99,98 p. 100. On n'a décelé aucune émission d'hydrocarbures chlorés à poids moléculaire élevé. Par contre, on a identifié trois hydrocarbures chlorés légers, soit le dichlorométhane, le chloroforme et le tétrachlorure de carbone, en concentrations inférieures à une partie par milliard. La quantité de poussières accumulées dans les précipitateurs et qu'il fallait éliminer, ainsi que les émissions de particules, ont augmenté au cours des expériences.

La portion de chlore provenant des déchets d'hydrocarbures chlorés a atteint environ 0,8 p. 100 du poids des clinkers, ce qui a réduit, en raison stoechiométriquement directe, la teneur en alcali de ces derniers. On a également remarqué une consommation réduite de fuels fossiles pendant la combustion des hydrocarbures chlorés.

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EXECUTIVE OUTLINE

Experiments using chlorinated hydrocarbon wastes in the manufacture of cement appear to have transformed a difficult waste disposal problem into a solution which is not only economically and environmentally satisfactory, but has a beneficial effect on the quality of the cement.

Safe disposal of the large volumes of the chlorinated hydrocarbon wastes which are generated in Canada each year is a difficult environmental problem. It is estimated conservatively that Canada generates some 25-30 million pounds annually of these highly toxic and persistent wastes. This figure does not include many toxic compounds such as insecticides and polychlorinated biphenyls (PCB's).

Environmentally safe disposal is difficult and expensive. Disposal on land, or underground, requires special and expensive precautions to prevent leaching into waterways. The favoured method of disposal, incineration with recovery of hydrogen chloride, can be very costly. Without recovery, scrubbing equipment is required to remove hydrogen chloride from the products of combustion to control its emission. This, in turn, usually necessitates a satisfactory disposal method for the scrubber liquid. Valuable fuel must be burned to maintain combustion while incinerating chlorinated hydrocarbon wastes, as extremely high temperatures with long residence times are required for their thermal destruction.

A long high-temperature flame is required in a cement kiln to achieve the desired product quality. During normal operations, the thermal conditions that are necessary effectively consume the toxic materials. The kiln also contains a considerable quantity of lime and thus has an intensive "scrubbing" action.

Recovery and re-use of hydrocarbon wastes is not always felt to be economic. The recycling of solvents is practiced when it is economically and technically feasible. However, this entails the control of segregation, storage, collection and ultimate treatment of the various hydrocarbon streams.

The report strongly urges that combustible liquid wastes, many of which are persistant environmental contaminants, be combined by means of a

single economical recovery system which would collect and later use the wastes as supplementary fuel for cement manufacture.

The experiments described in this report were monitored by the Department of Fisheries and Environment, the Ontario Ministry of the Environment, the United States Environmental Protection Agency, and the Ontario Research Foundation.

For these experiments, industrial chlorinated hydrocarbon wastes including polychlorinated biphenyls (PCB's) were burned during the commercial manufacture of cement.

This not only utilized the thermal value of the wastes, with a reduction in oil consumption, but the results showed that almost all the toxic wastes were completely destroyed in the kiln. Emissions of toxic materials into the atmosphere were negligible.

Calcium chloride is often used in cement manufacture to reduce the alkali content of the product. The only apparent effects that the experimental burn had on the quality of the cement were the beneficial effects due to the incidental addition of chloride ion.

SUMMARY

Chlorinated hydrocarbon wastes were burned in a carefully controlled experimental trial as a partial fuel at the St. Lawrence Cement Co., Mississauga, Ontario. The experiment was conducted to determine whether chlorinated hydrocarbon wastes could be burned in a cement kiln without adverse effects on air pollution levels.

The wastes used included a variety of chlorinated hydrocarbons in the series of program phases designed to progress from easily combusted chlorinated hydrocarbons to those which are combusted only with difficulty. The last phase consisted mainly of polychlorinated biphenyl wastes. These materials were processed and formulated from chemical wastes as required for the different phases and supplied by Chemtrol Pollution Services Inc.

Atmospheric emission measurements were made before, during and after the burning of each blend of chlorinated waste. Two methods of emissions sampling were used during each phase, the method normally used for measuring emissions of particulate matter, and a sampling train designed specially for determining emissions of organic material. All samples from both systems were analyzed for unburned chlorinated hydrocarbons. It was concluded that the combustion efficiency was at least 99.986 percent for the chlorinated hydrocarbons. Approximately 50 ppb of volatile low molecular weight compounds were found in the emission samples. There were no detectable quantities of high molecular weight chlorinated compounds in the stack gases.

A mass balance was carried out on chlorine and potassium. This showed that the chlorine input as chlorinated hydrocarbon was completely reacted with the process solids.

The alkali content of the clinker showed a reduction which corresponded exactly with the quantity of chlorine input to the system. This agreement further confirms the data from emission testing and the mass balance.

While burning chlorinated hydrocarbons with approximately 40 percent chlorine, a decrease in oil consumption equivalent to 65 percent of the Btu content of the chlorinated hydrocarbons was obtained.

The only differences in the quality of clinker produced while burning chlorinated hydrocarbons were the beneficial effects which were expected through the reduction in alkali content.

It was concluded that chlorinated hydrocarbon wastes may be used in cement kilns, replacing other forms of chlorine used for reduction of alkali content. A small proportion of fossil fuel required for cement manufacture is conserved through use of these materials. Burning chlorinated hydrocarbon wastes is considered a valuable means of destroying persistent and toxic forms of pollutants while recovering useful heat values.

RECOMMENDATIONS

The experiments have shown that there is virtually no adverse effect on air pollution levels by burning chlorinated hydrocarbon wastes in a cement kiln. These wastes include polychlorinated biphenyls and other materials which are difficult to destroy. When other methods, such as incineration, are used hydrogen chloride and chlorine may be emitted and, if the incinerator operation is poorly controlled, uncombusted material may be released into the environment.

The following recommendations are the outcome of the present report:

(1) Burning chlorinated hydrocarbon wastes in a cement kiln is considered a valuable means of destruction of persistent and toxic materials which are members of this family of compounds. Since flame temperatures and retention times are similar for all cement plants regardless of type of kiln or fuel used, chlorinated hydrocarbons should be destroyed in any cement kiln. The feasibility of doing so in a particular kiln installation can be determined by a technical and economic review.

(2) Due to lack of familiarity with organic chemicals, it is considered essential that instructions on safe handling procedures be given to cement industry personnel.

(3) Since problems such as precipitation, solidification, heat or gas release can arise through mixing incompatible waste materials in storage tank, it is considered advisable to obtain such materials from one reliable source of supply at any given time.

LIST OF ABBREVIATIONS

APCD	Air Pollution Control Directorate (EPS)
BLA	Baseline A, designates emission tests before waste burns
BLB	Baseline B, designates emission tests after waste burns
DCM	Dichloromethane
EC	Electron capture (detector)
EPA	Environmental Protection Agency (U.S.)
EPS	Environmental Protection Service (Fisheries and Environment Canada)
FID	Flame ionization detector
GC	Gas chromatography
MOE	(Ontario) Ministry of the Environment
MS	Mass spectrometry
ORF	Ontario Research Foundation
PCB	Polychlorinated biphenyl
SLC	St. Lawrence Cement Co.
TRW	TRW Systems Group
T1, T2, T3	Test one, Test two, Test three
WBA	Waste Burn A (chlorinated aliphatics)
WBB	Waste Burn B (WBA plus chlorinated aromatics and alicyclics)
WBC	Waste Burn C (WBB plus polychlorinated biphenyls)
XRF	X-ray fluorescence

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1 INTRODUCTION

In Canada each year an estimated 25-30 million pounds of chlorinated hydrocarbon wastes require disposal or destruction, 17-20 million pounds being generated in Ontario [1]. These figures are based on 5-6% of annual production and may be conservative. Experience in Europe indicates that 10% of production is a more reliable estimate of waste material.

There are waste streams from plants manufacturing, processing, or using chlorinated hydrocarbons which must be disposed of, the method of disposal frequently being incineration. Chlorinated wastes other than those directly from chemical plants also present a serious disposal problem. Among these latter chemicals are polychlorinated biphenyls (PCB's) and insecticides which may require disposal.

Many of these wastes are toxic and persistent, and all pose a serious disposal problem. Among the methods presently used are incineration and land disposal. Incineration with recovery of hydrogen chloride can be costly. Without recovery, combustion gases must be scrubbed, thereby generating a liquid waste requiring disposal. Both incineration methods require additional fuel. Deep welling and other similar methods of disposal are environmentally unsound because of the risk of water contamination.

In cement manufacture, the kiln operates at higher temperatures and for longer residence times than those used in incinerators for destruction of these waste materials. It is also common practice in the cement industry to add chlorides to the kiln to reduce the alkali concentration of the final product. Use of chlorinated hydrocarbon wastes in a cement kiln would provide useful recovery of chlorine and energy and, at the same time, solve a serious disposal problem.

The present research program was carried out to determine whether waste chlorinated hydrocarbons can be burned in a rotary cement kiln without causing adverse air pollution. The approach taken was to analyse stack emissions for uncombusted chlorinated hydrocarbon. A material balance on chlorine was undertaken to confirm the emission findings.

2 CEMENT MANUFACTURE

2.1 General Principles

While a variety of raw materials may be used in cement manufacture, materials containing calcium, silicon, aluminum and iron without an excess of certain other elements are required. These materials are ground to a fine powder called raw meal, the chemical composition of which is carefully controlled by proper blending of the various materials. Normally, blending is achieved by grinding all the raw materials together (intergrinding). Raw meals required for wet and dry processes are similar except that the raw meal for the wet process is in the form of a slurry containing approximately 35% water, while raw meal for the dry process contains less than 0.5% water.

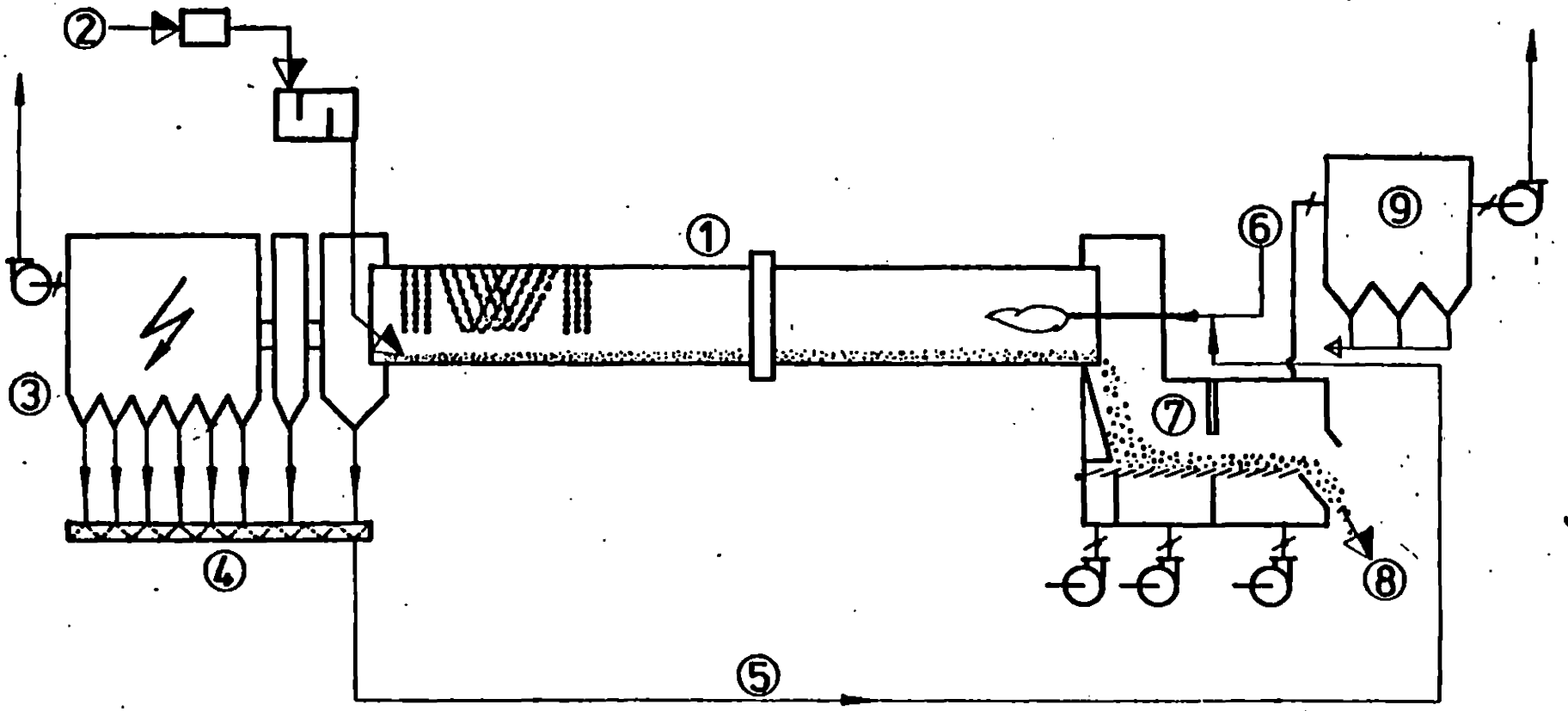
The raw meal is fed into the kiln (see Figures 1 and 2) and is burned in the kiln to produce an intermediate product called clinker.

The kiln slopes towards the burning zone and rotates slowly, causing the raw material to gradually move into the burning zone. Reactions which occur during gradual heating in the kiln are: evaporation of free water, evolution of combined water, evolution of carbon dioxide from carbonates, and combination of lime with silica, alumina and iron to form the desired compounds in the clinker. These reactions require a final material temperature of 1450°C (2650°F). Four main compounds are present in Portland cement clinker:

Name Of Compound	Chemical Formula	Common Abbreviations Used In The Cement Industry
Tricalcium Silicate	$3\ CaO \cdot SiO_2$	C_3S
Dicalcium Silicate	$2\ CaO \cdot SiO_2$	C_2S
Tricalcium Aluminate	$3\ CaO \cdot Al_2O_3$	C_3A
Tetracalcium Aluminoferrite	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

Minor compounds are also formed in clinker, commonly magnesia (MgO), potassium sulfate (K_2SO_4) and sodium sulfate (Na_2SO_4).

Traces of other elements present in either the raw materials or fuel are also found in clinker. Upon leaving the kiln, the clinker is



1-KILN
2-SLURRY FEED
4-PRECIPITATOR DUST SCREW
3-PRECIPITATOR
5-DUST RETURN
6-FUEL
7-CLINKER COOLER
8-CLINKER
9-FILTER

WET PROCESS KILN

FIGURE 1.

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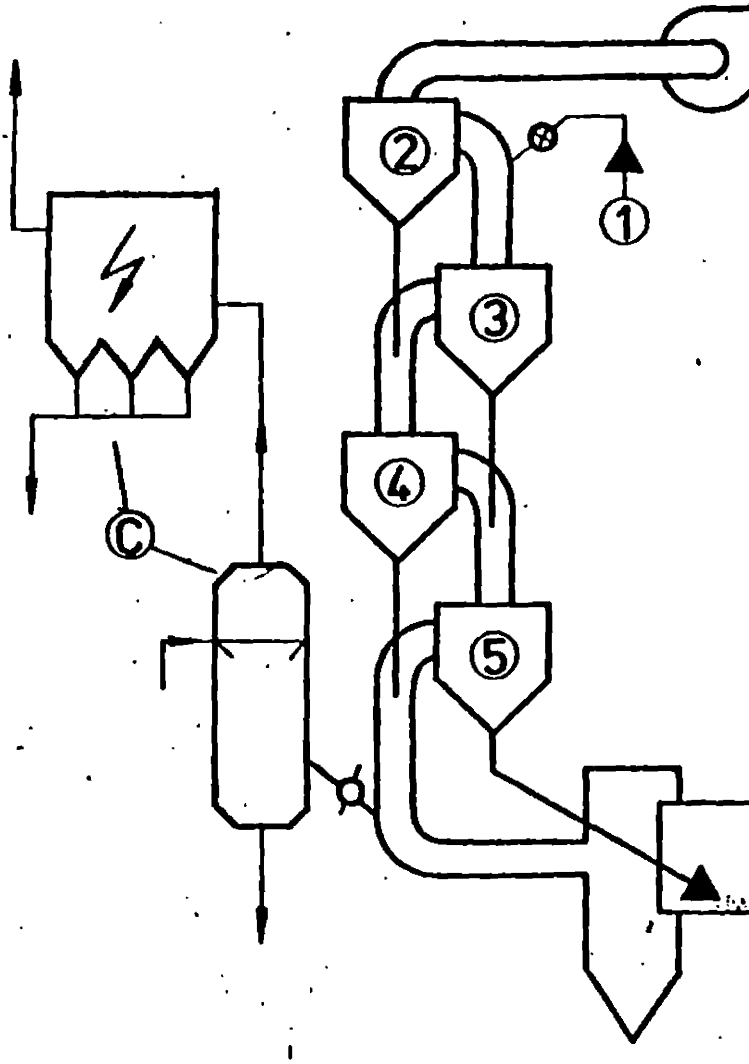

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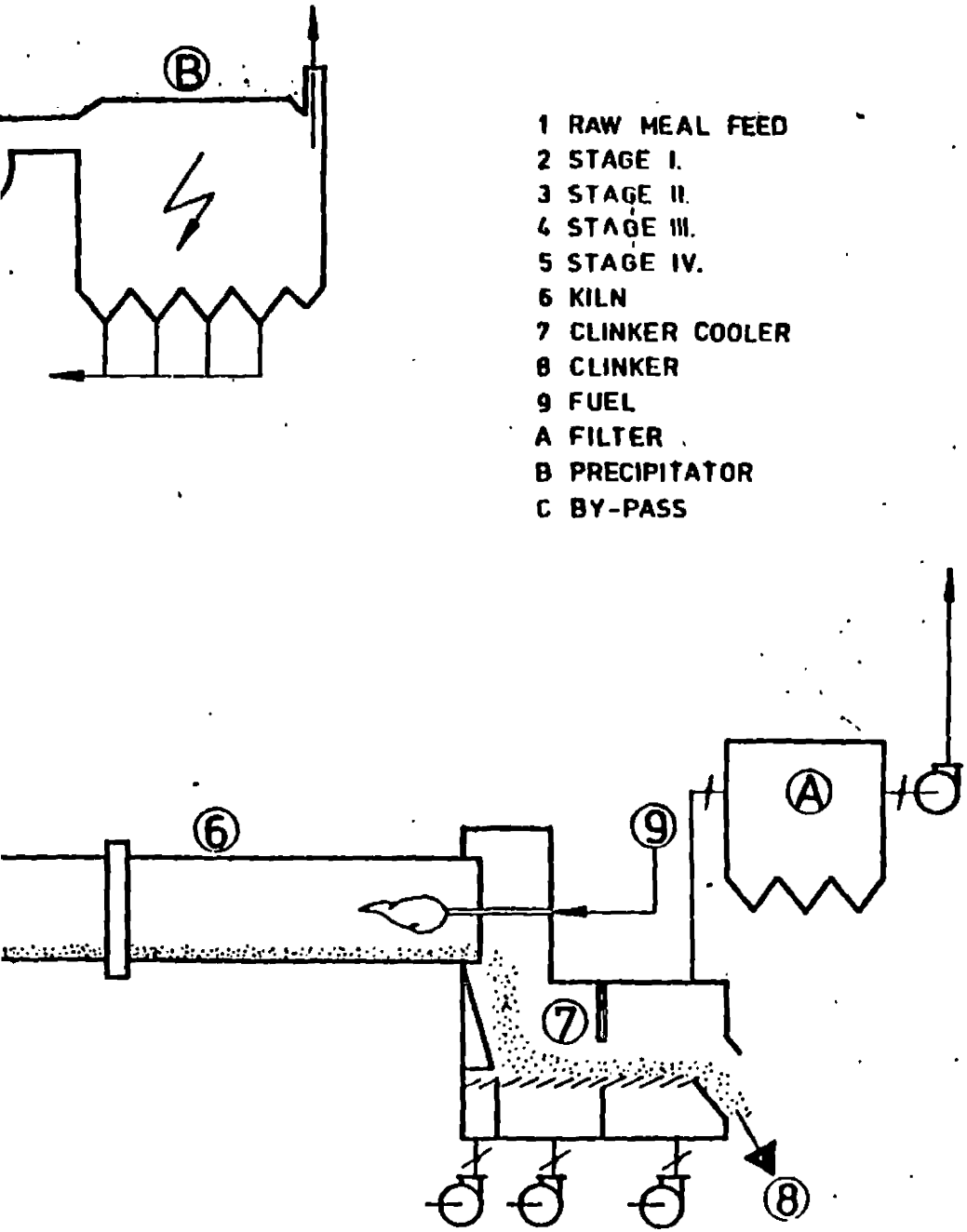
SCRUBBERS

DRY



PROCESS KILN

FIGURE 2.

rapidly cooled to avoid undesirable crystal forms of the above compounds. After cooling, the clinker is ground and blended, normally by intergrinding, with gypsum to a fine powder. The final product, called Portland cement, is the basic ingredient of concrete.

In the burning process, considerable CO_2 is driven from the raw meal. Any elements not driven off are increased in the clinker in proportion to the quantity of CO_2 evolved. Throughout most of this report, the analyses have been reported on a natural basis, i.e. reported results are actual concentrations present in samples as received. In some cases, results have been reported on an ignited basis, i.e. on CO_2 free basis, and have been indicated as such in the report.

2.2 Effect of Alkalies

In cement manufacture, reference to alkalies implies potassium and sodium oxide (K_2O and Na_2O). Both alkalies are frequently combined and reported as equivalent Na_2O for purposes of specification. The raw materials at St. Lawrence Cement are such that Na_2O is low and practically constant (see Table A.10). For this reason, only potassium oxide (K_2O) is considered in detail in this report.

The effect of alkalies on cement quality has been well documented [2, 3, 4]. While some alkali may be desirable for early strength development [3], an excess can be problematic. The most extensively reported of these problems is the alkali-aggregate reaction [5, 6]. Certain glassy silicates and some dolomites react slowly with alkalies and cause expansion and disruption of concrete. It has been found by experience that cement containing less than 0.60% total alkalies reported as Na_2O performs satisfactorily with such aggregates. This specification is imposed with sufficient frequency in the United States that it is found as an optional specification under ASTM C-150 [7]. Strength attained and setting characteristics are also related to the alkali concentration of the cement [3, 8].

It is common practice in the cement industry to add chlorides such as calcium chloride or waste hydrochloric acid to the raw meal to reduce alkalies [9, 10]. Alkalies are normally present as sulphates which at kiln operating temperatures are not readily volatilized, but are retained in the clinker. Alkali chlorides are volatile at normal kiln operating

temperatures. These are evolved from the material in the kiln and carried in the gas stream to the precipitator. The high alkali dust from the precipitator can then be discarded.

2.3 The St. Lawrence Cement Co.

The St. Lawrence Cement Co., Mississauga Plant, has a nominal production capacity of 1,750,000 short tons per year. The company operates two wet processes and one dry process suspension preheater kiln. General information on the company and the plant has been published in two articles [11, 12].

2.3.1 Relevant unit processes - wet process kiln

Each of the two wet process kilns are dumbell-shaped Allis Chalmers kilns 402' long with a diameter of 11'6", having nominal capacity of 1050 short tons per day (see Figure 1). The chain system in the drying zone has 57 tons of loose hung carbon steel chains with a radiation curtain at the front (flame end) of stainless steel chains. The chain system extends through 87' of kiln length. The slurry feed system is a bucket wheel conveyor with a variable speed drive taking slurry from a constant level box. Gases from each kiln (maximum capacity 150,000 CFM at 450°F) pass through a six-section electrostatic precipitator. Gases from the precipitators are exhausted via a common stack 554' in height with 13' exit inside diameter. No. 6 fuel oil is burned in a single burner at the centre of the burner pipe. For the test, chlorinated hydrocarbons were fed just above and to one side of centre using different size nozzles for proper atomization at different flow rates. A detailed description of the chlorinated hydrocarbon system is given in Appendix E.

2.3.2 Relevant unit processes - suspension preheater kiln

The kiln (Figure 2) is a 17' x 276' Traylor unit normally fired through three nozzles with No. 6 fuel oil. For the test, chlorinated hydrocarbons were injected via a nozzle at the centre of the triangle formed by the three oil nozzles.

The suspension preheater (Figure 3) consists of a system of cyclones through which hot exit gases from the kiln are drawn by a fan. The raw meal passes through the system in counterflow to the gas. Kiln feed is introduced into the duct between the first and second stage cyclones. It is swept with the hot exhaust gases into the uppermost (Stage 1) cyclones

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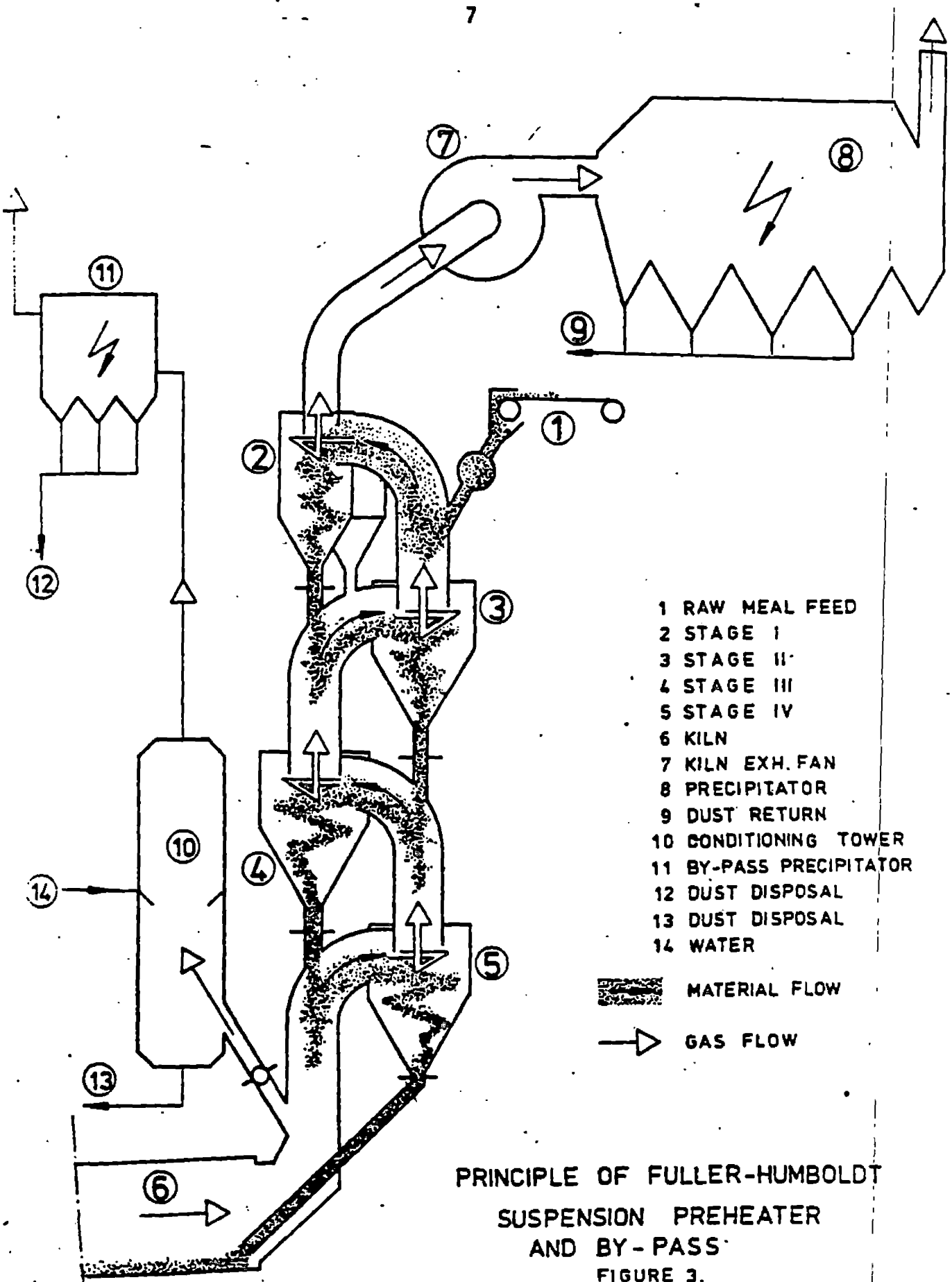

PRINCIPLE OF FULLER-HUMBOLDT SUSPENSION PREHEATER AND BY-PASS

FIGURE 3.

where gas and material are separated. The raw feed from the cyclone drops into the duct between the second and third stage cyclones and is again suspended and separated. This procedure, being swept up with hot gases and then being dropped into the stream entering the next lowest stage, is repeated in Stages III and IV before the partially calcined feed enters the kiln. The average retention time of the system is approximately 30 seconds. A detailed description of the Humboldt preheater has been given by G.A. Schroth [13] from which article these notes have been prepared. The raw material entering Stage I is preheated to approximately 300°C (600°F), while the gas temperature drops from 530°C (990°F) to 340°C (650°F). At each stage, corresponding heat exhanges occur such that the material enters the rotary kiln at approximately 800°C (1475°F) having been partially decarbonated. The gas temperature at the point of exit from the kiln into the preheater is 1040°C (1900°F) to 1090°C (2000°F). The St. Lawrence Cement Co. preheater is a dual Fuller-Humboldt unit with four stages in each.

The alkali bypass system (Figure 4) is an important unit in relation to this study. In common with other plants using suspension preheater systems, special measures have to be taken to reduce the buildup of chlorides and alkalies in the system. At the St. Lawrence Cement Co. plant, a system is in use where a fraction of the kiln exhaust gases is removed from the preheater and passed through a conditioning tower. In the conditioning tower, water is sprayed into the gas stream to lower the temperature and condition the gases for precipitation. Concurrently, the gas velocity is reduced, since the cross section of the tower is greater than that of the bypass duct. The net effect of cooling and velocity reduction is to divide the particulate matter carried in the gas stream into two fractions. One fraction, of lower alkali content, is separated in a conditioning tower and returned to the raw meal silos. The other fraction, of higher alkali content, is collected in an electrostatic precipitator, pelletized and discarded.

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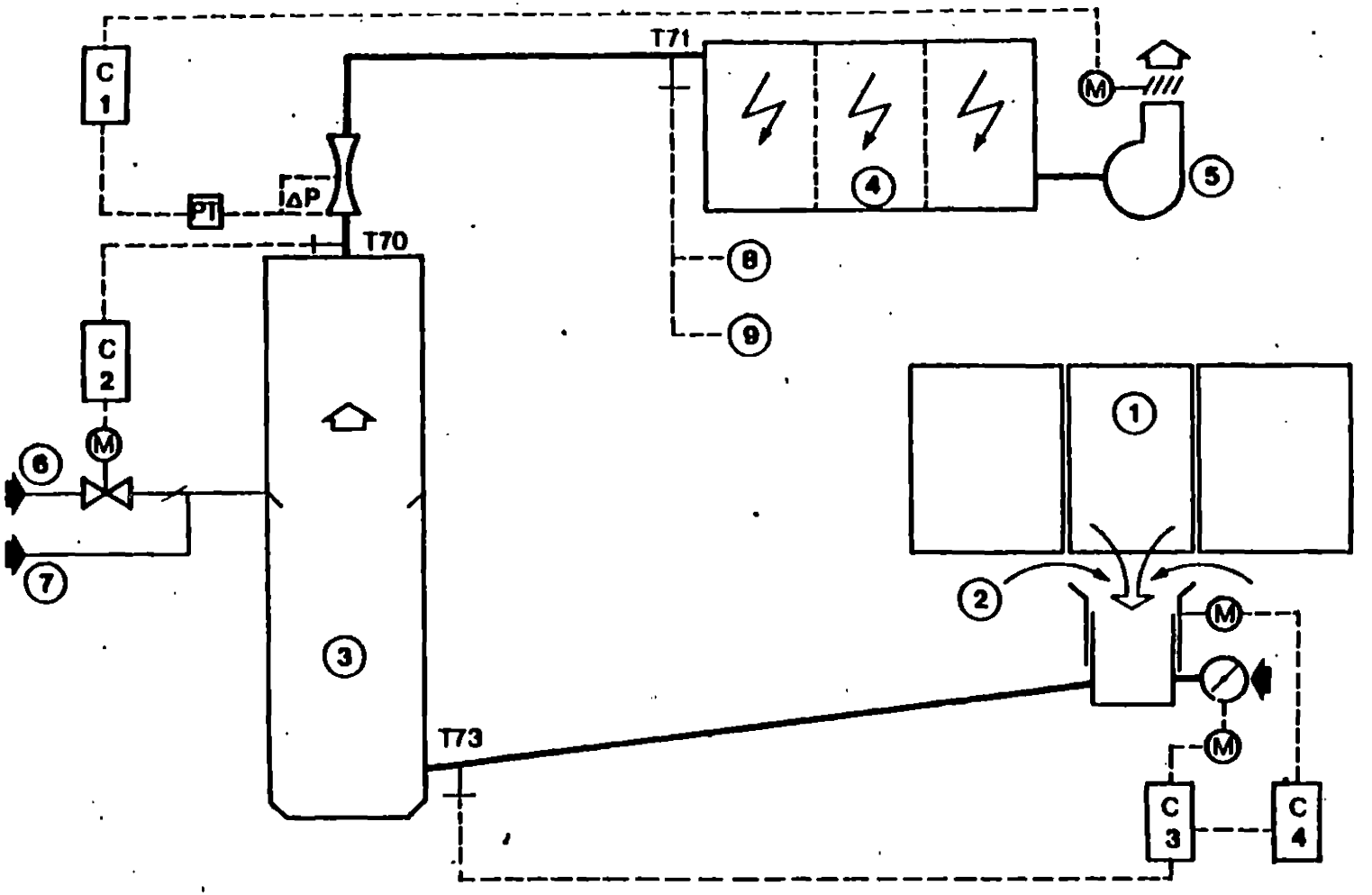

ALKALI BY-PASS

FIGURE 4

1 PREHEATER TOWER BY-PASS HOOD
2 QUENCH AIR
3 CONDITIONING TOWER
4 PRECIPITATOR
5 EXHAUST FAN
6 WATER
7 AIR
8 650°F CAT OFF CONTROL
9 AIR QUENCH NOZZLE CONTROL (450°F)
C CONTROLLER
PT PRESSURE TRANSMITTER
M MODULATOR

3 CONSIDERATIONS AT THE PROGRAM PLANNING STAGE

The history of suspension preheater kilns in the United States indicates a trend to this system [14]. Thirteen preheater kilns were installed in the years 1953-1955. Because of inadequate knowledge about the basic process and effects of raw materials on this system, numerous operating difficulties were encountered. These difficulties, possibly combined with emphasis on alkali reduction, caused the shut down of six of these units. From 1956 to 1969, only two suspension preheater kilns were installed, one of which has since been shut down. However, with increasing fuel costs and emphasis on energy conservation, 22 suspension preheater kilns have been commissioned since 1970. Another indication of this trend is that five of the eleven new kilns installed in 1975 were preheater-rotary kilns [15]. In addition, three existing rotary kilns were converted to suspension preheater units. All five kilns planned for completion in 1976 will be preheater kilns. While the situation in Canada is similar, there are fewer plants and such trends are difficult to follow.

Any study concerned with future use of the technology developed must take into consideration the suspension preheater kiln. Flame characteristics are identical in all cement kiln systems, hence, demonstration that destruction of chlorinated hydrocarbons occurs in one cement kiln implies destruction in all cement kilns. Reduction of alkalies in a straight rotary kiln system by addition of chlorides (calcium chloride and hydrochloric acid) has been extensively demonstrated.

It was decided to conduct the experiment in the suspension preheater kiln despite knowledge that the preheater is prone to plugging problems at high alkali chloride levels.

The primary purpose of the study was to determine whether chlorinated hydrocarbons were destroyed in a cement kiln. It was considered desirable to conduct the experiment in stages with materials of increasing difficulty of destruction. After each stage, normal operation was resumed, thus giving time to analyze samples in order to determine that no waste chlorinated hydrocarbons were emitted. For this study, it was agreed to use four different formulations of industrial chlorinated wastes:

1) aliphatics;
2) aromatics;
3) aliphatics plus aromatics and alicyclics; and,
4) aliphatics, aromatics, alicyclics and large complex molecules such as polychlorinated biphyenyls (PCB's).

Generally these are filtered, processed and blended to obtain specific formulations for control of energy value, chlorine content and viscosity.

4 TRIAL ON THE SUSPENSION PREHEATER KILN

The first phase of the trial was done in the suspension preheater kiln to determine whether alkali reduction could be accomplished on this unit by burning of chlorinated hydrocarbons. Reduction of alkalies by addition of chloride is achieved by increasing the amount of alkali volatilization. Alkali carbonates and chlorides are almost entirely volatilized at the normal operating temperature of the kiln. Alkali sulphates and alkalies which are complexed in the calcium silicate and aluminate structures are preferentially retained in the clinker.

The addition of chloride ion causes formation of the easily volatilized alkali chloride. Intimate mixing of hot kiln gases and countercurrent cooler raw meal causes alkali chlorides to condense on the raw meal thereby being returned to the kiln. Alkali chlorides are trapped between the burning zone of the kiln (volatilization) and the bottom stage of the preheater (condensation), causing increasing concentrations in the gas stream. At high concentrations of alkali chlorides, sufficient quantities condense in Stages III and IV of the preheater to cause plugging of this system. To alleviate this situation, the bypass is used to withdraw a fraction of the gases leaving the rotary kiln and with these gases a fraction of the alkali chlorides. As greater quantities of alkali chloride are volatilized in the kiln, high withdrawal rates through the bypass are required.

Samples of the raw meal entering the kiln from the preheater can be taken to monitor the alkali chloride concentration. Prior to the burn, it was estimated that equilibrium alkali chloride concentration at this point would be reached in approximately two hours.

Gases exhausted via the bypass have a temperature of approximately 1000°C (1830°F). To cool these gases, they are mixed initially with ambient air, then passed through a conditioning tower in which water spray is used for further cooling and conditioning of the gases. In the conditioning tower, the coarser fraction of the dust, which has the lower alkali concentration, settles to the bottom of the conditioning tower and is returned to the process. The finer fraction, which has the higher alkali concentration, is carried with the gas stream to the bypass precipitator. Dust collected from this precipitator is discarded.

Initially, attempts to operate the bypass at the level required to compensate for addition of chlorides resulted in high emission rates of particulate matter. Weighings of materials showed that 50-60 tons per day of dust were collected in the precipitator (normally 6-10 tons per day), while 4 tons per day settled in the conditioning tower (normally 20 tons per day). The reversal of solids fraction removed in the two units and the larger amount of material carried forward to the electrostatic precipitator was attributed to the increased quantity of ambient air used for cooling the bypass stream. This increased gas flow gave higher velocities in the conditioning tower, lowered its settling efficiency and resulted in particulate entrainment in the gas stream.

The burning of chlorinated aliphatic material was begun on June 3, 1975 with a mixture having a specific gravity of approximately 1.2 and a chlorine content of about 55% w/w.

On June 5, the bypass duct between the kiln and the conditioning tower was plugged. The trial was suspended while the duct was cleaned. A second attempt was begun on June 10 using the same parameters used in the June 3 trial. On June 13, similar buildup again caused the bypass to fail. It was apparent that the addition of chlorides to the suspension preheater kiln could not be done without major portions of the bypass system being rebuilt.

Due to high particulate emissions, plugging of the bypass system and the cost of the equipment changes envisaged to alleviate the short comings, it was decided to continue the trial in one of the two existing wet kilns.

The trial on the dry process kiln did show, however, that chlorinated hydrocarbons were destroyed in this kiln. Chlorinated hydrocarbons used are volatile at temperatures found in Stage IV (980°C), and could not have condensed upon the material. The expected increase in chlorine concentration of Stage IV dusts was confirmed by analyses (Table 8.4). Equilibrium concentrations of chloride at Stage IV were obtained in approximately four hours (Appendix B). Some slight alkali reduction was apparent. During the five days on which chlorinated hydrocarbons were burned, the raw meal feed K_2O on ignited basis averaged 1.47%, while the average clinker K_2O was 1.27%. With the same quantity

of gases being removed by the bypass, but without addition of any chlorinated material, the raw meal feed contained on average 1.44% K_2O and the clinker contained on average 1.29% K_2O. While the difference is slight, the duration of the experiment was short.

Complete details and analytical results from the experiment on the suspension preheater kiln are given in Appendix B.

5 TRIAL ON THE WET PROCESS KILN

5.1 Discussion

The test program for this section of the study was designed to determine if kiln emissions contained any chlorinated organic compounds when chlorinated organic wastes were burned as supplemental fuel to reduce the alkali content of the clinker.

From a knowledge of kiln zone temperatures and gaseous product retention times in the kiln, it was anticipated that combustion of the waste chloride fuel would produce predominantly CO_2, H_2O, HCl (hydrochloric acid), Cl^- (chloride ion) and a negligible amount of free Cl_2 (chlorine gas).

$$H_2O + Cl_2 \rightleftharpoons 2HCl + \tfrac{1}{2}O_2$$

$$Kp = \frac{(P_{HCl})^2 \quad (P_{O_2})^{\frac{1}{2}}}{(P_{H_2O}) \quad (P_{Cl_2})}$$

= 15 at 1000°C (1832°F)
= 68 at 1500°C (2732°F)
=150 at 1500°C (3452°F) [28].

This shows that amount of free chlorine gas decreases with:

a) increase in temperature;
b) increase in water vapor content;
c) decrease in oxygen content; and,
d) decrease or removal of hydrochloric acid.

The hydrochloric acid will react and the chlorine will be retained as alkali chlorides in the process solids. From a knowledge of orthodox incineration systems, the combustion conditions in a cement kiln were expected to provide a very favourable means for the destruction of waste chlorinated hydrocarbons. In order to determine the effect, if any, of burning waste chlorinated organic material on air quality, emissions from the kiln were monitored before, during and after three separate periods of burning the supplemental waste fuels. Prior to each sampling period, emissions were checked for the presence of

HCl and Cl_2 with detector tubes at sensitivity limits of 2 ppm and 0.5 ppm, respectively.

- A mass balance for chlorine was carried out by analyzing all feed and process samples collected during each waste burn for this element, to confirm the emission data.

Prior to the trial on the wet process kiln, light oil was put into the chlorinated feed system for the purpose of calibrating and testing the proportioning and metering devices. Some light oil remained in the system when chlorinated aliphatic material was received, causing the chloride content to increase as the test progressed. While emissions were tested, chlorinated aliphatic material was burned at different rates while attempting to compensate for the changing chloride content, the rates being equivalent to:

October 28, 1975, 0.31% chlorine relative to clinker;
October 29, 1975, 0.32% chlorine relative to clinker; and
October 30, 1975, 0.63% chlorine relative to clinker.

Due to excessive quantities of chlorine input, a ring was formed, which required a kiln shutdown for its removal. A ring is caused by the buildup of material on the inside of the kiln to such an extent that it restricts the flow of process materials.

Due to production scheduling, the delay caused by the shutdown made it necessary to drop the burning of aromatics alone and immediately progress to the mixture of aromatic and complex molecules. The conductivity of this latter material was too low (0.3×10^{-6} mhos) for the magnetic flow meter to function properly.

Control of flow rates was therefore achieved by measuring the depth of liquid in the tank. While accurate over a long period of time, short term control was difficult because one inch of liquid in the tank is 196 imperial gallons. Variable flow rates were encountered during emission testing, the quantity added each day being:

December 10, 1975, 0.45 to 0.71% chlorine relative to clinker;
December 11, 1975, 0.31 to 0.51% chlorine relative to clinker; and,
December 12, 1975, 0.79% chlorine relative to clinker.

A ring also formed during this burn but broke away after the sampling sequence had been completed, thus avoiding another kiln shutdown. The presence of this ring restricted the burning of the residual quantity of this material (aromatic plus complexes) to intermittent burns.

Due to the above mentioned upset and requirements of the production schedule, it became necessary to add 13,000 gallons of the polychlorinated biphenyl blend to the 12,000 gallons of material remaining in the tank. The resulting mixture contained a significant quantity of solids and also had very low conductivity, thus requiring tank measurements as the method used for flow control.

The problem with solids separation and settling became more severe as the test progressed. This caused burner nozzle restrictions and pluggages which, in turn, caused interruptions and irregularities in waste liquid flows.

For the last day of emission testing, the nozzle was removed completely to permit uninterrupted flow rates of polychlorinated biphenyls. Quantities added during emission tests were:

January 7, 1976, 0.06 to 0.14% chlorine relative to clinker;
January 8, 1976, 0.13 to 0.33% chlorine relative to clinker; and,
January 9, 1976, 0.61% chlorine relative to clinker.

5.2 Organic Chloride Waste Burned

The chemical compositions of the three waste materials burned, the labelling used to identify each burn and the time periods during which they were fed to the kiln are given below:

Chlorinated aliphatics	WBA	October 23 - November 4/75
WBA plus chlorinated aromatics and alicyclics	WBB	December 5 - December 15/75
WBB plus polychlorinated biphenyls (PCB's)	WBC	January 3 - January 9/76

It was anticipated that complete combustion of these materials would occur in the kiln. However, a knowledge of the major constituents of each of the fuels was necessary in order to determine which trace components might be detected in the sampled emissions should incomplete combustion occur. Previous studies on the incineration of waste

chlorinated hydrocarbons [16] had shown that trace quantities of low molecular weight compounds such as carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) were detected in the combustion product gases. It was decided, therefore, to analyze collected emission samples for the presence of the major components of each composite waste fraction, and for the low molecular weight organochlorides referred to above.

Samples of the chlorinated wastes were taken from the line between the tank and the kiln. Typical component analyses of the three composite wastes burned during the program are recorded in Tables 1, 2 and 3.

The quantitative values given in the tables are based upon an assumed equal response of all the components to a flame ionization detector (FID). While this assumption is not very accurate, it was considered sufficient to provide the needed compositional data. Identification of components at concentrations greater than one percent was achieved by use of gas chromatography-mass spectrometry (GC-MS). Identification of components at concentrations less than one percent was not routinely performed. Analyses of samples collected on different days during a burn showed some variation in the concentration of individual components. However, the overall chemical composition of the feeds remained the same.

Two of the waste burn sample feeds (WBB and WBC) were also analyzed by the Ontario Ministry of the Environment (MOE), and the TRW Systems Group. The results obtained by these agencies are reported in detail in Appendices F and G, respectively. The TRW Systems Group analyzed composite samples of the daily feeds for both waste burns by GC-MS. The MOE group analysed individual daily samples for both waste burns using GC-FID operating conditions. The chromatographic parameters used by the MOE group to analyse for aromatic and PCB components precluded the identification of aliphatic organochlorine compounds such as $CHCl_3$ and CCl_4.

Some variation in the percent composition of the waste burn samples was apparent between the TRW and ORF results, especially with respect to the amounts of aliphatic organochlorine compounds present in waste burn B (WBB). The discrepancies observed are due to the fact that TRW received a composite sample of all daily feeds for each of the

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TABLE 1. COMPOSITION OF ALIPHATICS (WBA)

Sample Feed - October 28, 1975

Peak # in GC Profile (cf Figure A.6)	Approximate Concentration %	Identification
1	17.4	Chloropropane & propene ethylchloride, dichloromethane
2	1.4	
3	0.8	Chlorobutane & butene
4	1.5	
5	3.2	
6	16.5	1, 2, Dichloroethane
7	6.6	Carbon tetrachloride
8	1.0	
9	10.5	1, 1, 2-Trichloroethane
10	0.7	
11	0.3	
12	1.9	Dichloropropanes
13	1.4	
14	1.4	
15	2.4	Tetrachloroethylene
16	7.3	Tetrachloroethane
17	15.6	Chlorobenzene
18	2.4	multichlorinated butanes, butenes hexanes, hexenes
19	0.2	
20	3.3	
21	0.3	
22	1.1	
23	0.6	
24	0.5	
25	1.6	
26	0.6	
27	0.7	

Note: No identification of compounds at concentrations of 1% or less was attempted.

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TABLE 2. COMPOSITION OF AROMATICS PLUS COMPLEX (WBB)

Sample Feed - December 12, 1975

Peak # in GC Profile (cf Figure A.7)	Approximate Concentration %	Identification
1	2.0	Chloropropane
2	0.1	-
3	0.1	-
4	1.4	Chloroform
5	1.5	1, 2-Dichloroethane
6	3.5	Carbon tetrachloride
7	0.4	-
8	1.1	-
9	1.9	1, 1, 2-Trichloroethane
10	0.2	-
11	0.2	-
12	0.4	-
13	0.6	-
14	0.5	Chlorobenzene
15	0.5	-
16	52.2	Chlorotoluene
17	0.2	-
18	0.1	-
19	0.1	-
20	6.3	Hexachlorocyclopentadiene
21	2.7	Heptachlorocyclopentene
22	0.1	-
23	1.0	Pentachlorobenzene
24	8.5	Octachlorocyclopentene
25	4.4	Complex associated with Hexachlorocyclopentadiene
26	6.9	
27	1.3	

Note: No identification of compounds at concentrations of 1% or less was attempted.

TABLE 3. COMPOSITION OF AROMATICS PLUS PCB's (WBC)

Sample Feed - January 8, 1976

Peak # in GC Profile (cf Figure A.8)	Approximate Concentration %	Identification
1	3.4	Chloropropane
2	0.3	-
3	1.4	1, 1,-Dichloroethane
4	1.3	Carbon tetrachloride
5	0.5	-
6	0.3	-
7	1.9	1, 1, 2-Trichloroethane
8	0.1	-
9	1.9	-
10	0.5	-
11	28.5	Chlorotoluene
12	< 0.1	-
13	< 0.1	-
14	1.8	
15	0.9	Hexachlorocyclopentadiene
16	2.8	+ complex
17	0.9	
18	2.2	
19	0.3	Dichlorobiphenyl
20	2.1	
21	0.9	
22	6.7	
23	3.4	Trichlorobiphenyl
24	5.9	-
25	1.6	
26	12.1	Tetrachlorobiphenyl
27	5.6	
28	4.0	
29	5.4	
30	2.1	Pentachlorobiphenyl
31	1.6	

Note: No identification of compounds at concentrations of 1% or less was attempted.

waste burns, and different chromatographic columns and a different detector system were used by the two laboratories.

Since the study was to evaluate the burning of waste chlorinated materials of variable composition, minor differences between the laboratories' results do not affect the conclusions of the study.

The agreement among all groups was good with respect to the identification of components present in the two waste fuels. The presence of chlorinated aliphatics was observed in both waste fuels. WBB samples were found to consist primarily of chlorinated aromatic compounds, in particular o-chlorotoluene. WBC samples were found to consist of approximately 50% polychlorinated biphenyls (Arocior 1242) plus the chlorinated aromatics and alicyclics found in WBB samples.

5.3 Emissions

Samples of the kiln emissions before (BLA), during (WBA, WBB, WBC), and after (BLB) the burning of waste organic chlorides were taken, using the equipment and methods described in Appendix A. The analytical techniques used to determine if any organic chloride compounds were present in the emissions samples are discussed with respect to both gaseous and particulate emissions.

5.3.1 Free chlorine and hydrogen chloride

Prior to each sampling period, analyses were made for the presence of free chlorine (Cl_2) and hydrogen chloride (HCl) in the kiln emissions. An MSA gas sampler and MSA detector tubes were used to determine the concentrations of these pollutants. In no instance, either during baseline or waste burn sampling periods, were Cl_2 or HCl detected. The sensitivity limits using this analytical procedure are 0.5 ppm for Cl_2 and 2.0 ppm for HCl.

5.3.2 Gaseous organic compounds

Emission samples were collected using two sampling trains. The first, a gaseous sampling train (Appendix H), was designed to collect any volatile low molecular weight organic chlorides, e.g. CCl_4, $CHCl_3$, CH_2Cl_2, by adsorption on an inert adsorbent. In this study Chromosorb 102 was used. The second, a particulate sampling train (EPA Joy #5), was expected

to collect higher molecular weight compounds, including any noncombusted starting materials in the impingers.

Components adsorbed on the sorbent were removed by thermal desorption prior to analysis. All other collected fractions, from both trains, were extracted with organic solvents prior to analysis. These included probe rinse water solubles and insolubles, filters and impinger solutions.

In considering the results obtained in this study it is important to keep in mind the following:

- The collection efficiency of Chromosorb 102 sorbent for low molecular weight chlorinated hydrocarbons was determined to be better than 90%. The collection efficiencies of filters and ice-water in the impingers of a Joy train for organochloride components was not determined.
- The methods of collection, followed by thermal desorption or solvent extraction, were designed to concentrate any organic compounds which may have been present. Such techniques allow detection and identification of compounds at much lower levels than would otherwise be possible. Concentration factors for each type of sample have been calculated for each phase of the burn and are given in Table 4. For the desorbed gas samples, organic compounds from several cubic feet of kiln emission gases were collected on Chromosorb 102 and then desorbed into 500 millilitres. The concentration factors are the ratios of these two volumes. In the case of the solvent extracted samples, molecular weights enter the calculation in the conversion of volume to weight. A complete discussion of these calculations is given in Section A.6.4.

5.3.2.1 Desorbed samples. The concentrations of volatile organic chlorides calculated for the kiln emissions from gas chromatography - electron capture (GC-EC) are recorded in Table 5.

The results reported were averaged for each test series. Dichloromethane (DCM) was tentatively identified as the major component of these desorbed gas samples. Others tentatively identified were $CHCl_3$

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TABLE 4. GAS SAMPLE VOLUMES AND SAMPLE CONCENTRATION FACTORS
(Gaseous Sampling Train)

Test #	Date	Test Duration (mins)	Volume* Sampled scf	Sample Concentration Factors: Desorbed Gas	Sample Concentration Factors: Solvent** Extracted
1 BLA	Oct. 20 (1975)	317	2.80	159	
2 BLA	Oct. 21	281	1.86	141	510
3 BLA	Oct. 22	320	2.83	160	
1 WBA	Oct. 28	362	3.22	181	
2 WBA	Oct. 29	286	2.53	143	500-1100
3 WBA	Oct. 30	285	2.53	143	
1 WBB	Dec. 10	260	2.30	130	
2 WBB	Dec. 11	317	2.80	159	600-2000
3 WBB	Dec. 12	250	2.21	125	
1 WBC	Jan. 7 (1976)	268	2.37	134	
2 WBC	Jan. 8	237	2.09	119	520-1500
3 WBC	Jan. 9	228	2.02	114	
1 BLB	Jan. 19	170	1.50	85	
2 BLB	Jan. 20	247	2.18	124	380
3 BLB	Jan. 21	240	2.12	120	

*Volume sampled per adsorbent tube.

**These values are based on the lowest and highest molecular weights of compounds found in the waste feeds. Figures given for both baseline series are based upon the molecular weight of dichloromethane (DCM).

TABLE 5. ESTIMATED KILN EMISSION CONCENTRATIONS (GC-EC) FOR SPECIFIC VOLATILE ORGANOCHLORINE COMPOUNDS

Test Series	Emission Concentrations					
	Dichloromethane		Chloroform		Carbon Tetrachloride	
	ppb	$\mu g/m^3$	ppb	$\mu g/m^3$	ppb	$\mu g/m^3$
BLA	4.1	14.5	0.004	0.020	0.0004	0.0026
WBA	5.4	27.3	0.015	0.080	0.0020	0.0128
WBB	18.0	19.1	0.038	0.190	0.0020	0.0128
WBC	7.7	102.7	0.069	0.345	0.0060	0.0385
BLB	29.0	63.7	0.018	0.090	0.0004	0.0160

and CCl_4. It was found that GC-EC profiles of blank determinations obtained with unused conditioned Chromosorb 102 were variable, and the peaks that were present in the profiles possessed similar retention times to the compounds of interest. Therefore, reported results are higher than actual concentrations in the emission gases. The differing concentrations for DCM quoted in Table 5, especially with respect to BLB versus BLA, WBA or WBB, are probably a result of this background contamination rather than real differences. It was still noted, however, that the maximum concentration calculated as DCM in the kiln emissions was no greater than 30 ppb even with this positive bias from background contamination.

The MOE results confirm the ORF findings with respect to the detection of low molecular weight chlorinated organics in the desorbed gas samples. TRW did not find any trace of these volatile chlorinated organics in their desorbed gas samples. However, TRW did not routinely perform specific analyses for compounds present at concentrations below 0.1 mg/m^3.

5.3.2.2 Organic solvent extracted samples. Due to the much higher gas flow rate through the particulate sampling train to maintain an isokinetic sampling rate, the concentration factors for solvent extracted samples for this train were greater than those collected with the gaseous train. Calculated average concentration factors for each test series are

given below:

BLA	7,000
WBA	6,000 - 13,000
WBB	7,000 - 23,000
WBC	7,000 - 20,000
BLB	6,000

For the waste burns, the two values given represent the highest and lowest molecular weight species present in the waste chlorinated hydrocarbons. Calculations for the baselines are based on the molecular weight of dichloromethane. Subtraction of background interference based on control blanks (Appendix A.6.3) was performed on solvent extracted samples. Comparison was then made with the appropriate waste feed sample chromatograms. It was concluded that no uncombusted waste fuel components were present in any of the organic solvent extract samples at the detection limits of the analytical procedure used. Representative chromatograms together with discussion are presented in Appendix A.6.5.

TRW performed analyses on portions of all the organic solvent extracts obtained from BLA, WBB, WBC and BLB emission samples. The samples were specifically searched for chlorinated compounds. Also, the Chemistry Division, Air Pollution Control Directorate (APCD), Department of the Environment, Ottawa, Canada carried out analyses on portions of the solvent extracts of WBC emission samples to search for high molecular weight chlorinated hydrocarbons. Detailed reports of the work undertaken by these groups are presented in Appendices G and I, respectively.

The noteworthy result with respect to both reports was that in none of the samples analyzed by either group were any chlorinated organic compounds detected. Their results thus confirm the ORF conclusion that no chlorinated organic residues were detectable in any of the organic solvent extracts of the emission samples collected during the various waste chlorinated hydrocarbon burns.

5.3.2.3 Results obtained by the participating laboratories. In gas chromatographic analyses, program parameters define the conditions used. The choice of detector and column makes the analysis specific to certain

groups of compounds. Four laboratories analyzed the emissions samples taken during this study.

One of the laboratories, APCD, was requested to search for high molecular weight chlorinated hydrocarbons. The TRW group were not requested to identify low molecular weight chlorinated compounds present at less than 0.1 mg/m^3 in the stack gases. TRW did, however, search for PCB's using techniques designed to detect small quantities of these compounds. ORF and MOE were assigned the task of detecting and identifying all possible chlorinated organic species. Analytical design, and hence results, reflect differences in the analyses requested of the different laboratories.

Both ORF and MOE found low molecular weight hydrocarbons, such as dichloromethane, to be present at microgram per cubic meter ($\mu g/m^3$) levels in the emissions. That TRW detected no such compounds is not contradictory. The levels in the emission gases were less than their required detection limits. Similarly, it was not within the terms of reference for the APCD work to determine these compounds.

Results of the four laboratories can be conveniently summarized. While burning chlorinated hydrocarbons, low molecular weight chlorinated compounds were emitted at levels of a few $\mu g/m^3$ (Table 5). None of the participating laboratories detected any high molecular weight chlorinated hydrocarbons from either air sampling train. At detection limits of 3 $\mu g/m^3$ in the stack gases, polychlorinated biphenyls were not found.

5.3.2.4 Estimated minimum combustion efficiencies. The maximum value for total chlorinated hydrocarbon content in the kiln emissions was obtained in test 2 of the WBC series. Ignoring background subtraction for the baseline samples and the interferences from control blanks a maximum value of 40 ppb was determined. If a collection efficiency of 80% is assumed, a maximum level of 50 ppb in the kiln emissions is obtained. Because of the high and uncertain background levels, the estimate is higher than actual levels in the emission gases.

An average molecular weight for each of the three composite feeds can be obtained from a knowledge of the composition of the feed. Using this information, together with the average fuel feed rates to the kiln and average gas volume flow rates in the duct, the maximum

chlorinated hydrocarbon content can be determined. These values are presented in Table 6. Minimum combustion efficiencies were then calculated using the estimated maximum value of 50 ppb derived above. These figures in Table 6 are considered very conservative estimates because of the method used to calculate them.

TABLE 6. ESTIMATED MINIMUM COMBUSTION EFFICIENCIES FOR EACH WASTE BURN

Waste Composite	Maximum Estimated Organic Content in Kiln Emissions				Minimum Combustion Efficiency % v/v
	Assuming no Combustion		From Sample Chromatograms		
	ppm	g/m^3	ppb	$\mu g/m^3$*	
WBA	550	2.40	50	177.1	99.990
WBB	470	3.37	50	177.1	99.989
WBC	350	3.02	50	177.1	99.986

*Based on the molecular weight of dichloromethane.

5.3.3 Particulate emissions

Summary data for the particulate tests made during each test period are provided in Table 7. For each series of tests, the particulate loadings and emission rates are quite consistent except for the third test in the WBA series. The very high loading obtained probably resulted from some temporary malfunction of the precipitator. It is noticeable that, when the chloride wastes were burned in the kiln, the particulate emission rate increased. For the WBA series, the emission rates were about four times the rates obtained during the baseline tests and for the WBB and WBC series the rates were twice those obtained during the baseline tests.

Increased emission rates were not unexpected since combustion of the chloride wastes produces HCl and Cl_2, which react with the alkali components in the raw feed to form volatile alkali chlorides. At the precipitator the particulate loading is, therefore, increased and, since the condensed alkali chlorides are very fine and have a different resistivity, the amount of material passing through the collector increases. Another factor influencing emissions of particulate matter

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TABLE 7: SUMMARY OF PARTICULATE TEST DATA

Test #	Date	Probe Rinse Gain (mg)	Filter Gain (mg)	Total Gain (mg)	% of Total Gain on Filter	Volume Sampled (std ft^3)	Flow rate ACFM	Concentration (grains/ft^3)	Emission Rate (lb/hr)
1 BLA	Oct. 20/75	57.6	285.7	343.3	83	141.04	157,000	0.0376	20.8
2 BLA	Oct. 21/75	58.8	366.0	424.8	86	135.86	155,000	0.0483	25.4
3 BLA	Oct. 22/75	35.8	291.8	327.6	89	132.83	153,000	0.0367	19.6
							Average	0.0409	21.9
1 WBA	Oct. 28/75	99.0	1242.6	1341.6	93	142.81	157,000	0.1458	83.9
2 WBA	Oct. 29/75	94.8	1261.7	1356.5	93	137.34	153,000	0.1524	84.6
3 WBA	Oct. 30/75	237.5	2193.8	2431.3	90	109.88	165,000	0.3415	200.0
							Average	0.2132	122.8
1 WBB	Dec. 10/75	143.0	424.1	567.1	75	106.64	148,000	0.0821	40.3
2 WBB	Dec. 11/75	06.1	468.4	554.5	84	117.06	162,000	0.0731	40.5
3 WBB	Dec. 12/75	145.6	621.6	767.2	81	116.24	161,000	0.1019	55.0
							Average	0.0857	45.3
1 WBC	Jan. 7/76	62.2	546.3	608.5	90	119.62	172,000	0.0785	45.3
2 WBC	Jan. 8/76	43.1	436.5	479.6	91	113.52	160,000	0.0652	34.5
3 WBC	Jan. 9/76	87.8	600.0	687.8	87	118.99	167,000	0.0892	52.2
							Average	0.0776	44.0
1 BLB	Jan. 19/76	65.2	251.7	316.9	79	126.88	183,000	0.0385	23.9
2 BLB	Jan. 20/76	51.4	240.1	291.5	82	116.60	163,000	0.0386	21.0
3 BLB	Jan. 21/76	11.9	183.5	195.4	94	116.45	168,000	0.0259	14.6
							Average	0.0343	19.8

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were the kiln rings formed while burning chlorinated hydrocarbons. Kiln rings, by their effect on gas velocities through the kiln, increase the amount of particulate material carried to the precipitator.

Extensive ring formation was noted during test WBA. The average emission rate for WBA was about 3 lb/ton of clinker produced, compared to the Canadian Federal Government objective of 0.9 lb/ton. The average value for the other phases of the test was about 1.1 lb of particulate emitted/ton of clinker produced and that of the baselines was 0.5. This apparent increase in the particulate emissions while burning chlorinated hydrocarbons is believed to be partially caused by the change in resistivity of the dust entering the precipitator due to its increased alkali content. A modification in the design of the precipitator could compensate for this change.

The higher emission rates did not significantly add to the suspended particulate in the ambient air in the vicinity of the plant. Computed maximum ground level concentrations using standard dispersion equations were less than 2 $\mu g/m^3$ for the baseline emission rates and, during the burning of waste chlorides, did not exceed 10 $\mu g/m^3$. The current Ontario standard is 100 $\mu g/m^3$.

5.4 Mass Balance on Wet Kiln

For the wet process kiln, the input streams are slurry feed, No. 6 fuel oil and, when burned, the waste chlorinated hydrocarbons. Clinker (the product) and a portion of the precipitator dust form the output streams. The major portion of the precipitator dust is immediately returned to the process. This stream, though not required for the mass balance, was monitored for information on kiln operation while burning chlorinated hydrocarbons. Balances of chlorine and potassium were calculated for both baseline periods and for each type of chlorinated waste burned. Methods of sampling and quantifying material streams are detailed in Appendix A. Details of analytical results, calculations and tables of daily mass balances are given in Appendix C.

5.4.1 Significance of the mass balance

In common with other material balance experiments on large scale production systems, the material accounting in this experiment showed apparent losses and gains when the data were expressed in percent retention.

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These should not be regarded as real system losses or gains. There are random and systematic errors in weighing and quantifying very large quantities of materials and in analytical results. In the case of alkali chlorides, a cycle is developed within the kiln whereby alkali chlorides volatilize in the hotter section of the kiln and condense in the cooler section. Should a kiln upset occur, the cycle may be broken by alkali chloride being retained in the clinker. Such an occurence may be of sufficiently short duration that clinker samples taken may not be indicative. This effect is evident from the data of October 11-14, 1975. A power failure on the eleventh caused a three hour kiln shutdown. The indicated very low retention of both chlorine and potassium occurred presumably while the cycle was being re-established. Since the equilibrium changes when burning of chlorinated materials begins or ends, this feature can also be seen with each phase of chlorinated waste burning. At the start of any chlorinated burn, the mass balance for chlorine indicates very low retention while the cycle is established. At the end of the chlorinated burn, a gain is indicated as chlorine is retained in process solids while the new equilibrium is established. Formation of kiln rings also caused an apparent loss of alkali chloride since a considerable quantity was contained within the ring.

5.4.2 Chlorine and potassium retained

The cumulative percentage of chlorine retained (Table 8) was low in all cases throughout the study, ranging from 50.7 percent for the chlorinated aliphatic burn to 92.2 percent for the final baseline. K_2O (Table 9) closely followed the pattern of chlorine retention, although at a different retention level, with 83.5 percent the lowest value found during the chlorinated aliphatic burn and 97.8 percent the highest value found during the final baseline. The reason is clearly that potassium chloride was being lost in ring formation and kiln cycle equilibrium fluctuations.

The cumulative percentage K_2O retained was less affected than that of chlorine by such losses because the quantity of K_2O was from 3 to 20 times greater than the quantity of chlorine. Random and systematic errors could also be expected to play a greater role in the chlorine balance for the same reason.

TABLE 8. ACCUMULATED MASS BALANCE FOR CHLORINE

Accumulated Period	Chlorinated Hydrocarbon Burned	Accumulated Input (lb) (T_I)	% of T_I From Chlorinated Hydrocarbon	Accumulated Retention (lb)	% Retention
7/10/75-22/10/75	---	28,249	0	20,768	73.5
23/10/75- 4/11/75	Aliphatic	134,379	83.2	68,088	50.7
2/12/75-14/12/75	Aromatic + Complex	135,705	85.0	112,640	83.0
3/ 1/76- 9/ 1/76	PCB	58,590	82.4	41,704	71.2
10/ 1/76-21/ 1/76	---	18,351	0	16,927	92.2

TABLE 9. ACCUMULATED MASS BALANCE FOR K_2O

Accumulation Period	Chlorinated Hydrocarbon Burned	Accumulated Input (tons)	Accumulated Retention (tons)	% Retention
7/10/75-22/10/75	---	240.99	229.37	95.2
23/10/75- 4/11/75	Aliphatic	199.67	166.72	83.5
2/12/75-14/12/75	Aromatic + Complex	194.59	186.68	95.9
3/ 1/76- 9/ 1/76	PCB	103.25	92.88	90.0
10/ 1/76-21/ 1/76	---	280.40	274.36	97.8

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While the chlorine balance does show discrepancies, in all cases while burning chlorinated hydrocarbons more chlorine was retained in process solids than the quantity input with materials other than these wastes. A major portion of the chlorine from the chlorinated hydrocarbon materials is thus accounted for. Considering the uncertainties involved with ring formation and kiln upsets; the mass balance for chlorine confirms the finding of the emission measurements that all chlorinated hydrocarbons are destroyed in the cement kiln.

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6 CONSIDERATIONS ON BURNING CHLORINATED HYDROCARBON WASTES IN A CEMENT KILN

6.1 Effect on Production

Kiln ring formation normally decreases kiln production, apart from any loss of production caused by downtime. However, the kiln rings formed during this study were attributed to poor control of feed rates of the chlorinated waste. Ring formation through chlorine addition rates higher than desirable were previously encountered at St. Lawrence Cement while adding waste hydrochloric acid. Adequate control would certainly eliminate this problem and, since this is a fairly simple proposition, kiln ring formation should not be considered a deterrent to use of this waste in the kiln.

During the study, average production rates (Table 10) were 1038 tons per day while not burning chlorinated hydrocarbons and 1025 tons per day while burning these materials.

There was also an increase of approximately 20 tons per day in the quantity of dust discarded (Table 11) while burning chlorinated materials.

While these values may be partly due to ring formation, it is probable that dust generated would increase due to increased volatilization of alkali chloride, and that this would have a corresponding effect on clinker production. Thus, if another form of chloride were being used for alkali reduction, it is unlikely that any change would be detected by use of chlorinated hydrocarbon wastes.

6.2 Alkali Reduction While Burning Chlorinated Hydrocarbon Wastes

As indicated earlier in this report, Na_2O is not considered in this study because it is low and practically constant in the St. Lawrence Cement Co. raw materials and products.

To determine the efficiency of alkali reduction, the following points require consideration. The percent K_2O reported in the slurry feed is on the natural or "as received" basis. To determine the quantity which would be present if none were volatilized in the burning process, the results must be calculated on the "ignited basis", that is, recalculated for the CO_2 evolved from the raw materials in the burning process. The

TABLE 10. AVERAGE REDUCTION IN K_2O CONTENT OF CLINKER

Accumulation Period	Clinker Prod. (t/day)	Chlorinated Hydrocarbon	Cl Input With Hydrocarbon % Relative to Clinker Prod.	Slurry K_2O (%) Natural Basis	Slurry K_2O (%) Ignited Basis	K_2O Clinker (%)	K_2O Reduction (%)	Calculated* K_2O Reduction (%)
7/10/75-22/10/75	1056	-	0	0.92	1.42	1.21	0.21	0
23/10/75- 4/11/75	1050	Aliphatic	0.41	0.92	1.42	0.87	0.55	0.58
2/12/75-14/12/75	1020	Aromatic + Complex	0.44	0.90	1.42	0.74	0.68	0.58
3/ 1/76- 9/ 1/76	1006	PCB	0.34	0.91	1.41	0.87	0.54	0.45
10/ 1/76-21/ 1/76	1020	-	0	0.91	1.40	1.25	0.15	0

*Based on chlorine input.

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TABLE 11. AVERAGE DUST DISCARDED

Period	Chlorinated Hydrocarbon	Average Dust Discarded (Tons Per Day)
7/10/75-22/10/75	---	22.2
23/10/75- 4/11/75	Aliphatic	42.7
2/12/75-14/12/75	Aromatic + Complex	74.0
3/ 1/76- 9/ 1/76	PCB	62.5
10/ 1/76-21/ 1/76	---	45.1

percent K_2O in slurry feed on the ignited basis minus the percent K_2O in the clinker yields the reduction through volatilization in the kiln. Since the K_2O reduction is achieved by formation of potassium chloride (KCl), the reduction expected while burning chlorinated hydrocarbons, based on the assumption that all chlorine is bound into potassium chloride, can be readily calculated. Comparison of actual and calculated values (Table 10) are excellent. If chlorine is added to reduce alkalies, the reduction is stoichiometric. However, the total reduction is relative to alkali levels in the slurry and not to the baseline content in the clinker. This result was confirmed both by this study and by previous experience using hydrochoric acid as the source of chlorine. This may be due to formation of potassium chloride from volatile compounds such as potassium carbonate. On average, without chloride addition, a reduction of 0.18 percent K_2O is apparent. While burning chlorinated hydrocarbons, the average reduction is that calculated on the basis of potassium chloride formation plus 0.05 percent.

The extremely good correlation between quantity of chlorine input by burning of chlorinated hydrocarbons and alkali reduction in the clinker gives better proof than the mass balance that chlorinated hydrocarbons are destroyed in a cement kiln. Otherwise, alkali chloride could not be formed, and volatilization to the extent noted could not occur. The high degree of correlation indicates that all of the chlorinated hydrocarbon was destroyed.

6.3 Heat Recovery From Chlorinated Hydrocarbon Wastes

Calculation of heat recovery from these materials, normally difficult due to the low flow rates involved, was made more difficult by the flow control problems encountered. During the aromatic plus complex chlorinated hydrocarbon burn, the oil meter did not function properly and assessment of heat recovery was made only over the first two days of burning. As near as can be established, approximately 65% of the heat of the chlorinated hydrocarbon was recovered (Table 12). This can be expected since volatilization of potassium chloride required energy. While the energy is recovered upon condensation, this occurs too far along the kiln to be completely recuperated. Weber [18] states "volatilization of alkalies consumes high grade heat in the sintering zone and calcining zone above a material temperature of 800°C and this heat is subsequently released only at lower temperatures. Thus, degradation of high-grade heat takes place".

When it is considered that potassium chloride forms a cycle within the kiln and may be volatilized several times before escaping to the precipitator, the heat consumed by this process becomes considerable.

In the suspension preheater kiln, an indication of the number of cycles of volatilization of alkali chlorides is given by the relationship between the Stage IV chloride level and quantity of chloride input. Since in this study, the K_2O at Stage IV was a factor of ten greater than the K_2O input, it follows that ten cycles of volatilization occur on average in the suspension preheater kiln. The situation in the wet process kiln, however, is dissimilar. There is no convenient method for determining the number of alkali cycles involved. That there will not be as many cycles as in the suspension preheater kiln is certain when consideration is given to the differences in the two processes.

It is assumed, for purpose of illustration, that a chlorinated hydrocarbon with 9300 Btu/lb and 42% chlorine is being burned with an alkali cycle of three times. For each pound of chlorinated material, there are 0.42 pounds of chlorine which will produce 0.88 pounds of potassium chloride. The heat of vaporization of potassium chloride is 38,840 cal/mol [19] or 938.6 Btu/lb. The 0.88 pounds of potassium

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TABLE 12. RECOVERY OF Btu FROM CHLORINATED HYDROCARBONS

Material	Average Reduction Input With Oil (10^6 x Btu/ton Clinker)	Average Input With Chlorinated Hydrocarbon (10^6 x Btu/ton Clinker)	% Useful Heat From Chlorinated Hydrocarbon
Aliphatic	0.125	0.205	61
Aromatic + Complex	0.128	0.217	59
PCB	0.157	0.228	69

chloride would require 2478 Btu for three cycles. On this basis we might expect to recover:

$$\frac{9300 - 2478}{9300} \times 100\% = 73\%$$ of the heat content of the chlorinated hydrocarbon.

While the above is only an approximation and ignores concurrent heat exchange processes, it indicates that the heat recovery of about 65% obtained in the present study is reasonable.

It should be emphasized that the addition of calcium chloride would require a similar quantity of heat to volatilize alkalies. In the case of calcium chloride, an increase in fuel quantity would be required.

6.4 Cement Quality

While the literature available [2, 3, 10] indicates that alkali reduction is beneficial with regard to cement quality, the possibility of unburned organic material being retained in the cement and having a deleterious effect was considered. Cements were ground in the laboratory with clinkers produced while burning only No. 6 fuel oil as well as clinkers produced during the aromatic plus complex and PCB burns. Detailed results are given in Appendix D. The results obtained indicated the only effects to be those due to alkali reduction.

6.5 Extrapolation to Other Kiln Types

Since all cement kilns have in common the requirement that uniformly high temperatures be maintained, the authors believe that

chlorinated hydrocarbons will be destroyed in all types of cement kilns regardless of fuel used. The only qualification to this statement is that the wastes must be injected into the burning zone. While it is advisable to atomize the chlorinated waste, there appeared to be no difference during the PCB burn with or without a nozzle for atomization.

For fuel economy, cement kilns are operated at low excess oxygen. This, combined with the high temperatures and hydrogen from the fuel, will in all cases ensure that hydrogen chloride (HCl) is preferentially formed rather than free chlorine. In all cement kilns, the lime will readily react with the hydrogen chloride. Based upon results of the present study, no detectable quantities of either compound are expected to be emitted from any type of cement kiln.

Since alkali chloride is volatilized and condensed in the gas stream as extremely fine particles, it would be expected that emission of particulate matter would increase by an amount depending on the efficiency of the precipitator. This would apply to any method of chloride addition. To overcome the plugging problem caused by condensation of these salts in suspension preheaters, design modifications to these units need to be installed and demonstrated.

6.6 Comparison of Cement Kiln Burning with Other Uses and Disposal Methods for Waste Chlorinated Hydrocarbons

Information on disposal methods used and actual quantities of chlorinated hydrocarbons requiring disposal is not readily available in Canada. While a conservative estimate of 25-30 million pounds of chlorinated hydrocarbon wastes was obtained, it seems likely that this quantity represents only wastes from plants manufacturing chlorinated hydrocarbon products. The magnitude of the problem of disposal of these wastes in North America can be inferred by some of the methods used. One method makes use of ships designed for burning of these wastes at sea, this method being described in studies monitored by the United States Environmental Protection Agency [20, 21]. Such a method of disposal is expensive, requires constant monitoring of temperatures within the furnace, uses additional fuel for combustion and emits hydrogen chloride (HCl) which is dissolved in the ocean.

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Another method of disposal in North America is incineration with production of hydrochloric acid [22].

One report from Europe [23] indicates that methods of disposal are:

1) illegal dumping of small quantities in barrels or other containers on uncontrolled refuse dumps;
2) deposition of larger quantities in barrels on refuse dumps which are supposedly sanctioned for this purpose;
3) combustion in simple facilities without hydrogen chloride scrubbing;
4) combustion of piles of barrels on remote beaches with an offshore wind;
5) dumping barrels on the open sea;
6) dumping liquids into the sea from moving vessels;
7) separation of waste materials and recovery of useful components;
8) combustion with recovery of hydrochloric acid; and,
9) combustion on the open sea at temperatures guaranteeing almost complete pyrolysis.

The same report states: "Only the last three procedures can be considered to be not harmful for the environment. But procedures 7) and 8) are possibly very expensive and in special cases unsustainable for the producer". Also from the same report, it is pointed out that combustion at sea requires extensive observation of a variety of safety procedures.

A study from France [24] indicates that a variety of legal and illegal means are used to dispose of chlorinated hydrocarbon wastes. Of illegal means: "the discharge of what in general are insignificant quantities is disposed of in drums, or by tankers, into waterways, former quarries now used for other purposes, or discharged with unsupervised wastes that reason suggests should be retained".

In comparing combustion in a cement kiln, with other methods of disposal which are considered not harmful to the environment, the following points become apparent:

- Incineration of these wastes is normally done at a flame

temperature of 1200°C to 1560°C [25] while cement kiln flame temperatures are 2100°C [18] or higher.

- The retention time in a cement kiln flame envelope is considerably longer than the 0.1 seconds normally found in an incinerator.
- For the production of cement clinker, the temperatures cited are necessary [26], thus removing the necessity for constant monitoring of temperatures as required when burning in an incinerator.
- To prevent operating difficulties, such as kiln rings, in a cement kiln, the amount of chlorine is restricted to approximately 0.4 percent relative to clinker. Besides maintaining constant temperature, this requirement ensures that sufficient hydrogen is available to form hydrogen chloride which is readily absorbed by lime.
- There is always a high quantity of lime in the cement kiln to react with hydrogen chloride and thus prevent emission of this compound to the atmosphere.
- Burning of these wastes in a cement kiln saves fossil fuels, as opposed to the necessity of using fossil fuels to ensure combustion of these wastes in an incinerator.
- Beneficial use is obtained in a cement kiln of persistent and toxic waste materials which normally require disposal.

7 CONCLUSIONS

The concept of using chlorinated hydrocarbon wastes in cement processing derives from knowledge of kiln operating temperatures and residence times in comparison with incinerators capable of destroying these compounds. The action of cement kilns as "dry-lime scrubbers" in relation to halogens in the kiln gases was already known.

In all cases, in the present study, analyses of kiln emissions indicated the efficiency of combustion of chlorinated hydrocarbon wastes to have exceeded 99.98 percent. Traces of volatile low molecular weight chlorinated hydrocarbons were found to be present at a maximum emission concentration of 50 ppb above baseline. All other starting materials, including polychlorinated biphenyls, were completely destroyed. There were no detectable emissions of hydrogen chloride, free chlorine or high molecular weight chlorinated hydrocarbons.

An increase in total particulate emissions was observed while burning chlorinated hydrocarbon wastes. This is apparently related to an increase in dust loading to the precipitator as indicated by the necessity of discarding more dust while burning chlorinated hydrocarbons.

Combustion in incinerators designed for destruction of chlorinated hydrocarbon wastes caused the emission of most of the hydrogen chloride except for those installations using expensive hydrochloric acid recovery or scrubbing systems. These incinerators require continous monitoring of temperature profiles and use fossil fuels to initiate or maintain combustion.

The present study indicates that useful recovery of about 65 percent of the heat value and approximately 100 percent of the chlorine is attained by the burning of these wastes in a cement kiln.

A mass balance on chlorine and the effective alkali reduction derived from the chlorine contained in the chlorinated hydrocarbon wastes confirms the air emissions data.

Consideration of the data from this study and examination of the general literature on cement manufacturing has led the authors to conclude that all chlorinated hydrocarbon wastes may be used in cement kilns without adverse effect on air pollution levels.

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APPENDIX A

QUANTIFYING, SAMPLING AND ANALYSIS OF PROCESS MATERIALS

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QUANTIFYING, SAMPLING AND ANALYSIS OF PROCESS MATERIALS

While analytical procedures used are identical for both wet and dry process kilns, only the wet process kiln material streams are considered in this Appendix. The dry process suspension preheater kiln system is detailed in Appendix B.

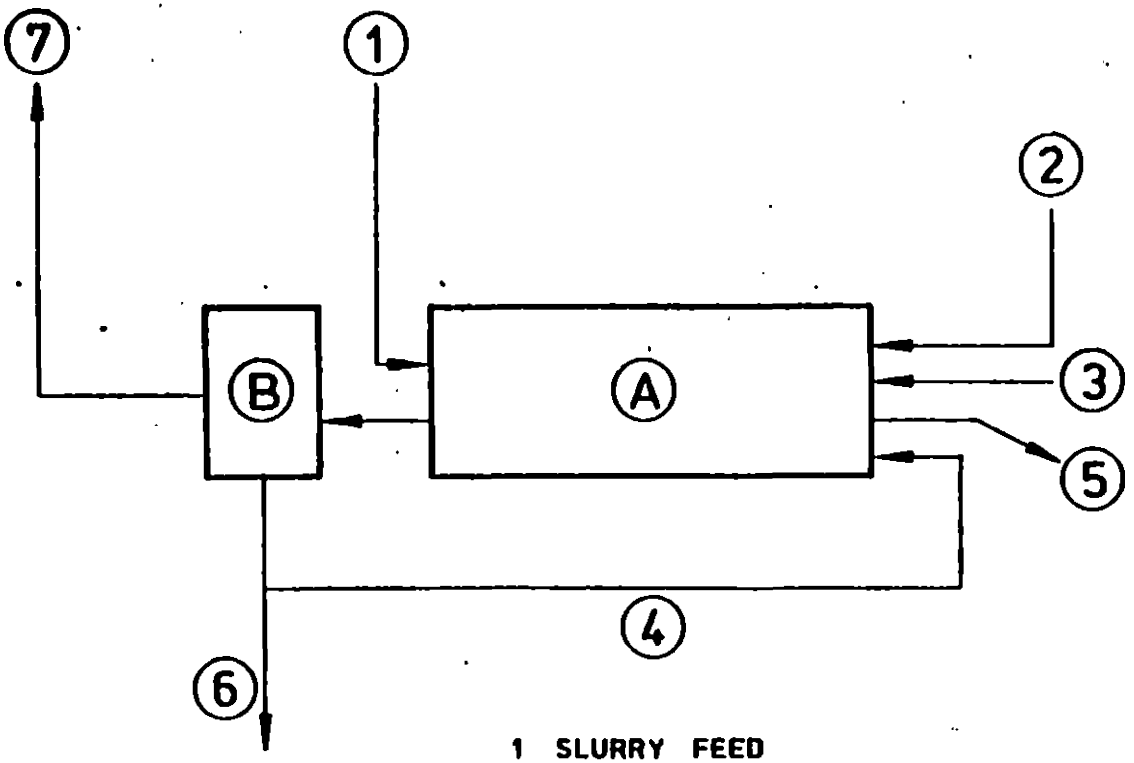
The material flow through the wet kiln production system is illustrated in Figure A.1. To obtain the material balance, six materials were quantified, sampled and analyzed. A seventh material, precipitator return dust, was monitored to obtain any additional operating data this stream might yield. Table A.1 lists the materials examined with approximate relative quantities under normal production conditions.

TABLE A.1. PROCESS MATERIALS STUDIED AND APPROXIMATE NORMAL PRODUCTION QUANTITIES

Material	Approximate Quantity
Slurry Feed	1540 dry tons/day
Clinker	1000 tons/day
Precipitator Discard Dust	0 - 140 tons/day
Precipitator Return Dust	350 tons/day
No. 6 Fuel Oil	20 gal/min
Chlorinated Hydrocarbons	1 - 2 gal/min
Kiln Exhaust Gases	160,000 ACFM

A.1 Quantifying and Sampling Slurry Feed and Clinker

There are four slurry basins, each of 6000 ton capacity, including slurry water. The product from the slurry grinding mills is pumped into these basins. The basins are supplied with air agitators for the purpose of blending the slurry and maintaining a uniform suspension of solids in liquid. Slurry is pumped from one basin at a time to the constant level box of the slurry feed system. The material which over-



1 SLURRY FEED
2 AIR
3 FUEL (OIL, CHLORINATED MATERIALS)
4 DUST RETURN
5 CLINKER
6 PRECIPITATOR DUST WASTED
7 STACK GAS

A KILN
B PRECIPITATOR

SCHEMATIC OF THE MATERIAL BALANCE

FIGURE A.1

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flows from the constant level box is returned to the slurry basins. Slurry feed for the kiln is taken from the constant level box by an Allis Chalmers "Ferris Wheel" bucket wheel feeder with variable speed drive. From the bucket wheel feeder, the slurry flows into a small basin with an outlet at the bottom from which the slurry goes directly into the kiln.

The slurry feed samples were taken every two hours from the overflow of the constant level box, and blended into a daily composite. A portion of the daily composite then was dried at 120°C for analysis.

Slurry feed quantities were obtained by multiplying the total number of revolutions of the "Ferris Wheel" per day by a factor. Measurement of the slurry basin levels while feeding the kiln but not allowing slurry to be fed into the basin gives an accurate quantity of slurry fed to the kiln. A second method, performed every two hours, is to close a valve at the outlet to the kiln of the small basin fed by the Ferris Wheel. By determining the time to fill this basin, the quantity fed to the kiln is known.

The clinker is fed to a bucket elevator by gravity through a chute from the cooler. Clinker samples are taken from this chute at intervals of two hours to form a 24-hour composite. The clinker composite sample is mixed, reduced by "cone and quartering" and a portion ground for analysis.

In common with general practice in the industry, there is no provision in the plant for continuous weighing of clinker. The water content of the slurry feed is determined thrice daily, from which the following calculation is made:

$$SFD = SF \left(\frac{100 - H_2O}{100} \right)$$

where SFD = quantity of slurry feed on a dry basis
SF = quantity of slurry feed including water
H_2O = % water in the slurry feed.

To obtain the quantity of clinker produced, the CO_2 which is lost in the burning process (determined by loss on ignition of the dry slurry feed) is deducted and a further correction is made for the quantity

of dust discarded from the system. A total material balance may then be written as follows:

$$\text{Clinker} = SFD\left(\frac{100 - LOI_{SFD}}{100}\right) - DD\left(\frac{100 - LOI_{DD}}{100}\right)$$

where SFD = quantity of slurry feed on dry basis

LOI_{SFD} = % loss on ignition on slurry feed on dry basis

DD = quantity of dust discarded

LOI_{DD} = % loss on ignition on dust discarded.

A.2 Weighing and Sampling Precipitator Dust

Dust from the precipitator is separated into two portions by a system of screw conveyers under the precipitator. The major portion is returned via a conveyor belt into a small holding silo from which the dust is returned into the burning zone of the kiln (return dust). Samples of the dust are taken at two-hour intervals from the conveyor belt to form a 24-hour composite. The composite is blended and a portion taken for analysis. A minor portion of the dust (discard dust) is fed into a second holding silo from which trucks are loaded directly. A sample of this dust is taken from each truck load, and all samples for each day are blended into a 24-hour composite. Each load of dust is weighed on the truck weigh scales before being disposed of.

A.3 Measurement and Sampling No. 6 Fuel Oil

While it was considered unlikely that No. 6 fuel used in the plant would contribute a substantial quantity of chlorine, samples of oil were taken daily. Fuel quantities are continuously monitored and recorded in the production data but are not given in this report. Chlorine content of the oil was determined, and the contribution to the chlorine mass balance due to oil was included.

A.4 Measurement and Sampling Waste Chlorinated Hydrocarbons

Sampling of chlorinated hydrocarbons was carried out by withdrawing material from the feed system twice daily and blending by vigorous mixing. Samples were split into equal portions after blending.

Initially, it was intended to meter chlorinated hydrocarbon flow continuously. For this purpose, a magnetic flow meter was installed in the line to monitor quantities of these materials. For this type of meter to function properly, it is required that the conductivity of the material be greater than 2×10^{-6} mhos. While this was the case for the chlorinated aliphatic wastes, the conductivities of the other materials were less than 0.3×10^{-6} mhos. As a result, chlorinated waste material quantities were determined by taking measurements of the volume of material in the storage tank. Tables A.2 through A.4 give detailed information on calculated chlorinated waste material quantities.

A.5 Emission Sampling

Separate sampling trains were used to collect representative samples of kiln emissions for analysis to determine the emission rates of particulate material and to determine if organic chloride compounds were present in the gas stream passing to the stack. Particulate and gaseous samples were collected from a duct downstream of the precipitator controlling dust emissions from kiln #1. The location is described below, followed by descriptions of sampling equipment and methodology.

A.5.1 Sampling location

Emissions from both #1 and #2 wet process kilns pass through electrostatic precipitators (Joy Manufacturing Co.) and then through sections of rectangular breeching before mixing in a common section of duct entering the stack. The stack, which is of height 554.0 feet and has an exit diameter of 13.0 feet, vents the exhaust gases to the atmosphere at a temperature of about 400°F and a velocity of almost 40 feet per second.

The rectangular breeching from the precipitator makes a 90° bend and then angles at about 30° upwards from the horizontal for a distance of approximately 45 feet to the common header which leads into the stack. This 45 foot section of duct was considered the most suitable for installation of sampling ports at a location which would meet both Federal and Provincial source testing codes. It was subsequently decided, therefore, to install five 4" diameter ports in the vertical side of the duct at a position 12 feet upstream of the bend into the

TABLE A.2. QUANTITIES OF ALIPHATIC MIXTURE BURNED DAILY

Date	Time From	To	Minutes	Igpm	Gallons	Gallons/Day
23/10/75	09:00	12:00	180	0.5	90	1170
	12:00	06:00	1080	1	1080	
24/10/75	06:00	06:00	1440	1	1440	1440
25/10/75	06:00	06:00	1440	1	1440	1440
26/10/75	06:00	06:00	1440	1	1440	1440
27/10/75	06:00	06:00	1440	1	1440	1440
28/10/75	06:00	06:00	1440	1	1440	1440
29/10/75	06:00	06:00	1440	1	1440	1440
30/10/75	06:00	09:30	210	1	210	2670
	09:30	06:00	1230	2	2460	
31/10/75	06:00	06:00	1440	2	2880	2880
1/11/75	06:00	06:00	1440	2	2880	2880
2/11/75	06:00	06:00	1440	2	2880	2880
3/11/75	06:00	06:00	1440	2	2880	2880
4/11/75	06:00	10:00	240	2	480	930
	10:00	17:30	450	1	450	
	OFF at 17:30					

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TABLE A.3. QUANTITIES OF AROMATIC PLUS COMPLEX MIXTURE BURNED DAILY

Date	Time	Tank Measurement	Difference gallons	Difference minutes	Gal/min
Dec. 6	15:00	12' 0"			
	2 loads in 60930 lb + 40690 lb @ 1.299 SG = 7823 gal				
Dec. 7	12:15	14' 6"	(7823-5886 = 1937 gal)		
			1937	1275	1.519
Dec. 8	15:00	14' 0"	1177	1605	0.733
Dec. 9	15:30	13' 6"	1177	1470	0.801
Dec. 10	12:00	12' 6"	2354	1230	1.914
Dec. 11	15:00	11' 8"	1962	1620	1.211
Dec. 12	09:00	11' 4"	785	1080	0.727
Dec. 12	15:30	11' 0"	785	390	2.013
Dec. 13	13:30	10' 3"	1373	1320	1.040
Dec. 14	13:20	9' 6"	1766	1430	1.235
Dec. 15	14:00	8' 8"	1962	1480	1.326

Gallons per Day

Date	From	To	Minutes	Igpm	Gallons	Total Gallons
Dec. 2	06:00	13:10	430	(1)	430	430
Dec. 5	10:00	12:00	120	1.519	182	1640
	14:00	06:00	960	1.519	1458	
Dec. 6	06:00	06:00	1440	1.519	2187	2187
Dec. 7	06:00	12:15	375	1.519	570	1351
	12:15	06:00	1065	0.733	781	
Dec. 8	06:00	15:00	540	0.733	396	1117
	15:00	06:00	900	0.801	721	
Dec. 9	06:00	15:30	570	0.801	456	2121
	15:30	06:00	870	1.914	1665	
Dec. 10	06:00	12:00	360	1.914	689	1997
	12:00	06:00	1080	1.211	1308	

TABLE A.3. (Cont'd)

Date	From	To	Minutes	Igpm	Gallons	Total Gallons
Dec. 11	06:00	15:00	540	1.211	654	1308
	15:00	06:00	900	0.727	654	
Dec. 12	06:00	09:00	180	0.727	131	1821
	09:00	15:30	390	2.013	785	
	15:30	06:00	870	1.040	905	
Dec. 13	06:00	13:30	450	1.040	468	1691
	13:30	06:00	990	1.235	1223	
Dec. 14	06:00	13:20	440	1.235	543	1869
	13:20	06:00	1000	1.326	1326	
Dec. 15	06:00	06:00	1440	1.326	1909	1909

TABLE A.4. QUANTITIES OF PCB MIXTURE BURNED DAILY

Date	Time	Tank Measurement	Difference gallons	minutes	Gal/min
3/1/76	14:30	11' 4"			
4/1/76	12:00	12' 6"	1962	1290	1.521
5/1/76	09:15	9' 8"	1962	1275	1.539
5/1/76	14:30	9' 6"	392	315	1.244
6/1/76	09:10	8' 7"	1766	1120	1.577
7/1/76	09:06	7'11"	1962	1436	1.366
7/1/76	16:00	7'10"	196	414	0.473
8/1/76	08:45	7' 9"	196	1003	0.195
8/1/76	15:45	7' 8"	196	420	0.467
9/1/76	08:45	7' 2"	1177	1020	1.154
9/1/76	05:45	6' 8"	1177	540	2.180

Gallons per Day

Date	From	To	Minutes	lgpm	Gallons	Total Gallons
3/1/76	07:45	14:30	405	1.521	616	2030
	14:30	06:00	430	1.521	1414	
4/1/76	06:00	12:00	360	1.521	548	2210
	12:00	06:00	1080	1.539	1662	
5/1/76	06:00	09:15	195	1.539	300	2159
	09:15	14:30	315	1.244	392	
6/1/76	06:00	09:10	190	1.577	300	2008
	09:10	06:00	1250	1.366	1708	
7/1/76	06:00	09:06	186	1.366	254	614
	09:06	16:00	414	0.473	196	
	16:00	06:00	840	0.195	164	
8/1/76	06:00	08:45	165	0.195	32	1215
	08:45	15:45	420	0.467	196	
	15:45	06:00	855	1.154	987	
9/1/76	06:00	08:45	165	1.154	190	1433
	08:45	18:15	570	2.180	1243	

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header, and positioned on a line perpendicular to the gas flow. The port locations are shown schematically in Figure A.2.

As agreed upon by the Ontario Ministry of Environment and Environment Canada, sampling was carried out at eight points on each of the five duct traverses for a minimum of five minutes per point. The sampling points were located at the centres of equal rectangular areas in the duct as shown in Figure A.3. The numbers given in each rectangle are typical gas velocities measured during the study and indicate the distribution of gas flow at that location.

A.5.2 Sampling equipment

Prior to setting up equipment for particulate and gaseous sampling, grab samples of the kiln emissions were taken using the equipment depicted in Figure A.4. A gas sample was pulled through an in-stack 47 mm glass fibre filter in a stainless steel holder to remove particulate material and then through a heated teflon line into a Tedlar bag. For each bag sample a clean bag was placed in the lung and the lid tightened to effect an air-tight seal. Valves A and C were closed and B opened so that, with the pump on, the sampling line was purged. Valve B was then closed and valve C opened to evacuate the sampling lung, making sure that the vacuum did not exceed 5" Hg. At a vacuum of 4" Hg, valve A was opened and the sample bag filled with emissions from the duct. Valve A was then closed and valve B opened. The pump was shut off and the line to the pump disconnected. Valve C was opened to bring the lung to atmospheric pressure and the bag was removed from the drum and quickly capped. Each bag sample was transported to the laboratory at ORF for analysis on the same day that the sample was collected.

A.5.2.1 Particulate train. Samples of particulate emissions were collected using a Joy Manufacturing Company EPA (Model CU-2) train, shown schematically in Figure A.5. This equipment conforms to that recommended by both the Ontario Source Testing Code [A.1] and the Environment Canada Code [A.2]. Prior to each test a velocity traverse was conducted across the duct through each port to determine an average gas velocity. Gas temperatures were also recorded at each sample point.

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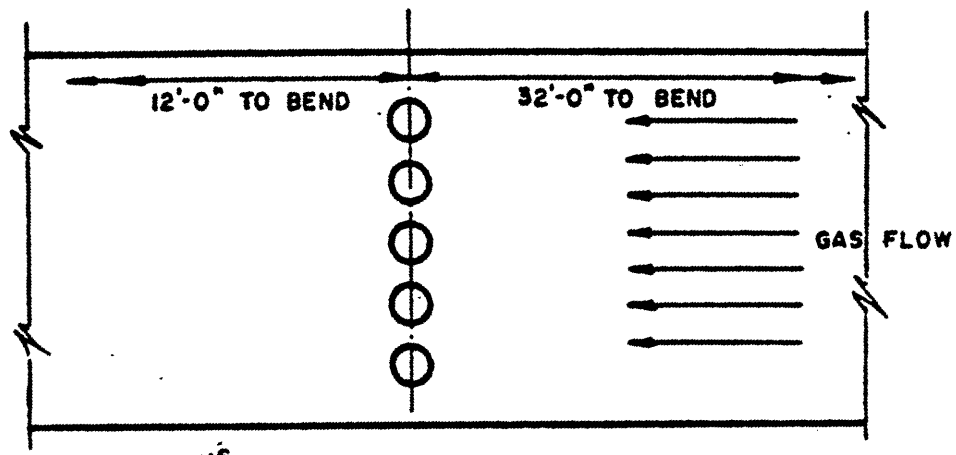

FIGURE A.2. SCHEMATIC OF PORT LOCATIONS

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108.9 x	110.6 x	118.6 x	118.6 x	117.6 x	114.7 x	107.8 x	103.2 x
92.5 x	107.8 x	112.0 x	113.3 x	110.6 x	110.6 x	108.9 x	107.8 x
78.2 x	89.2 x	92.6 x	91.9 x	94.5 x	100.2 x	102.0 x	104.9 x
72.5 x	74.2 x	78.2 x	78.2 x	82.0 x	91.2 x	97.7 x	97.7 x
42.8 x	51.9 x	66.4 x	73.4 x	78.2 x	80.5 x	74.8 x	80.5 x

Velocity in feet per second

FIGURE A.3. GAS FLOW DISTRIBUTION AT SAMPLING POINTS

An Orsat analysis was made to find the concentrations of CO, CO_2, O_2 and N_2 in the gas stream and a gas moisture determination was carried out using an established procedure [A.1]. With the preliminary data obtained, the isokinetic sampling rate was calculated using known standard equations [A.1].

For each particulate test, sampling was made for five minutes at each of the eight points across the duct through the five ports. Specified data [A.1] were recorded every 2.5 minutes on a test data sheet. The high flow rates encountered at the far wall of the duct and across the top of the duct necessitated use of probe nozzles of diameter less than 0.25 inches. Nozzles of diameter 0.219 inches and 0.188 inches were used during certain tests.

At the conclusion of a test the glass fibre filter was removed from its holder and placed in a labelled petri dish. The volume of water in the impingers was measured and the contents transferred

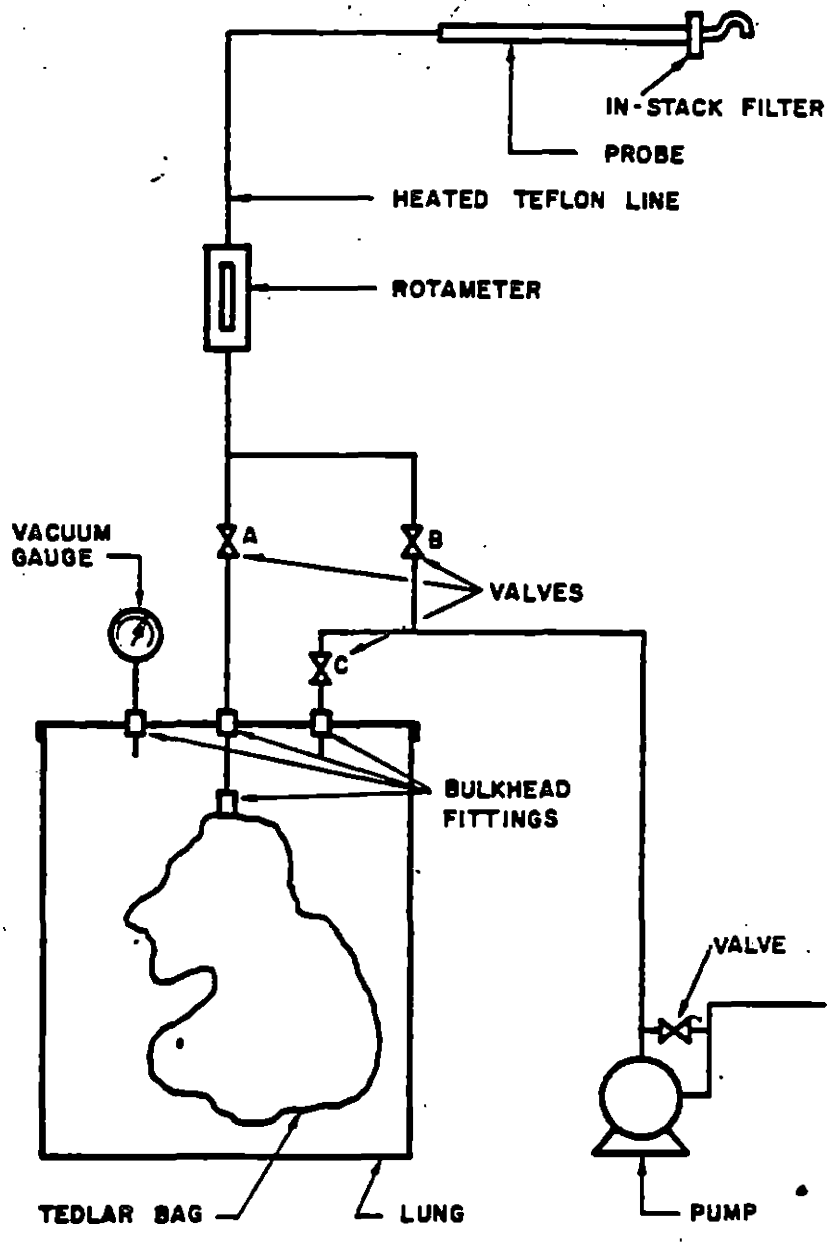

FIGURE A.4. GRAB BAG SAMPLING EQUIPMENT

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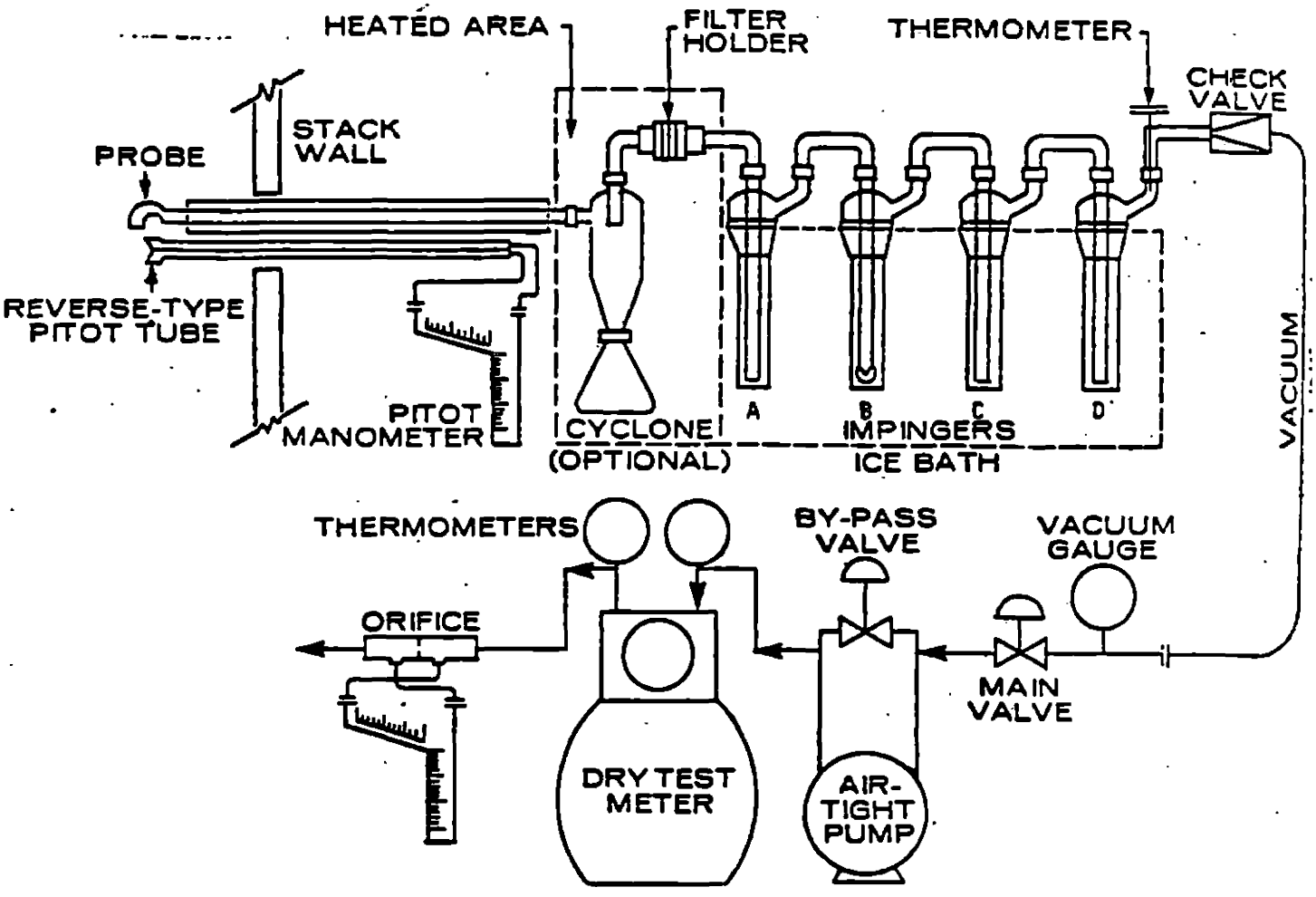

FIGURE A.5. PARTICULATE SAMPLING TRAIN

to polyethylene bottles, which were then labelled. The probe and nozzle were rinsed with distilled water as the inside of the probe was carefully brushed. The rinsings were collected in a polyethylene bottle. The glassware between the end of the probe and top of the filter holder was washed with distilled water and these washings added to the probe rinse. The bottom of the filter holder and glassware between filter and impingers was also washed and the contents added to the impinger catch.

After filtering the probe rinse, drying and weighing the insoluble particulate material, weighing the reconditioned filter, and determining the soluble portion of particulates in the probe rinse by aliquot evaporation, the total weight of collected particulate material was obtained. The moisture removed from the sampled gas was found by adding the gain in weight of the silica gel to the volume of additional water collected in the impingers. The volume of gas sampled was corrected to standard conditions and the particulate loading and emission rate calculated by use of appropriate equations [A.1].

A.5.2.2 Gaseous train. It was originally intended to sample for gaseous organic chloride compounds using the EPA-type particulate train, with specific absorbents replacing water in the impingers. Due to the high flow rates (0.5 - 1.0 cfm) required for isokinetic sampling, however, it was considered that the collection efficiency of any absorbent for volatile organic compounds would be very low. An experimental program was, therefore, devised and carried out at ORF to evaluate collection methods and develop a suitable sampling train for gaseous organic chlorides. Details of this study, performed under contract to the Ontario Ministry of the Environment, are given in Appendix H. Data obtained which are relevant to this section are described below.

A particulate train was set up in the laboratory and heated air was pulled through the complete system at a flow rate of 0.5 cfm. Water was placed in the first impinger and solvents such as xylene, toluene and decane, containing a few ppm of $CHCl_3$, CH_2Cl_2 or $CHCl_2CH_2Cl$, were placed in the second impinger. The third impinger was left empty and the fourth contained silica gel. After a period of three to four hours, the time anticipated for a particulate test, the impingers were

examined with respect to solvent volume and organic chloride concentration. In all cases, it was found that the loss of chloride compounds was considerable. For the polar solvents, such as toluene or xylene, the chloride concentration was retained but the total loss of solvent plus chlorides was in the range of 50%-70%. For the non-polar solvents, such as decane, the volume loss of solvent was negligible but the chloride loss was in the range of 60%-90%. Even if efficient collection of trace organic chlorides from the gas stream by specific solvents were possible, these compounds would not be retained in solution at gas flow rates of 0.5 cfm or higher.

Recent studies have shown that collection and retention of trace organic compounds is possible using specific adsorbent materials [A.3]. Inert materials, such as the Chromosorbs, are considered to have certain advantages over activated carbons in that water vapour present in the gas does not hinder organic compound adsorption, and adsorbed compounds are readily removed by thermal desorption. Experiments using the particulate train with Chromosorb 102 or activated carbon in the third impinger were carried out, passing heated air containing a few ppm of $CHCl_3$ through the system at a flow rate of 0.5 cfm. Neither adsorbent removed more than 70% of the $CHCl_3$ initially and, after about thirty minutes, almost all of the $CHCl_3$ was passing through the system. It was concluded, therefore, that efficient collection and retention of volatile organic compounds was not possible with gas flow rates of 0.5 cfm or higher and the particulate train could not be used for this purpose.

After further studies in the laboratory with both Chromosorb 102 and activated carbon, the sampling train for gaseous organic compounds depicted in Figure A.6 was constructed. Tests made with an air stream containing 15 ppm of $CHCl_3$ showed that either adsorbent would remove better than 95% of the $CHCl_3$ over a sampling period of four hours. Chromosorb 102 was selected on the basis of the advantages previously mentioned.

A 47 mm fibreglass filter was placed directly behind the probe nozzle to remove particulate material at the duct gas temperature. The sample gas was passed through midget impingers containing water and

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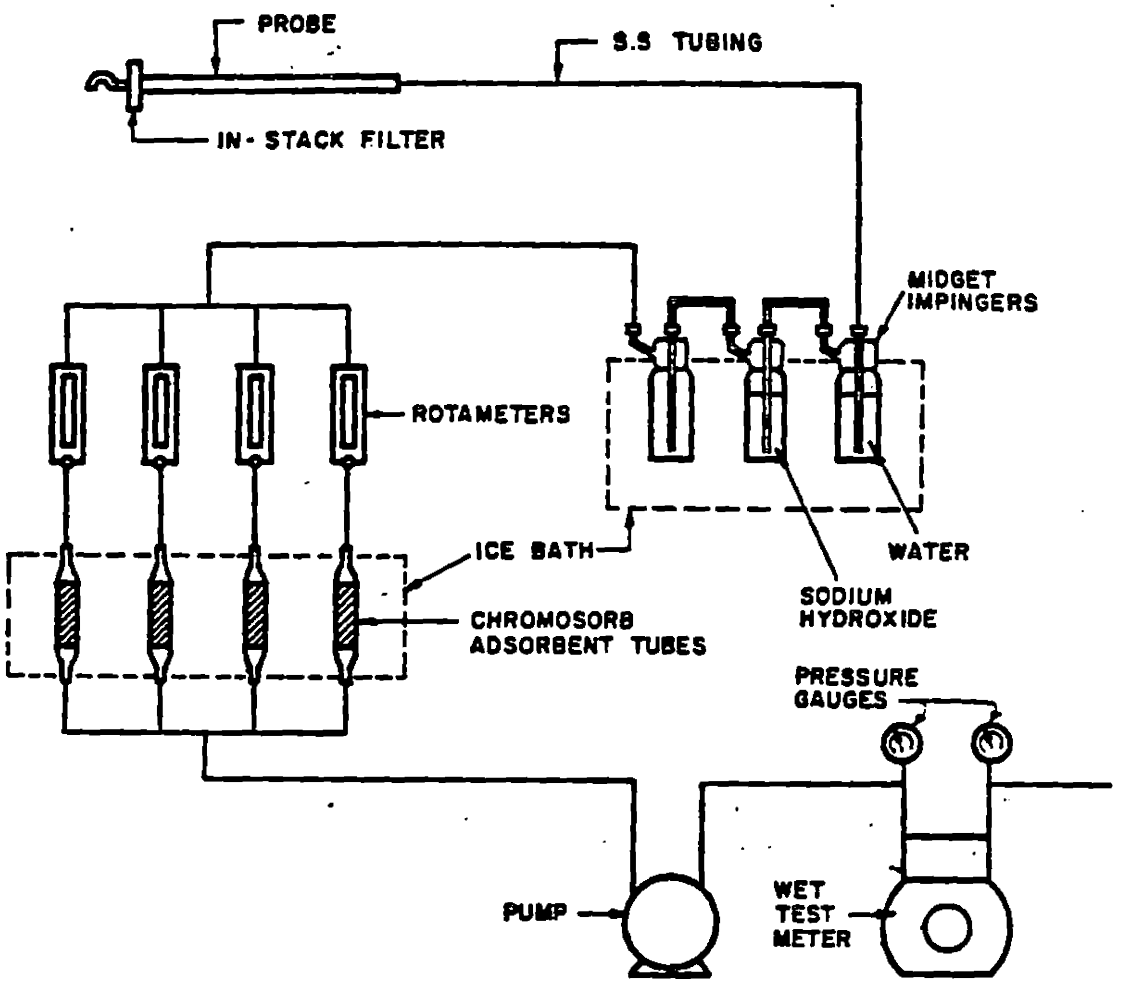

FIGURE A.6. GASEOUS SAMPLING TRAIN

caustic soda (5% solution), respectively, to remove any HCl and Cl_2 present in the kiln emissions. After the impinger, the gas was filtered through four Chromosorb adsorbent traps placed in parallel at a flow rate controlled by rotameters. A flow rate of 250 ml per minute was selected for each trap, giving a total flow of one litre per minute through the train. The total flow over each test period was also monitored by a wet test meter placed after the pump. Impinger solutions and adsorbent traps were maintained at ice temperature to effect a better collection of chloride compounds.

After each test the in-stack filter and impinger solutions were stored in labelled containers. The adsorbent traps were removed, capped and labelled. The probe was rinsed and the rinsings placed in a polyethylene bottle. All samples were then transferred directly to the ORF laboratory for analysis. The gaseous sampling train was operated simultaneously with the particulate sampling train for each test.

A.6 Organic Chloride Analyses

The methodology used to collect kiln emission samples, in baseline or waste burn test periods, provided four distinct types of samples for analysis of chlorinated organic compounds. These sample types and the analyses required were:

- chlorinated waste feeds for compositional analysis;
- grab bag samples for any chlorinated organic species;
- Chromosorb adsorbent samples for volatile low molecular weight organic compounds; and,
- solvent extracts of filters and solutions for noncombusted waste components.

A.6.1 Sample preparation

Waste feed. Samples of the prospective WBA feed material were supplied in advance of the test burn for analyses. When the test period arrived, however, insufficient quantities of some components were available to make up the specific blend of waste feed. The composition of material actually delivered to SLC was, therefore, different from the sample supplied to ORF in advance. In order to obtain a true compositional analysis of the material being supplied to the kiln, and to determine

feed consistency, aliquots of the waste feed were collected on specific sampling days during the burn.

Grab bag. Emission samples collected in Tedlar bags were analyzed directly for gaseous chlorinated hydrocarbons by injecting syringe samples taken from the bag into a gas chromatograph. After direct analysis, the contents of each bag were drawn through a glass tube containing Chromosorb 102 adsorbent by means of a small pump. Any trapped organic compounds were then thermally desorbed from the adsorbent tube into an evacuated gas jar. The gas jar contents were then subjected to GC analysis.

Adsorbent tubes. Chromosorb 102, being readily available in amounts required for this study, was selected as a suitable adsorbent for low molecular weight organohalides. Experiments were performed in the laboratory to confirm the suitability and efficiency of this adsorbent for the collection of volatile organohalides from an air stream. Thermal desorption of adsorbed components into an evacuated gas jar was selected as a method for preparing samples for GC analysis. Initial tubes were prepared with fresh Chromosorb 102 from the bottle without conditioning. It was determined after the first baseline test period that conditioning of the adsorbent would be necessary to reduce the amount of bleed produced on heating which tended to produce excessive background noise during GC analysis.

Adsorbent tubes were made up by packing Chromosorb 102 in glass containers 11.5 cm in length and 11.0 mm inside diameter, using silanized glass wool plugs at either end for support. Tubes for the WBA and WBB burns were preconditioned by heating to 200°C and passing a stream of nitrogen at 40 ml/min through them for four hours. Chromosorb 102 used in tubes for the WBC and BLB tests was extracted with acetone in a Soxhlet for 18 hours and then treated at 240°C with nitrogen for 12 hours prior to use.

Adsorbed components on the Chromosorb 102 after each test were removed by thermal desorption into an evacuated gas jar of 500 ml capacity. The adsorbent tube and gas jar were connected by Teflon

tubing and the tube heated to a fixed temperature of 170°C using a heating tape controlled by a variable transformer. When the fixed temperature was reached the stopcock of the gas jar between the jar and the tube was opened, and heating of the tube continued for a further 15 minutes. The stopcock was then closed, the jar removed from the connecting tubing and taken outside the laboratory to fill up with clean air. Previous studies of thermal desorption using this removal technique in the laboratory have shown that recoveries in excess of 90% may be expected for adsorbents with adsorbed organohalides.

Solution and filter extracts. Pentane or hexane was used as an extractant for organic compounds from all filters and probe rinse insoluble fractions, using a Soxhlet apparatus. The same solvents were used to extract probe rinse solutions, and aqueous sodium hydroxide and impinger solutions, using a liquid/liquid partitioning procedure. The extracts were then dried over anhydrous Na_2SO_4, filtered, and concentrated by evaporation using a combination of rotary and Kontes tube heaters. The concentrate was made up to a known small volume with solvent for GC analysis.

Pentane was used as extractant for BLA, WBA and WBB test samples, since its high volatility would minimize sample loss of low molecular weight compounds during evaporation. Hexane was used as extractant for WBC and BLB test samples.

A.6.2 Sample analysis

All samples were analyzed by gas chromatography with flame ionization (FI) or electron capture (EC) detectors. Gas chromatography - mass spectrometric (GC-MS) analysis was performed on waste feed samples to confirm the identity of major components. The various conditions and columns used are summarized in Tables A.5 to A.7. The mass spectrometer used was an AEI MS-30 instrument equipped with an electron bombardment ion source. Between the GC and the MS the interface is of all glass design with a silicone molecular membrane. GC columns similar to those described in Tables A.5 to A.7 were used at approximately the same instrument conditions.

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TABLE A.5. GC ANALYSIS - SYSTEM A

Column	- Chromosorb 102 (80/100 mesh) 6' x 1/8" SS
Column Temperature	- 180°C
Injector Temperature	- 215°C
Detector Temperature	- 215°C
Detector	- FID and EC
Flow Rates	- N_2 at 40 ml/min Air and H_2 adjusted for maximum sensitivity
Range and Attenuation	- As required
Chart Speed	- As required

TABLE A.6. GC ANALYSIS - SYSTEM B

Column	- 15% SE 30 on Chromosorb W (AW; HDMS; 60/80 mesh) 12' x 1/4" SS
Column Temperature	- 60°C isothermal for 20 minutes then programmed at 10°C/min to maximum temperature
Injector Temperature	- 190°C
Detector Temperature	- 230°C
Detector	- FID
Flow Rates	- N_2 at 40 ml/min Air and H_2 adjusted for maximum sensitivity
Range and Attenuation	- As required
Chart Speed	- As required

TABLE A.7. GC ANALYSIS - SYSTEM C

Column	- 4% SE 30/6% QF 1 on Chromosorb W (HP; 60/80 mesh) 6' x 1/8" SS
Column Temperature	- 200°C
Injector Temperature	- 250°C
Detector Temperature	- 230°C
Detector	- Linearized EC
Flow Rates	- N_2 at 25 ml/min
Range and Attenuation	- As required
Chart speed	- As required

These conditions are used for routine PCB analyses. The same parameters were used for WBB waste feed except that an isothermal temperature of 155°C was maintained.

A.6.3 Blanks and standards

For trace analytical studies it is necessary to avoid contamination of samples at all stages of sample collection and preparation. Though extreme care was taken during the study it was not possible to pre-extract all hardware and chemical reagents used. Due to the high sensitivity of the EC detector to many compounds, some of the blank extracts, therefore, gave complex GC-EC profiles, which had to be subtracted as background from the sample chromatograms. The following blanks were obtained and analyzed for this purpose.

i) Particulate train:
   (a) Particulate filter + probe rinse filter + Soxhlet thimble.
   (b) Water

ii) Gaseous train:
   (a) In-stack filter + probe rinse filter + Soxhlet thimble
   (b) Water
   (c) Aqueous NaOH

iii) Solvents:
   (a) Pentane (100 ml concentrated to 1 ml)
   (b) Hexane (100 ml concentrated to 1 ml)

iv) Polyethylene containers: (a) Solvent extracts (100 ml concentrated to 1 ml)

Standard gas samples of various components of interest, such as CCl_4, $CHCl_3$, CH_2Cl_2 and 1,2-dichloroethane, were made by injecting 50 µl aliquots of these compounds into an evacuated 500 ml gas jar through a silicone septum. Clean air was then allowed to enter the jar to attain atmospheric pressure. The sealed gas jar, therefore, represented nominally a 100 ppm standard. Gas standards of lower concentration were made by dilution of the 100 ppm standard using a similar procedure. These standards were used immediately after preparation and were not retained for use on the following day.

Solution standards were made by weighing accurately known amounts of the components of interest and dissolving them in a known volume of pentane.

A.6.4 Concentration factors

Desorbed compounds from the adsorbent tubes were concentrated into a 500 ml gas jar. For each particular test, therefore, the concentration factor would be the volume of emission passed through the tube divided by 500 ml. The volumes sampled for each tube varied from 1.5 cubic feet to 3.22 cubic feet during the complete test program giving a range of concentration factors from 85 to 181. Thus, a concentration for a particular component of 1 ppm in the gas jar sample would mean a concentration of about 10 ppb in the kiln emission, assuming a 100 percent collection efficiency, and subsequent desorption of the adsorbent.

Most of the extracted samples were concentrated into a 2 ml volume of solvent. The following example illustrates how the concentration factors were determined for various components detected. Assume that CH_2Cl_2 was detected at a concentration of 1 ppm in the solvent extract. This corresponds approximately to a weight of 2 ug of the compound in 2 ml of solvent. The molecular weight of CH_2Cl_2 is 85. Therefore, 2 ug of CH_2Cl_2 at 70°C, the temperature at which the emission sample was measured, occupies a volume of:

$$\frac{2}{85 \times 10^6} \times 24 \text{ litres, or } \frac{2}{85 \times 10^6} \times \frac{24}{28.3} \text{ cubic feet.}$$

For test WBA 1, for example, a volume of 142.81 scf was sampled. Thus, the concentration of CH_2Cl_2 in the kiln emission is:

$$\frac{2}{85 \times 10^6} \times \frac{24}{28.3} \times \frac{10^6}{142.81} \text{ ppm or } 0.14 \text{ ppb.}$$

The concentration factor is therefore $\frac{10^3}{0.14} = 7140$.

Factors were calculated for feed compounds of lowest and highest molecular weight.

A.6.5 Sample chromatograms

Analysis for low molecular weight organohalides and noncombusted chlorinated organic compounds present in any collected samples was made using GC techniques only, by selecting appropriate GC parameters and using retention time data. No specific cleanup or separation procedures were performed in order to segregate components of interest from possible interfering compounds because, although GC profiles obtained were quite complex, very low concentrations of organic compounds were evident from the peak heights obtained for the attenuations used. Estimates of specific compound concentrations in waste burn samples were made by subtracting blank and baseline levels and comparing with a standard for that compound.

Waste feeds. GC-FID profiles for the three waste feed materials burned in this study are given in Figures A.7 to A.9. Identification of the main components in the respective waste feeds are presented in Tables 1, 2 and 3 in Section 5 of the report.

It was anticipated that the levels, if any, of uncombusted components in the stack emissions would be very low. Therefore GC-EC analysis was used to evaluate the organic solvent extracts of the various impinger samples from the sampling trains for the presence of any uncombusted components. Figures A.10 and A.11 represent GC-EC profiles for diluted waste feed material for WBB and WBC, respectively. WBB also contained approximately 50% o-chlorotoluene which has a weak response to the EC detector. Therefore, in this instance the solvent extracts were also analyzed by GC-FID in order to determine whether any uncombusted o-chlorotoluene was present.

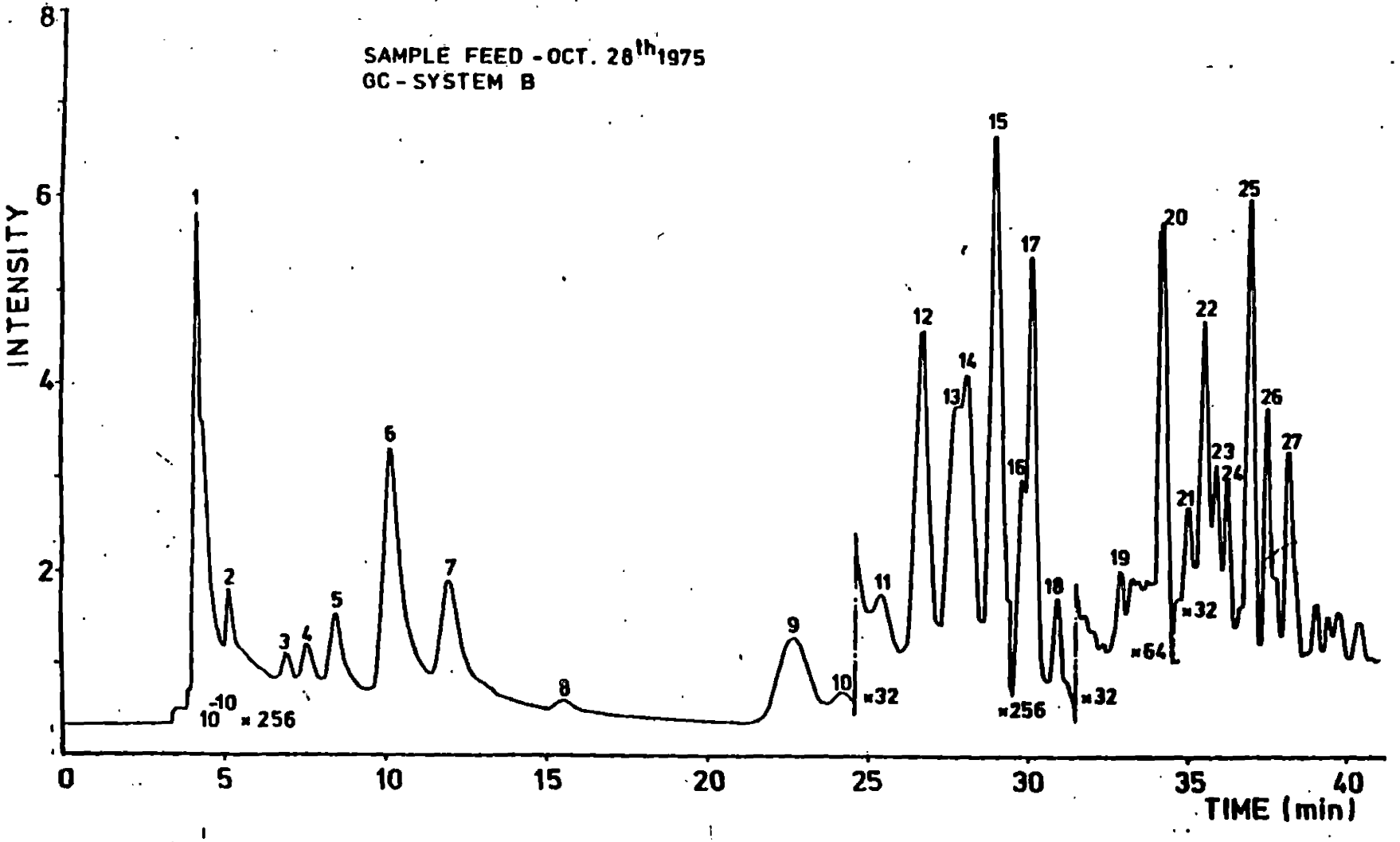

FIGURE A.7 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR CHLORINATED ALIPHATICS (WBA) SAMPLE FEED

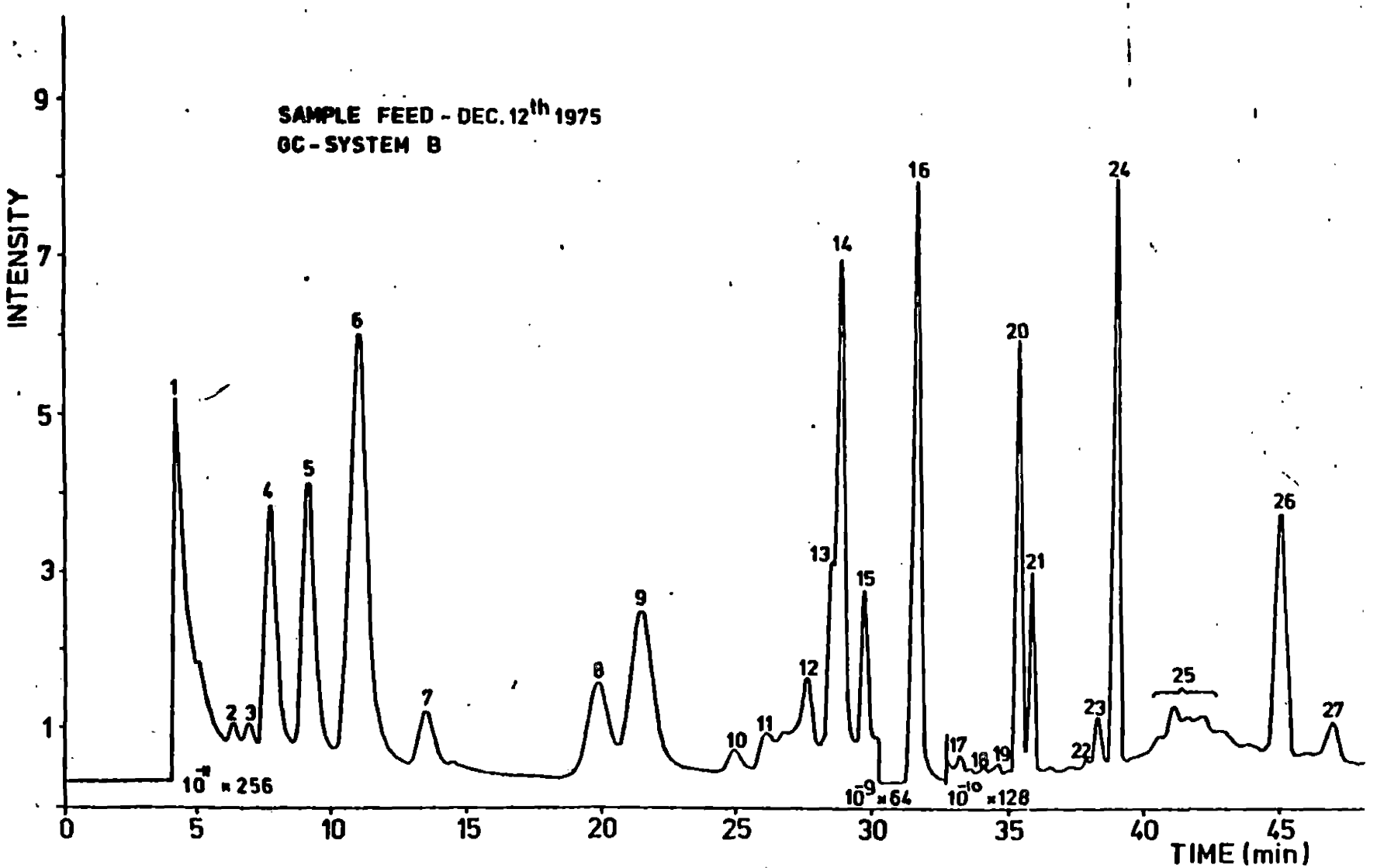

FIGURE A.8 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR CHLORINATED ALIPHATICS PLUS AROMATICS AND ALICYCLICS (WBB) SAMPLE FEED

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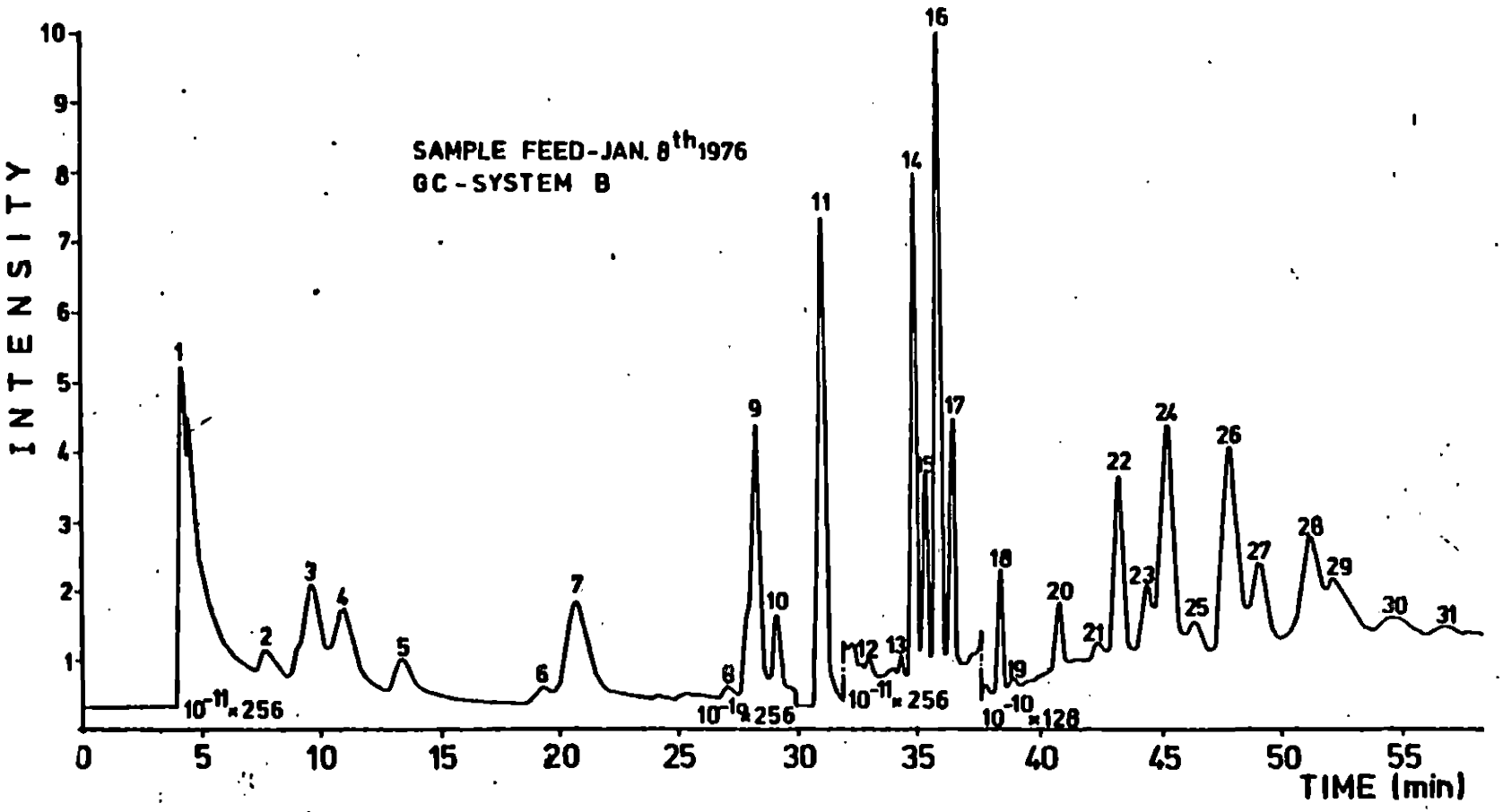

FIGURE A.9 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR CHLORINATED ALIPHATICS PLUS AROMATICS, ALICYCLICS AND POLYCHLORINATED BIPHENYLS (WBC) SAMPLE FEED

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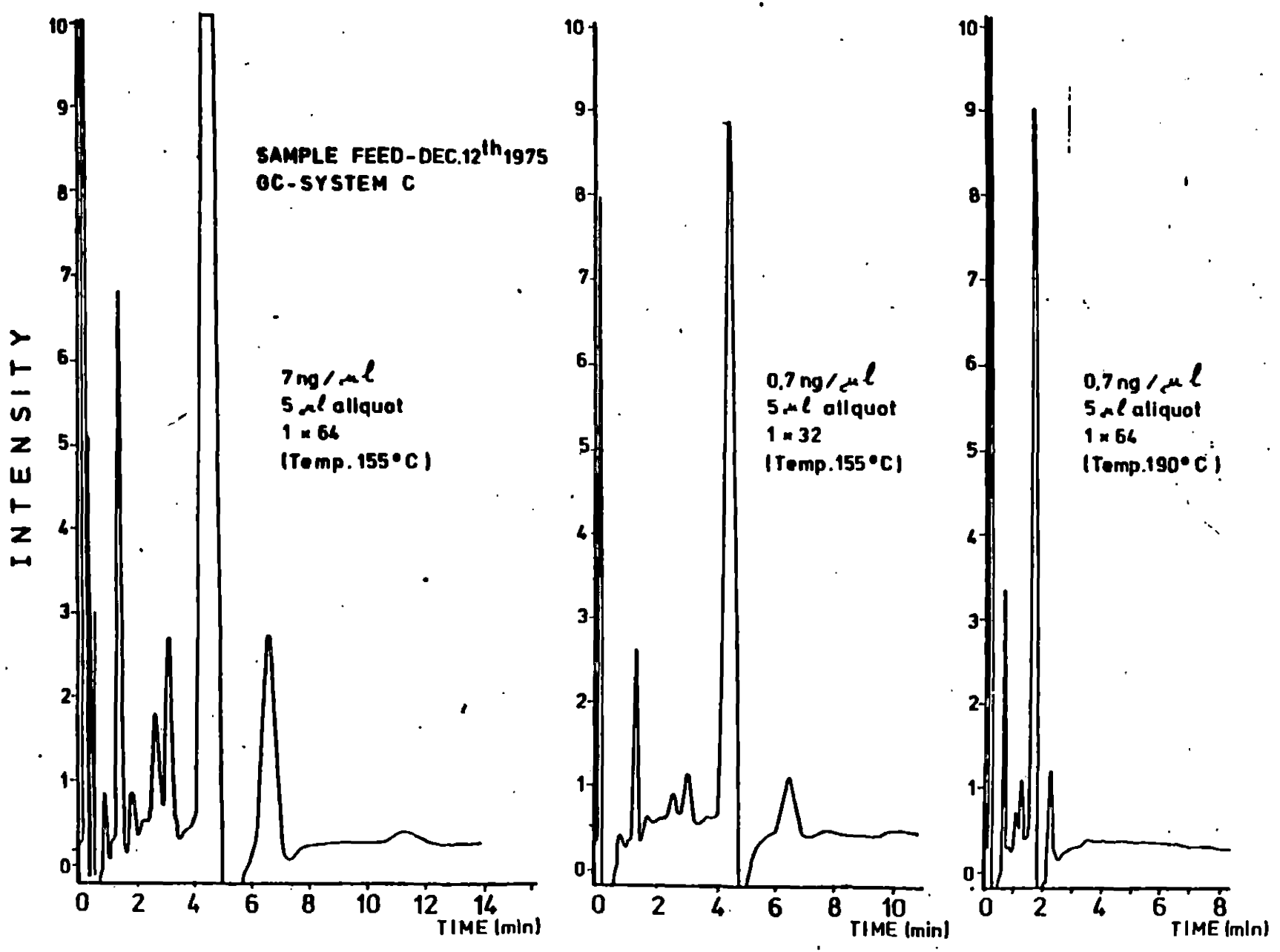

FIGURE A.10 GAS CHROMATOGRAPHIC PROFILES FROM ELECTRON CAPTURE DETECTOR FOR WBB SAMPLE FEED

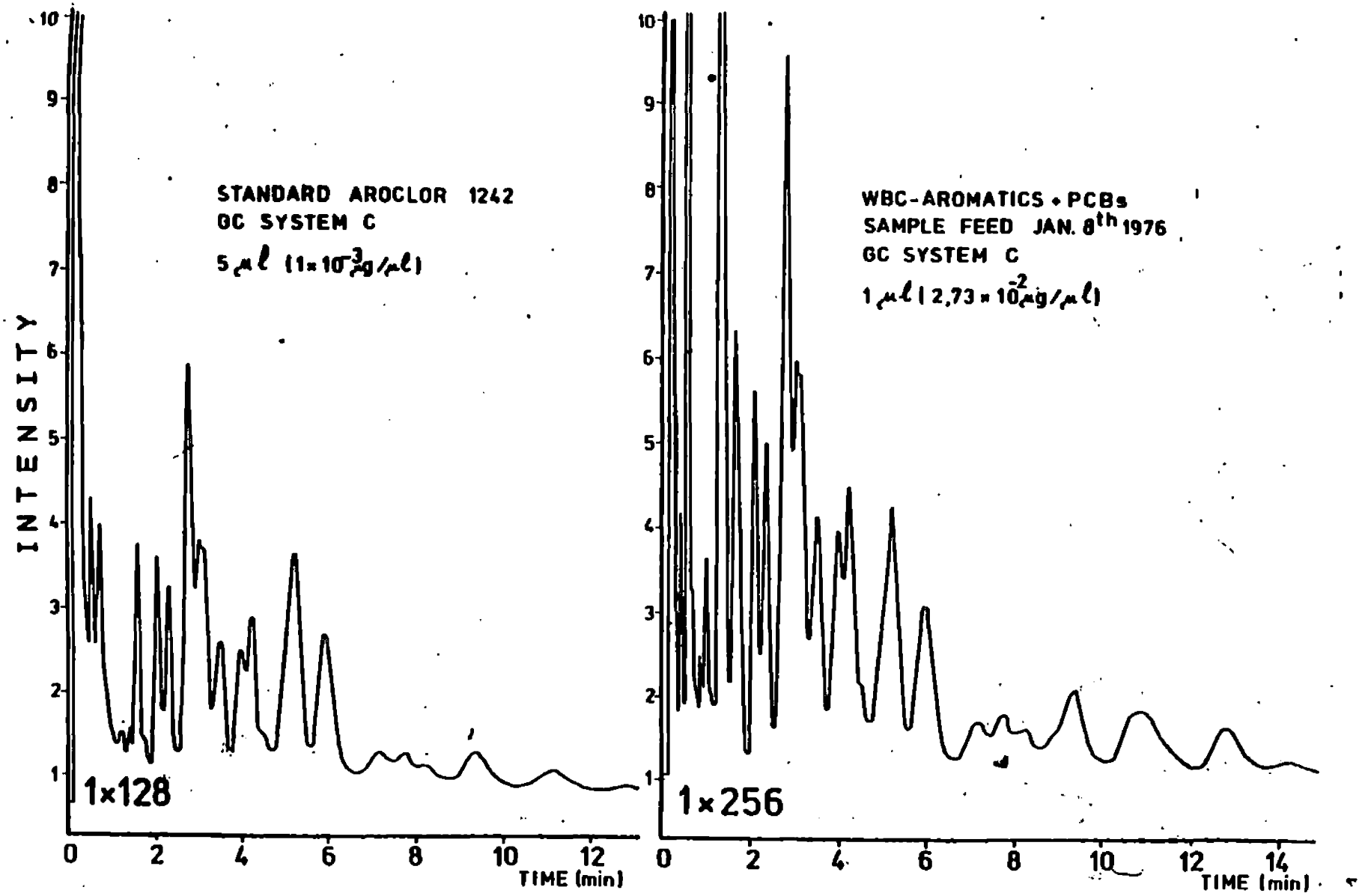

FIGURE A.11 GAS CHROMATOGRAPHIC PROFILES FROM ELECTRON CAPTURE DETECTOR FOR STANDARD AROCLOR 1242 AND SAMPLE FEED WBC

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Standards. Figure A.12 shows the GC-EC profile for the low molecular weight chlorinated hydrocarbons, e.g. CH_2Cl_2, $CHCl_3$, CCl_4 and 1,2-dichlorethene. Figure A.13 shows the GC-FID profile for the same compounds to indicate the greater sensitivity of the EC detector.

A GC-EC profile for 5 ng of standard Aroclor 1242 injected into the column is shown in Figure A.11.

Waste Burn Samples. Figure A.12 shows GC-EC profiles for desorbed gas samples for BLB and WBC test samples. The main difference between the samples is in the intensity of the peaks of interest.

The GC-EC profiles for all the solvent extract samples showed the presence of small peaks. When the profiles were compared to those obtained from the BLA samples and the various control blanks (cf. Section A.6.3), no peaks peculiar to the waste burn samples were detected. BLB samples became contaminated with WBC feed material and were discarded.

In most instances, the EPA impinger extracts showed the largest response to the EC detector. Figures A.14 and A.15 show GC-EC profiles for the organic solvent extracts of the EPA impinger samples obtained for BLA-T3 and WBC-T3, respectively. Profiles obtained for the two samples are quite similar. There is a large EC response occurring as an unresolved peak in the early portion of the chromatographic profile. This limited the sample size that could be used for injection, and restricted the use of high sensitivity settings on the gas chromatograph.

It is normal practice when analysing for PCB's to perform cleanup and separation procedures in order to segregate the PCB's from interfering components and thus facilitate their analysis. Such a cleanup and separation procedure was performed on WBC-T3 using Florisil adsorbant (27) in order to determine whether the early unresolved peak (Figure A.15) could be removed. After cleanup, it was possible to use a larger aliquot for injection and higher sensitivity settings on the chromatograph. The GC-EC profile of the cleaned up WBC-T3 sample is shown in Figure A.16.

The GC-EC profile shown in Figure A.16 was obtained on an organic solvent extract of a sample that should contain PCB's if any were present in the kiln emissions. The profile shows the presence of a few small peaks. When compared with the Standard Aroclor profile (Figure A.11),

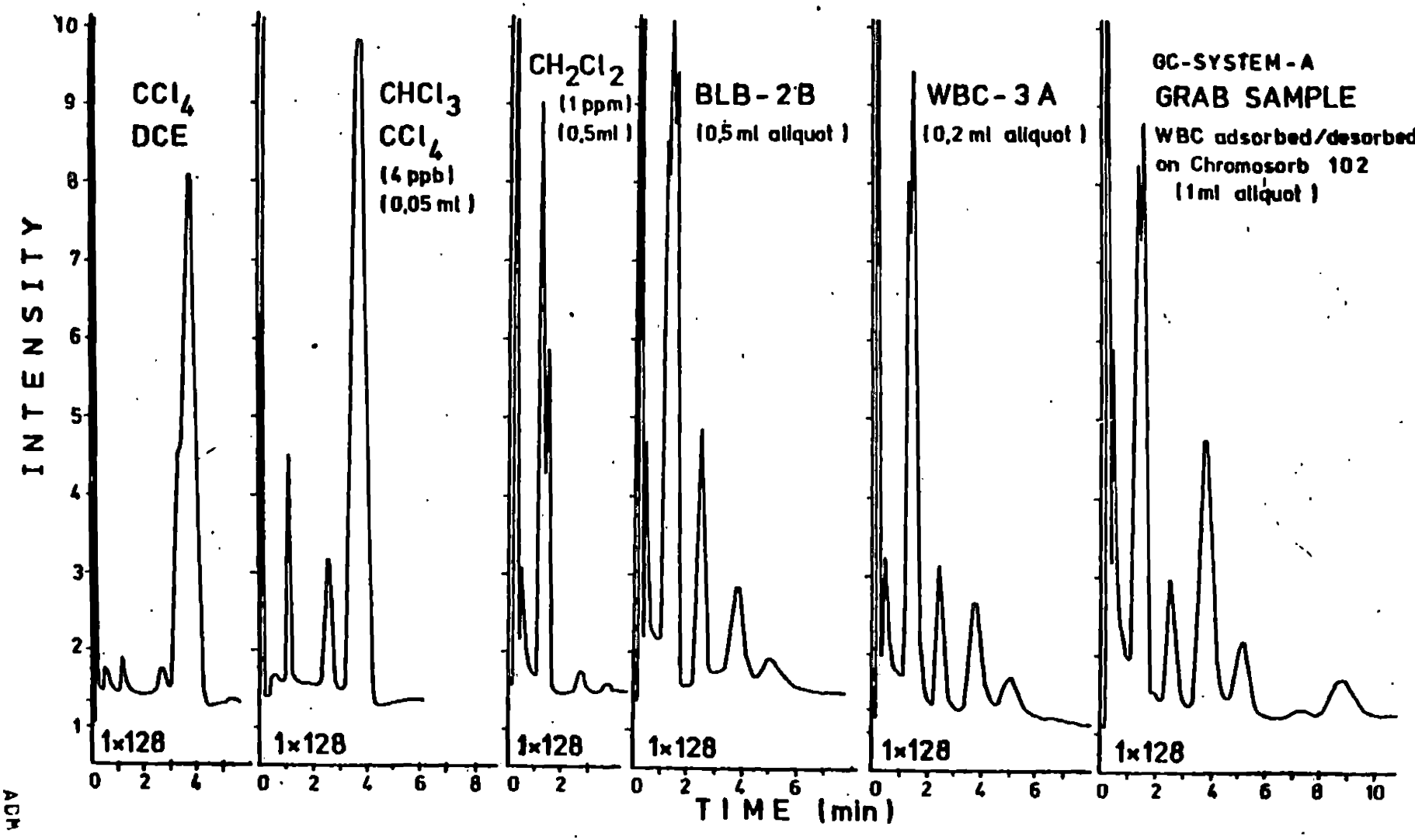

FIGURE A.12 GAS CHROMATOGRAPHIC PROFILES FROM ELECTRON CAPTURE DETECTOR FOR LOW MOLECULAR WEIGHT CHLORINATED HYDROCARBONS AND FOR BLB AND WBC TEST SAMPLES

ACM C0818E3

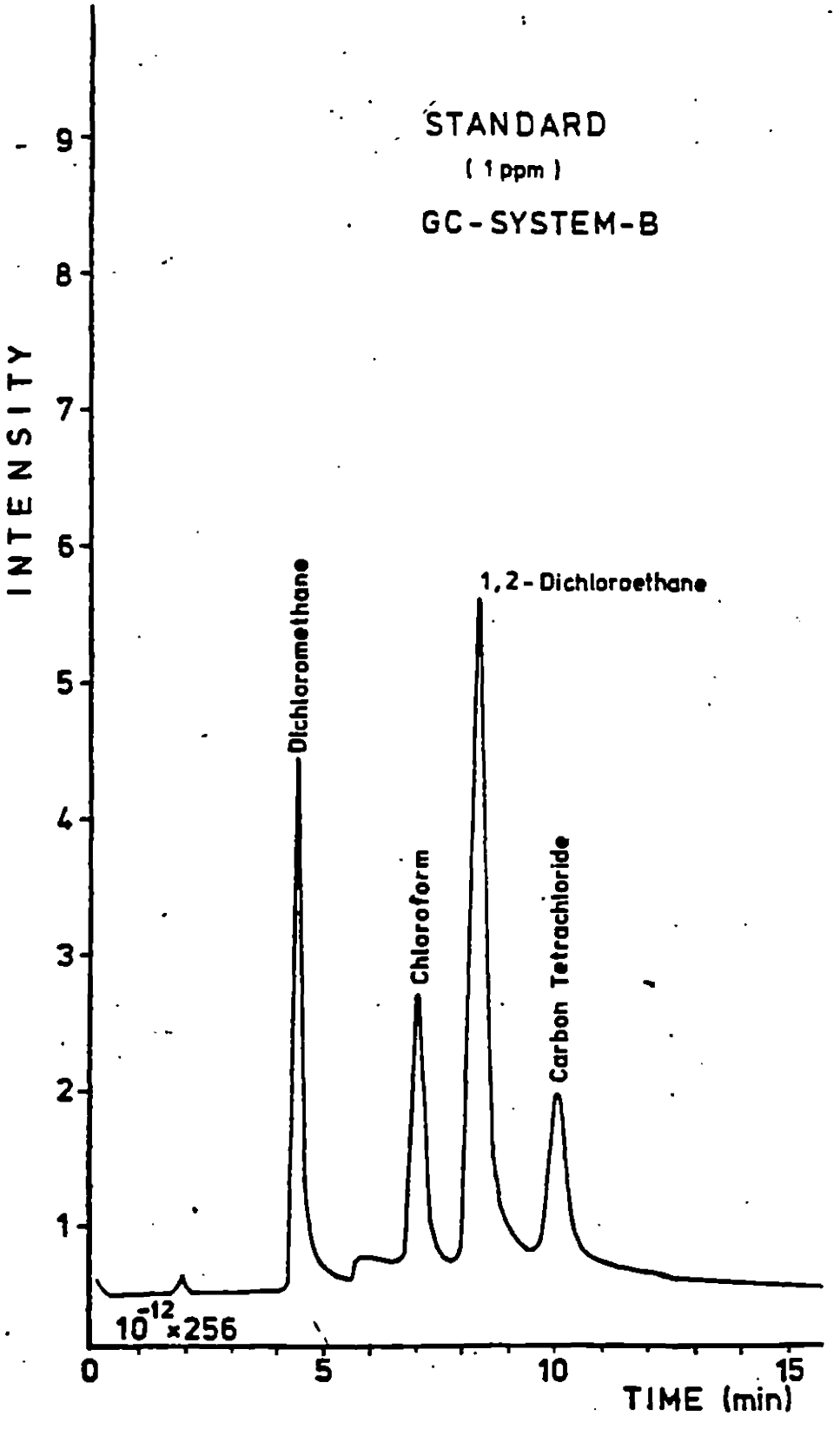

FIGURE A.13 GAS CHROMATOGRAPHIC PROFILE FROM FLAME IONIZATION DETECTOR FOR LOW MOLECULAR WEIGHT HYDROCARBONS

ADM CC&I64

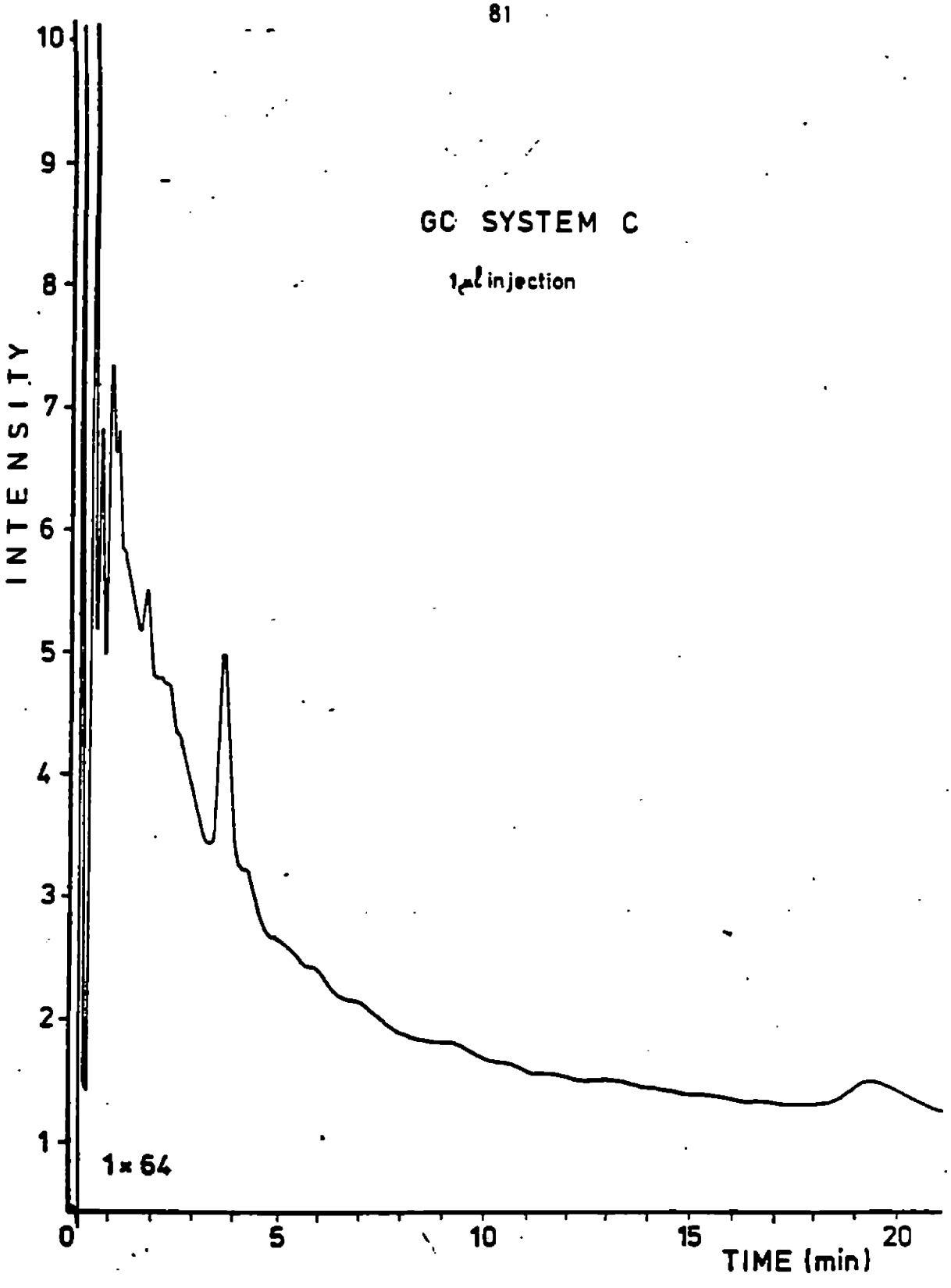

FIGURE A.14 GAS CHROMATOGRAPHIC PROFILE FROM ELECTRON CAPTURE DETECTOR FOR IMPINGER EXTRACT FROM BLA TEST 3

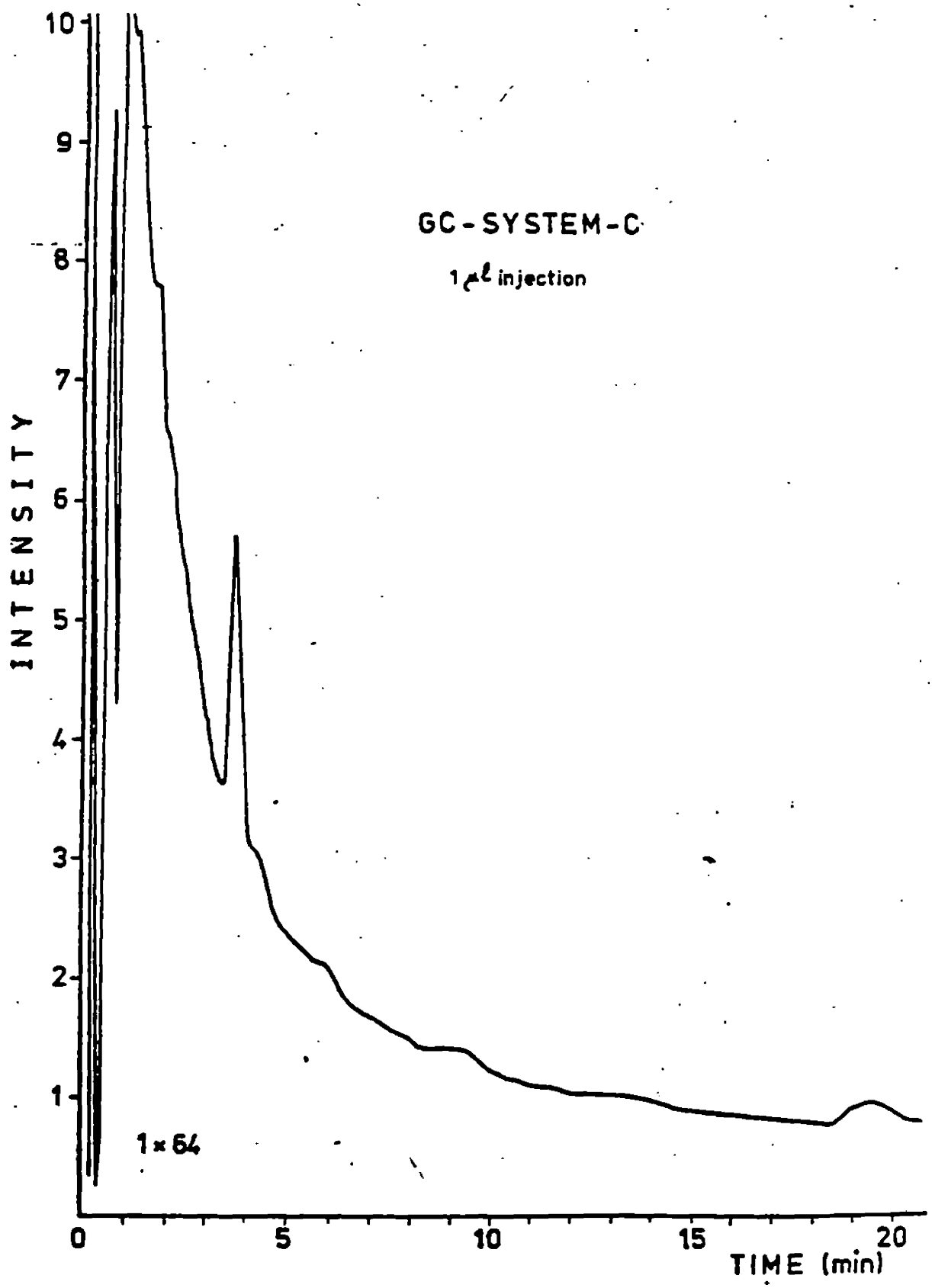

FIGURE A.15 GAS CHROMATOGRAPHIC PROFILE FROM ELECTRON CAPTURE DETECTOR FOR IMPINGER EXTRACT FROM WBC-TEST 3

ACM CC8186

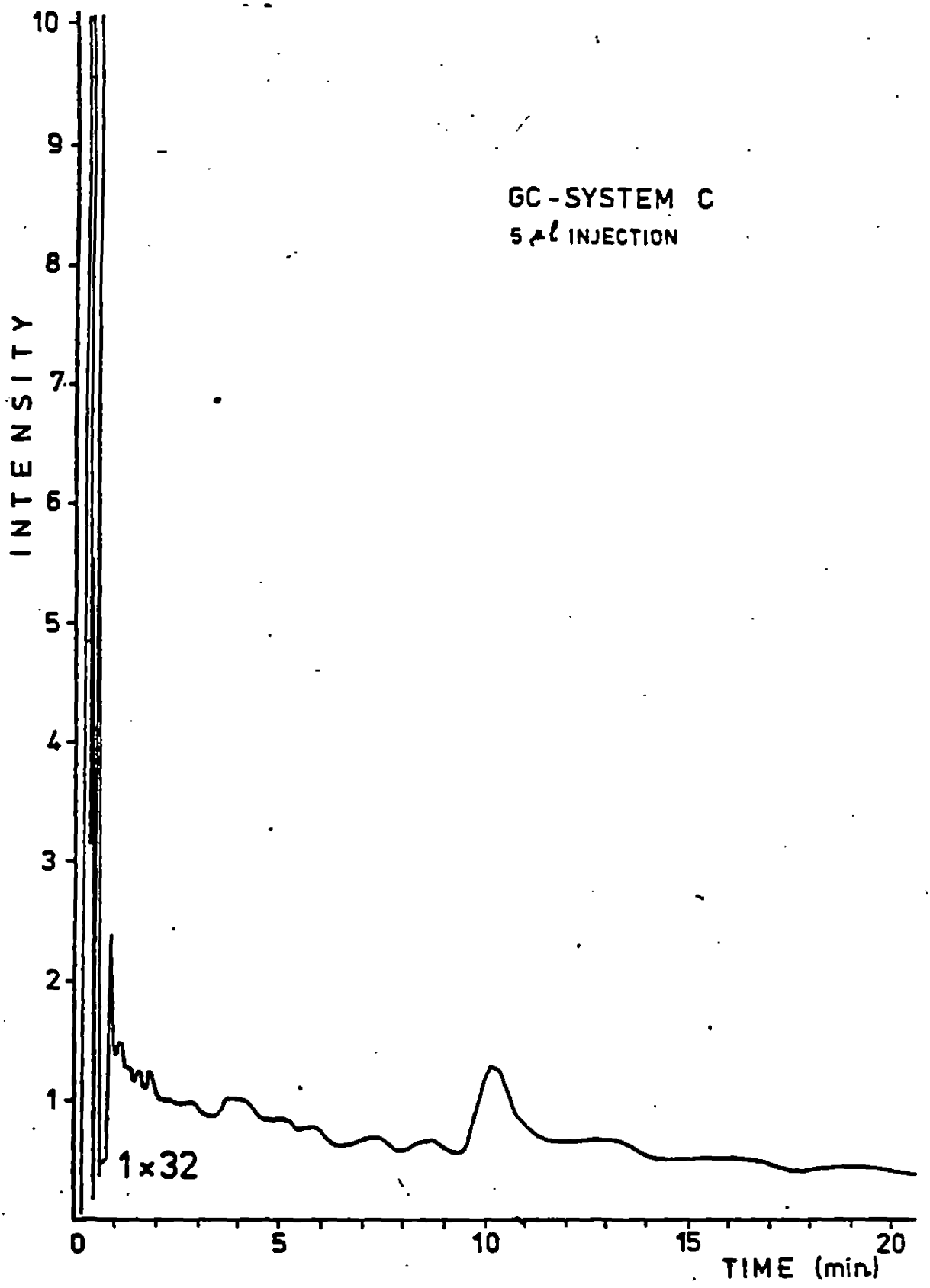

FIGURE A.16 GAS CHROMATOGRAPHIC PROFILE FROM ELECTRON CAPTURE DETECTOR FOR IMPINGER EXTRACT FROM WBC TEST 3 AFTER CLEANUP AND SEPARATION

ALM C08187

and taking into account that the extract represents a >7000 concentration factor, if any of the peaks in Figure A.16 represent PCB components the levels must be extremely low.

A.7 Analysis of Process Solids

For the purpose of obtaining a mass balance during the experimental chlorinated hydrocarbon burn, it was required to carry out chemical analyses of clinker, slurry feed and discard dust for chlorine and potassium. Sulphur was determined on process solids and the return dust samples were analyzed for changes which may have affected kiln operation.

X-ray fluorescence (XRF) analysis has been extensively used for determination of sulphur, potassium and chlorine in cement, cement raw materials and related materials, and was selected for use in this study.

A.7.1 Analytical procedures

Samples were prepared by grinding 10 grams of sample for 90 seconds in a SPEX Shatterbox with tungsten carbide containers and pucks. From this material a 1.25 inch diameter pellet at 8 tons pressure was made in SPEX aluminum sample caps.

For the X-ray fluorescence method to be applied, there must be a linear relationship between elemental concentration (over the full range of concentration required) and the measured fluorescence intensity. The slope of the line representing this relationship then can be used directly as a calibration constant, usually in the form of the ratio, counts per second:percent element. When a calibration line is generated by known additions of the test element to a material being analyzed ("spiking"), the line intercept gives the percent of the element present in the original sample prior to any additions.

In addition to linearity, reproducibility of the calibration constant is a prerequisite if it is to be applied across a range of materials having some degree of matrix variability. Both conditions were examined prior to the final development of the analytical procedure.

The calibration curves for chlorine content of clinker and raw meal-slurry feed were prepared by addition of standard lithium

ADM CCElec

chloride in alcohol solution to samples of these materials. Dust samples were analyzed by the standard Volhard method for calibration of the chlorine curve and the standard gravimetric method of precipitation with barium for calibration of the sulphur curve (Table A.8). For calibration of curves for sulphur in clinker and raw meal/slurry feed, determinations were made on a Leco Induction Furnace Model 523CS with Leco Automatic Titrator Model 517 (Table A.9). For calibration of the potassium curve, all potassium results, as well as those for sodium, were obtained from analyses on a Perkin-Elmer Model 460 Atomic Absorption Spectrophotometer in the flame emission mode (Table A.10).

Examination of these samples yielded linear calibration relationships between X-ray fluorescence count rates and percent element. The least squares computations for each set of data gave the slopes, intercepts and regression (correlation) coefficients listed in Table A.11.

TABLE A.8. GRAVIMETRIC DUST ANALYSES

Dust Type	Date	% Cl	% SO_3
Discard	19/10/75	2.00	-
"	11/11/75	2.08	3.17
"	31/11/75	5.97	2.36
"	4/12/75	2.89	6.53
"	5/12/75	7.11	12.12
"	6/12/75	4.69	7.27
"	7/12/75	6.18	6.90
"	5/ 1/76	4.71	5.08
"	6/ 1/76	3.72	4.23
"	9/ 1/76	4.43	4.18
"	14/ 1/76	0.46	4.65
"	16/ 1/76	0.90	4.32
Return	5/12/75	2.11	7.35
"	13/12/75	4.34	4.22
"	1/ 1/76	2.10	4.99
"	18/ 1/76	1.00	5.66

TABLE A.9. RESULTS FROM LECO INDUCTION FURNACE ANALYSES

Material	Date	% SO_3 (Total S as)
Clinker	19/10/75	0.93
"	21/10/75	1.34
"	23/10/75	0.75
"	31/10/75	0.30
"	1/11/75	0.16
"	5/11/75	0.66
"	8/12/75	0.93
"	31/12/75	1.39
"	1/ 1/76	1.43
"	11/ 1/76	1.04
"	20/ 1/76	1.42
Slurry Feed	13/10/75	0.45
"	20/10/75	0.42
"	27/10/75	0.41
"	9/11/75	0.45
"	6/12/75	0.52
"	9/12/75	0.48
"	13/12/75	0.60
"	14/12/75	0.55
"	31/12/75	0.43
"	3/ 1/76	0.47
"	8/ 1/76	0.46
"	21/ 1/76	0.47

TABLE A.10. RESULTS FROM ATOMIC ABSORPTION ANALYSES

Material	Date	% K_2O	% Na_2O
Discard Dust	11/11/75	6.36	0.32
"	31/11/75	10.30	0.39
"	4/12/75	7.14	0.36
"	6/12/75	8.23	0.44
"	7/12/75	9.96	0.45
"	5/ 1/76	8.12	0.43
"	6/ 1/76	6.43	0.34
"	9/ 1/76	7.94	0.39
"	14/ 1/76	4.84	0.35
"	16/ 1/76	4.18	0.34
Return Dust	5/12/75	7.79	0.42
"	13/12/75	5.54	0.41
"	1/ 1/76	6.02	0.41
Clinker	19/10/75	1.32	0.23
"	21/10/75	1.61	0.25
"	23/10/75	1.00	0.20
"	31/10/75	0.54	0.21
"	1/11/75	0.40	0.21
"	5/11/75	1.01	0.21
"	8/12/75	0.64	0.20
"	31/12/75	1.18	0.21
"	1/ 1/76	1.31	0.24
"	11/ 1/76	1.10	0.22
"	20/ 1/76	1.45	0.26
Slurry Feed	13/10/75	0.93	0.19
"	20/10/75	0.93	0.22
"	27/10/75	0.89	0.18
"	9/11/75	0.88	0.20
"	6/12/75	0.91	0.19
"	9/12/75	0.90	0.22
"	31/12/75	0.90	0.18
"	3/ 1/76	0.91	0.22
"	8/ 1/76	0.93	0.19
"	21/ 1/76	0.94	0.22

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TABLE A.11. LEAST SQUARES DATA FOR CALIBRATION LINES

Material	Element	Correlation Coefficient	Slope	Intercept
Raw Meal + Slurry Feed	Potassium (as K_2O)	0.9172	27128	-0.01
	Chlorine	0.9995	5260	0.060
	Sulphur (as SO_3)	0.9913	739	0.27
Clinker	Potassium (as K_2O)	0.9829	24980	-0.01
	Chlorine	0.9999	4781	0.011
	Sulphur (as SO_3)	0.9917	400	-0.23
Dust	Potassium (as K_2O)		3166	-0.12
	Chlorine	0.9893	1927	-0.14
	Sulphur (as SO_3)	0.9548	278	-0.10

A.8 Determination of Heat Value, Chlorine Content and Sulphur Content in No. 6 Fuel

The heat value was determined using standard methods on a Parr Calorimeter Model 1241 equipped with Parr oxygen bomb Model 1108. Sulphur was determined using the standard barium precipitation method on the washings from the bomb. Where chlorine content was required, the washings were analyzed for chlorine by the standard Volhard method.

A.9 Determination of Heat Value and Chlorine Content in Chlorinated Hydrocarbons

The heat value was determined on a Parr calorimeter model 1241 equipped with Parr oxygen bomb model 1108 following standard operating procedures for determining heat value of oil. Due to the corrosive nature of the combustion products, it is recommended that the chlorinated materials be diluted with standard oil. It has been found that, while corrosion of the interior of the bomb is extensive, burning these materials without dilution gives similar results. Time between weighing and igniting is extremely important due to the volatile nature of some of these compounds.

After igniting and determining the heat value of the chlorinated material, the interior of the bomb is thoroughly washed with distilled water into a volumetric flask. Aliquots of the proper size for the chlorine content expected were taken. Nitric acid is added to allow a more distinct end point, and the chlorine is determined by the standard Volhard titration.

REFERENCES

A.1 Ontario Ministry of the Environment, Source Testing Code. January, 1973.

A.2 Standard Reference Methods for Source Testing: Measurement of Emissions of Particulates from Stationary Sources. Environmental Protection Service Report EPS 1-AP-74-1, Air Pollution Control Directorate, Environment Canada, February, 1974.

A.3 Pellizan, E.D., J.E. Bunch, and B.H. Carpenter. Env. Sci. Technology 9 (6), 552-560 (1975).

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APPENDIX B

ANALYTICAL DATA, CALCULATION AND DETAILS OF EXPERIMENT ON THE SUSPENSION PREHEATER KILN

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APPENDIX B

ANALYTICAL DATA, CALCULATION AND DETAILS OF EXPERIMENT ON THE SUSPENSION PREHEATER KILN

B.1 Theoretical

The excellent article by Weber cited in the body of the report describes in detail the problem of alkali reduction in a suspension preheater kiln, and was used in preparing the following notes.

At material temperatures above 800°C in the rotary kiln, alkalies (K_2O and Na_2O) are volatilized from the material being burned and are carried along with the exit gases to the kiln inlet. These condense at gas temperatures below 900°C. In part, they are recaptured by the material, particularly in the preheater, and are thus carried back to the sintering zone, so that an internal alkali cycle is established. The alkalies are in part also precipitated at the transition from the preheater to the kiln.

Coatings thus formed interfere with material and gas flows and, in the most severe cases, completely plug the system.

In preheater kilns, the raw meal is heated in the finely divided condition in the gas stream and these particles act as condensation nuclei for the alkalies. Between 81 and 97% of the K_2O volatilized in the kiln is trapped in the preheater.

The greater the alkali cycle, and therefore the concentration of alkali in the gas, the more alkali will condense on the bottom ducts and cyclone stages. If the alkali is very volatile, accretions are likely to occur in the preheater. However, the alkali cycle can be reduced by the provision of a bypass, that is by drawing off a portion of the gas at the bottom of the preheater. (See Figure 3, Section 2 of the report.)

Of alkali which enters the kiln system with the raw meal, a proportion (ε_1) will be volatilized and the remaining ($1-\varepsilon_1$) will be discharged with the clinker. If the proportion of gas withdrawn through the bypass is V, then of the volatilized alkalies, the proportion $\varepsilon_1 \cdot V$ will be removed by the bypass. The remaining portion $\varepsilon_1 (1-V)$ will return with the feed, thereby giving rise to the internal cycle in the kiln.

The alkali in the internal cycle has a different volatility ε_2 than alkali from the raw meal which has not yet been volatilized. By defining total alkali including raw meal alkali into the kiln by K, then the quantity of alkali from the cycle alone is K-1. Of this quantity, $(K-1)\cdot\varepsilon_2\cdot V$ is removed by the bypass.

Equilibrium is attained when the total quantity of alkali input with raw meal and fuel is equal to the quantity output by the bypass and retained with the clinker. This is most easily determined by considering only alkali in the cycle. Entering the cycle is the volatile raw meal alkali = ε_1; leaving the cycle are a proportion in the clinker = $(K-1)\cdot(1-\varepsilon_2)$ and a proportion through the bypass = $[\varepsilon_1 + (K-1)\ \varepsilon_2)]\cdot V$.

By setting the quantities input and output from the cycle as equal, the equation may be solved to determine the amount of gas the bypass must remove to keep the alkali cycle from becoming excessive.

B.2 Experience at St. Lawrence Cement

At St. Lawrence Cement, samples are taken of the material between the Stage IV cyclone and the kiln inlet (see Figure 3), this material being called, not quite appropriately, "Stage IV dust". From experience at St. Lawrence Cement, it was known that a chloride content of 2.5% chlorine in this material (natural basis) is excessive. The quantity of gas required to be withdrawn by the bypass to maintain lower chloride levels was calculated on the assumption that the chloride volatilities were $\varepsilon_1 = 0.99$ and $\varepsilon_2 = 1.0$ (completely volatile). These quantities are given in Table B.1.

While the bypass was designed to remove the quantities of gas required for the program, attempts to reach this level resulted in excessive emissions of particulate matter from the bypass precipitator. These were attributed to excessive gas flows. To alleviate this problem, measures to increase cooling water and decrease the quantity of ambient air were undertaken, with limited success.

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TABLE B.1. PERCENT BYPASS GAS REQUIRED TO MAINTAIN CHLORIDE LEVELS

Chloride addition relative to clinker	% K_2O in clinker	Bypass percent required to maintain Stage IV Cl at: 1.56% or 2.0% nat. / ign.	2.0% or 2.56% nat. / ign.	2.5% or 3.2% nat. / ign.
0	1.31	2.1	1.6	1.3
0.05	1.24	4.6	3.6	2.9
0.10	1.18	7.1	5.5	4.4
0.15	1.11	9.6	7.5	6.0
0.20	1.04	12.1	9.4	7.0
0.30	0.91	17.1	11.7	10.6
0.40	0.77	22.2	17.2	13.8

B.3 Equation of Approximated Time for Equilibrium

It was essential to the success of the program to determine the time required to attain the equilibrium state. To obtain an approximation of the time required, and realizing that it is only an approximation since retention time in kiln and absorption phenomena influence this time, the following approach was taken:

$$\frac{dQ}{dt} = Cl_{RM} - Cl_{clinker} - Cl_{bypass}$$

where:

$\frac{dQ}{dt}$ = change in quantity with time (pounds/minute)

Cl_{RM} = chlorine/time in with raw meal (pounds/minute)

$Cl_{clinker}$ = chlorine/time out with clinker (pounds/minute)

Cl_{bypass} = chlorine/time out through bypass (pounds/minute)

Cl_{RM} and $Cl_{clinker}$ are approximately constant, hence they can be combined as:

$$I_{cl} = Cl_{RM} - Cl_{clinker}$$

and $Cl_{bypass} = VQ(t)$

where:

$Q(t)$ = quantity in transition chamber at time (t) in pounds

V = bypass valve proportion.

Then:

$$\frac{dQ}{dt} = I_{cl} - VQ(t)$$

Solving for time gives:

$$t = \frac{\ln [I_{cl} - VQ(t)]}{V} \frac{Q_0}{Q_F} \text{ minutes.}$$

Since $\ln 0 = \infty$, Q_F must be taken as a very small distance from the true equilibrium.

The sampling sequence at Stage IV was planned from this model.

B.4 Sampling and Analytical Methods

Analytical methods were those described in Appendix A. Samples of clinker, raw meal feed, bypass precipitator dust and conditioning tower dust were taken at two hour intervals. These were then blended into 24-hour composite samples. On the basis of the calculation in Section B.3, samples were taken from Stage IV at 3 to 10 minute intervals when attempting to start the chlorinated burn. These latter samples were analyzed individually.

B.5 Discussion

In both cases described, the bypass was operated to withdraw 9 percent of the gases from the preheater tower. This was the maximum attainable due to the emission rate of particulate matter. On the first attempt to burn chlorinated hydrocarbons, the quantity to yield 0.24 percent chlorine relative to clinker was fed starting at 09:38, June 3, 1975. Plugging of the duct between the kiln and the conditioning tower caused a bypass shutdown on June 5, 1975. It was not possible to maintain feed of chlorinated material to the kiln unless the bypass was functioning. On June 10, 1975 a second and similar attempt was started

at 11:20. The bypass again failed due to accretion on the duct on June 13, 1975. On the second attempt, sampling of Stage IV material was continued for a longer period on the basis of the first set of results.

It was realized with the failure that major revisions to the bypass system would be required to continue this experiment on the suspension preheater kiln.

B.6 Analytical Results

Analytical results are given in Tables B.2 through B.4. The raw meal feeds showed a gradual increase in both the content of chlorine and K_2O. The results from the clinker analysis (Table B.3) showed that the burning of chlorinated hydrocarbons resulted in a reduction in the K_2O content (June 3-5, 1975 and June 10-12, 1975).

The results of the analyses from Stage IV dusts (Table B.4) show that the chlorinated hydrocarbons were destroyed in the burning process. Chloride content of these samples increased while burning chlorinated wastes. This finding could not have resulted without breakdown of the hydrocarbons since the raw material is at too high temperature at this position in the preheater for the chlorinated hydrocarbons to condense upon it. By the methods described in Section B.3, the approximate time to equilibrium was calculated to be about 90 minutes. It was also expected that an additional time of approximately 20 minutes would be required to travel through the kiln. The actual curve is less steep and equilibrium is reached in about four hours. For the June 3, 1975 burn, the curve was extrapolated to the calculated equilibrium (Figure B.1). On June 10, 1975 samples were taken for a longer period. Although there are points above the calculated curve (Figure B.2), the data from June 11, 1975 show that equilibrium was reached; the higher values found indicate random sampling or analytical errors.

TABLE B.2. RESULTS FROM ANALYSES OF DRY PROCESS KILN RAW FEEDS

Date	% Cl	% SO_3 (Total S as)	% K_2O
30/5/75	0.067	0.60	0.92
31/5/75	0.069	0.60	0.95
1/6/75	0.073	0.60	0.93
2/6/75	0.071	0.60	0.93
3/6/75	0.074	0.60	0.93
4/6/75	0.082	0.60	0.95
5/6/75	0.079	0.60	0.96
6/6/75	0.094	0.62	0.98
7/6/75	0.087	0.60	0.97
8/6/75	0.093	0.60	0.97
9/6/75	0.088	0.58	0.97
10/6/75	0.084	0.60	0.95
11/6/75	0.092	0.60	0.98
12/6/75	-	NO SAMPLE	-
13/6/75	0.084	0.60	0.96
14/6/75	0.104	0.60	1.00
15/6/75	0.102	0.62	1.00

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TABLE B.3. RESULTS FROM ANALYSES OF DRY PROCESS KILN CLINKER

Date	Time	% Cl	% SO_2	% K_2O
30/5/75	Average	0.03	1.05	1.27
31/5/75	"	0.03	1.15	1.29
1/6/75	"	0.03	1.15	1.31
2/6/75	"	0.21	1.16	1.30
3/6/75	"	0.03	1.10	1.24
4/6/75	"	0.05	1.19	1.30
5/6/75	"	0.04	1.23	1.33
6/6/75	"	0.04	1.34	1.44
7/6/75	"	0.07	1.33	1.48
8/6/75	"	0.05	1.31	1.43
9/6/75	"	0.06	1.50	1.63
10/6/75	"	0.04	1.22	1.29
10/6/75	12:00	0.06	1.38	1.25
10/6/75	14:00	0.04	1.00	0.97
10/6/75	16:00	0.04	1.07	0.87
10/6/75	18:00	0.05	1.30	1.10
10/6/75	20:00	0.05	1.03	0.96
10/6/75	22:00	0.05	1.11	1.05
11/6/75	Average	0.06	1.29	1.24
11/6/75	00:00	0.04	1.18	1.27
11/6/75	02:00	0.06	1.36	1.25
11/6/75	04:00	0.07	0.98	1.00
11/6/75	06:00	0.06	0.96	0.99
11/6/75	08:00	0.06	1.10	1.10
11/6/75	10:00	0.05	1.08	1.08
11/6/75	14:00	0.05	1.18	1.15
11/6/75	16:00	0.05	1.08	1.13
11/6/75	18:00	0.06	1.12	1.14
11/6/75	20:00	0.05	1.23	1.21
11/6/75	22:00	0.05	1.01	1.06
12/6/75	Average	0.07	1.28	1.29
12/6/75	00:00	0.07	1.07	1.15
12/6/75	02:00	0.05	1.12	1.16
12/6/75	04:00	0.05	1.11	1.15
12/6/75	06:00	0.05	1.10	1.16
12/6/75	08:00	0.05	1.11	1.18
12/6/75	10:00	0.10	1.25	1.36
12/6/75	12:00	0.05	1.11	1.15
12/6/75	14:00	0.06	1.23	1.28
12/6/75	16:00	0.05	1.11	1.17
12/6/75	18:00	0.05	1.14	1.18
13/6/75	Average	0.05	1.29	1.40
14/6/75	"	0.05	1.40	1.52
15/6/75	"	0.04	1.35	1.41

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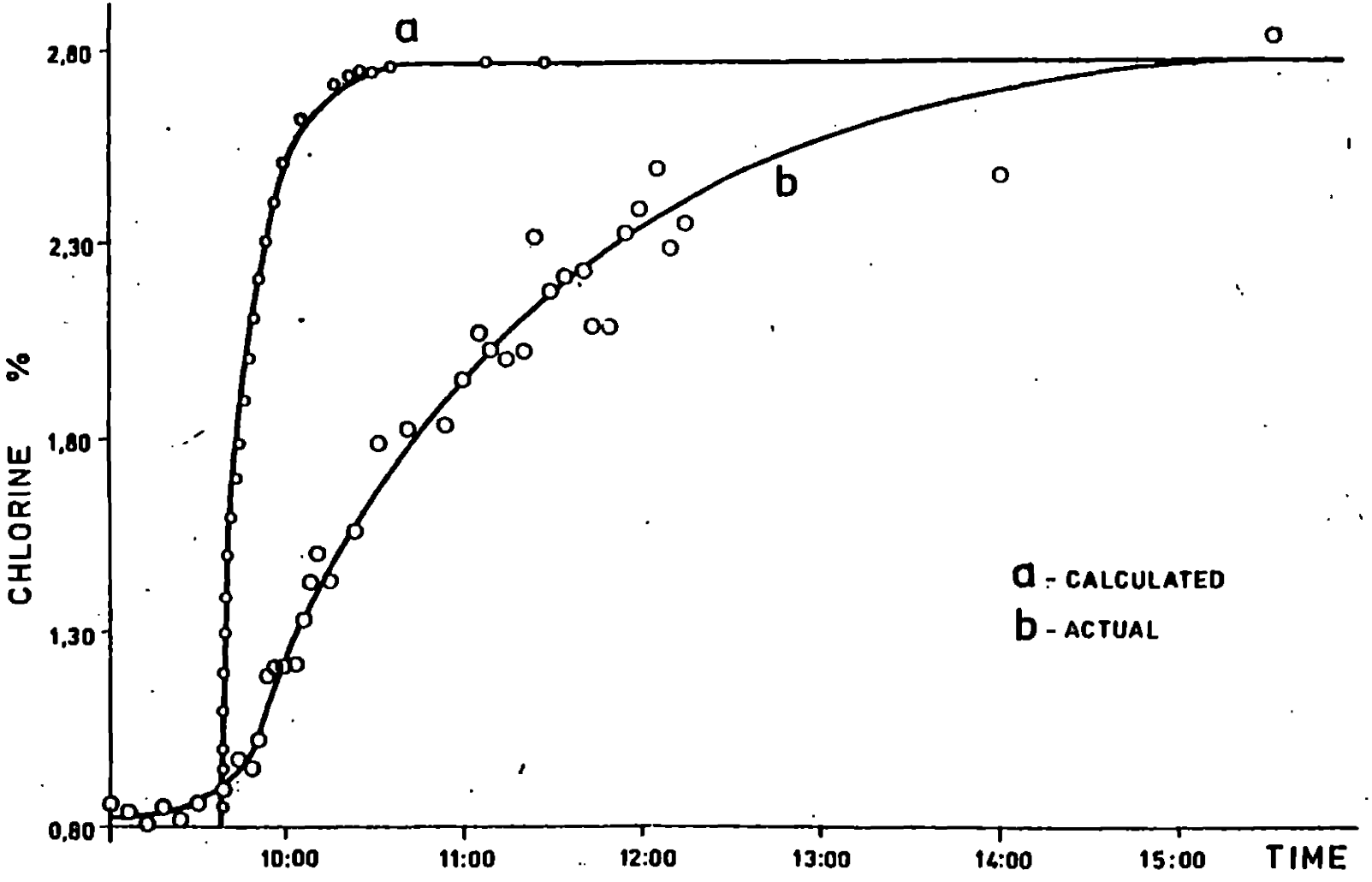
TABLE B.4. RESULTS FROM ANALYSES OF STAGE IV DUSTS

Date	Time	% Cl	% SO_3 (Total S as)	% K_2O
30/ 5/76	-	0.67	1.14	1.77
2/ 6/75	-	0.82	1.30	2.26
3/ 6/75	09:00	0.86	1.23	2.11
3/ 6/75	09:06	0.84	1.25	2.03
3/ 6/75	09:12	0.81	1.19	2.03
3/ 6/75	09:18	0.85	1.22	2.14
3/ 6/75	09:24	0.82	1.18	2.06
3/ 6/75	09:30	0.86	1.30	2.17
3/ 6/75	09:38	0.90	1.34	2.15
3/ 6/75	09:44	0.97	1.32	2.21
3/ 6/75	09:47	0.96	1.35	2.38
3/ 6/75	09:50	1.02	1.38	2.39
3/ 6/75	09:53	1.20	1.29	2.37
3/ 6/75	09:56	1.21	1.31	2.42
3/ 6/75	09:59	1.21	1.34	2.51
3/ 6/75	10:02	1.22	1.30	2.55
3/ 6/75	10:05	1.34	1.46	2.68
3/ 6/75	10:08	1.44	1.38	2.66
3/ 6/75	10:11	1.51	1.52	2.95
3/ 6/75	10:14	1.44	1.29	2.91
3/ 6/75	10:23	1.56	1.41	2.94
3/ 6/75	10:32	1.79	1.37	3.38
3/ 6/75	10:41	1.83	1.34	3.43
3/ 6/75	10:54	1.85	1.32	3.35
3/ 6/75	10:59	1.95	1.46	3.74
3/ 6/75	11:04	2.08	1.59	3.85
3/ 6/75	11:09	2.03	1.35	3.72
3/ 6/75	11:14	2.00	1.39	3.66
3/ 6/75	11:19	2.03	1.41	3.70
3/ 6/75	11:24	2.30	1.47	4.15
3/ 6/75	11:29	2.17	1.36	3.93
3/ 6/75	11:34	2.21	1.37	4.04
3/ 6/75	11:39	2.22	1.43	4.00
3/ 6/75	11:44	2.29	1.51	4.18
3/ 6/75	11:49	2.29	1.57	4.11
3/ 6/75	11:54	2.32	1.66	4.24
3/ 6/75	11:59	2.38	1.47	4.36
3/ 6/75	12:04	2.49	1.51	4.45
3/ 6/75	12:09	2.28	1.46	4.12
3/ 6/75	12:14	2.34	1.44	4.21
3/ 6/75	14:00	2.47	1.45	4.44
3/ 6/75	15:30	2.84	1.58	5.07
4/ 6/75	09:00	1.92	1.42	4.17
4/ 6/75	14:00	1.59	1.28	3.48
5/ 6/75	-	0.97	1.44	2.54
6/ 6/75	-	1.14	1.17	2.71

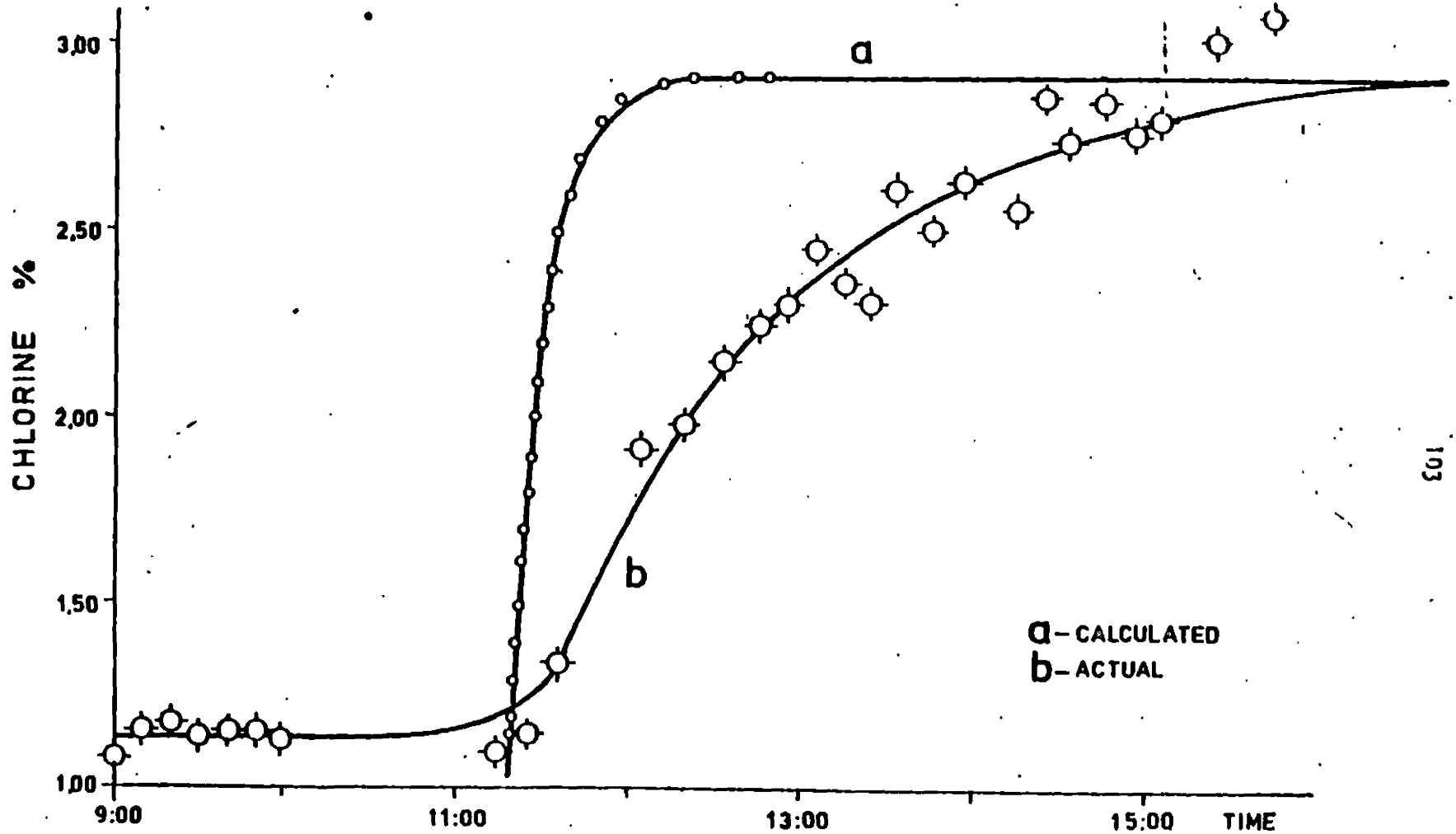
TABLE B.4. (Cont'd)

Date	Time	% Cl	% SO_3 (Total S as)	% K_2O
9/ 6/75	-	1.66	1.20	3.79
10/ 6/75	09:00	1.09	1.18	2.64
10/ 6/75	09:10	1.17	1.22	2.93
10/ 6/75	09:20	1.19	1.36	3.07
10/ 6/75	09:30	1.15	1.39	2.92
10/ 6/75	09:40	1.16	1.29	3.01
10/ 6/75	09:50	1.16	1.27	2.99
10/ 6/75	10:00	1.14	1.29	2.95
10/ 6/75	11:15	1.11	1.29	2.91
10/ 6/75	11:25	1.20	1.34	3.04
10/ 6/75	11:35	1.46	1.41	3.22
10/ 6/75	12:05	1.91	1.49	4.02
10/ 6/75	12:25	1.99	1.46	4.07
10/ 6/75	12:35	2.15	1.64	4.50
10/ 6/75	12:45	2.25	1.59	4.54
10/ 6/75	12:55	2.31	1.66	4.65
10/ 6/75	13:05	2.45	1.79	4.98
10/ 6/75	13:15	2.37	1.71	4.75
10/ 6/75	13:25	2.32	1.47	4.48
10/ 6/75	13:35	2.62	1.67	5.10
10/ 6/75	13:45	2.51	1.54	4.83
10/ 6/75	13:55	2.63	1.69	5.12
10/ 6/75	14:15	2.57	1.69	5.02
10/ 6/75	14:25	2.87	1.81	5.53
10/ 6/75	14:35	2.74	1.67	5.18
10/ 6/75	14:45	2.85	1.70	5.35
10/ 6/75	14:55	2.77	1.77	5.23
10/ 6/75	15:05	2.79	1.52	5.23
10/ 6/75	15:25	3.02	2.41	5.66
10/ 6/75	15:35	3.28	1.59	6.07
10/ 6/75	15:45	3.09	1.62	5.78
11/ 6/75	-	2.58	1.51	5.23
12/ 6/75	-	2.42	1.49	5.13



CHLORINE LEVEL IN STAGE IV 3/6/1975

FIGURE B.1



CHLORINE LEVEL IN STAGE IV 10/6/1975

FIGURE B.2

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APPENDIX C

RESULTS AND CALCULATIONS FOR WET PROCESS SYSTEM

APPENDIX C

RESULTS AND CALCULATIONS FOR WET PROCESS SYSTEM

C.1 Mass Balance Experimentation

C.1.1 Results of analyses of process materials

Analyses of process materials for the mass balance were carried out at the St. Lawrence Cement Co. plant. Analytical results are given in Tables C.1 to C.6.

C.1.2 Calculation of material balances

A daily record of production and material consumption is given in Table C.7 for the period October 7, 1975 to January 21, 1976. Production was disrupted during this period by a kiln shutdown for the removal of a kiln ring.

The program was further disrupted by formation of a ring, not requiring kiln shutdown, but time to reduce the quantity of aromatic plus complex chlorinated hydrocarbon in the tank and difficulty in scheduling deliveries. From the daily composite analysis of each material for each element, and the total daily quantity of each material, daily elemental quantities (as pounds or tons per 25 hour period) were determined by the relationship:

$$X_{ij} = M_{ij} \times \frac{C_{ij}}{100}$$

where

X_{ij} = total daily weight of element x in material i on day j

C_{ij} = concentration of element x in the composite sample material I on day j.

These data were then used to form the separate individual elemental balance accounts given in Tables C.8 and C.9. Due to process fluctuations and the very low concentrations in the case of chlorine, little significance should be attached to individual daily balance results, except as they indicate the responsiveness of the system to major changes in input of chlorinated hydrocarbons. Significant assessment of the

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balance is available by considering prolonged periods of plant operation. Summary balances for this purpose are given in the body of this report (see Section 5.4, Tables 8 and 9).

Materials entering the mass balance calculations (see Figure 1, Section 2) were slurry feed, No. 6 fuel oil and chlorinated hydrocarbon materials as input streams with clinker and discard dust forming the output streams. The return dust is returned almost immediately to the system and does not form a part of the mass balance.

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TABLE C.1. RESULTS FROM ANALYSES OF CLINKER SAMPLES

Date	% Cl	% SO_3	% K_2O
7/10/75	0.033	0.88	1.13
8/10/75	0.032	0.79	1.12
9/10/75	0.034	0.86	1.14
10/10/75	0.042	0.62	0.88
11/10/75	0.032	0.93	1.27
12/10/75	0.029	0.80	1.08
13/10/75	0.030	0.80	1.09
14/10/75	0.031	0.86	1.15
15/10/75	0.031	1.27	1.47
16/10/75	0.031	0.90	1.16
17/10/75	0.035	1.11	1.31
18/10/75	0.029	0.99	1.24
19/10/75	0.032	0.97	1.21
20/10/75	0.042	1.03	1.28
21/10/75	0.030	1.32	1.51
22/10/75	0.029	0.99	1.28
23/10/75	0.030	0.77	1.06
24/10/75	0.030	0.92	1.20
25/10/75	0.029	0.59	0.83
26/10/75	0.031	1.06	1.24
27/10/75	0.031	0.82	1.00
28/10/75	0.034	1.16	1.31
29/10/75	0.032	1.27	1.37
30/10/75	0.039	0.88	0.96
31/10/75	0.034	0.34	0.49
1/11/75	0.039	0.18	0.36
2/11/75	-	NO SAMPLE	-
3/11/75	0.032	0.26	0.48
4/11/75	0.028	0.30	0.56
5/11/75	0.031	0.64	1.00
6/11/75	0.031	0.70	1.18
7/11/75	0.037	0.71	1.20
8/11/75	0.029	0.68	1.15
9/11/75	0.035	0.72	1.19
2/12/75	0.031	1.13	0.94
3/12/75	0.029	1.39	1.28
4/12/75	0.034	1.02	1.01
5/12/75	0.033	1.23	1.16
6/12/75	0.029	1.18	0.90
7/12/75	0.028	1.18	0.84
8/12/75	0.038	0.91	0.74
9/12/75	0.040	0.71	0.56
10/12/75	0.034	0.47	0.36
11/12/75	0.035	0.70	0.48
12/12/75	0.032	0.92	0.54
13/12/75	0.032	0.75	0.39
14/12/75	0.031	0.73	0.48

TABLE C.1 (CONT'D)

Date	% Cl	% SO_3	% K_2O
31/12/75	0.029	1.40	1.20
1/ 1/76	0.029	1.48	1.34
2/ 1/76	0.029	1.49	1.37
3/ 1/76	0.033	1.12	0.77
4/ 1/76	0.030	1.68	1.42
5/ 1/76	0.035	1.14	0.78
6/ 1/76	0.031	0.70	0.58
7/ 1/76	0.029	1.14	1.26
8/ 1/76	0.030	0.88	0.83
9/ 1/76	0.028	0.46	0.46
10/ 1/76	0.028	0.91	1.05
11/ 1/76	0.030	0.92	1.12
12/ 1/76	0.030	0.94	1.15
13/ 1/76	0.029	1.13	1.35
14/ 1/76	0.030	1.14	1.28
15/ 1/76	0.029	1.12	1.22
16/ 1/76	0.030	1.38	1.45
17/ 1/76	0.037	1.36	1.42
18/ 1/76	0.028	1.20	1.27
19/ 1/76	0.028	1.06	1.15
20/ 1/76	0.029	1.42	1.46
21/ 1/76	0.029	0.94	1.12

ACM GC6210

TABLE C.2 RESULTS FROM ANALYSES OF SLURRY FEED SAMPLES

Date	% Cl	% SO_3 (Total S as)	% K_2O
7/10/75	0.080	0.48	0.92
8/10/75	0.056	0.48	0.91
9/10/75	0.052	0.45	0.91
10/10/75	0.058	0.46	0.91
11/10/75	0.060	0.46	0.92
12/10/75	0.068	0.45	0.92
13/10/75	0.050	0.50	0.93
14/10/75	0.044	0.44	0.92
15/10/75	0.046	0.44	0.93
16/10/75	0.043	0.43	0.93
17/10/75	0.051	0.43	0.93
18/10/75	0.055	0.43	0.93
19/10/75	0.046	0.44	0.93
20/10/75	0.043	0.42	0.93
21/10/75	0.038	0.41	0.92
22/10/75	0.040	0.40	0.93
23/10/75	0.040	0.40	0.93
24/10/75	0.050	0.40	0.93
25/10/75	0.043	0.41	0.92
26/10/75	0.055	0.42	0.93
27/10/75	0.042	0.43	0.91
28/10/75	0.047	0.41	0.92
29/10/75	0.055	0.43	0.93
30/10/75	-	NO SAMPLE	-
31/10/75	0.050	0.42	0.91
1/11/75	0.047	0.42	0.91
2/11/75	0.043	0.42	0.92
3/11/75	0.043	0.43	0.93
4/11/75	0.044	0.44	0.92
5/11/75	0.042	0.41	0.93
6/11/75	0.042	0.43	0.92
7/11/75	0.044	0.41	0.92
8/11/75	0.042	0.40	0.91
9/11/75	0.050	0.43	0.94
2/12/75	0.046	0.48	0.90
3/12/75	0.042	0.48	0.90
4/12/75	0.041	0.47	0.89
5/12/75	0.040	0.52	0.91
6/12/75	0.040	0.51	0.90
7/12/75	0.052	0.53	0.91
8/12/75	0.041	0.51	0.91
9/12/75	0.040	0.51	0.89

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TABLE C.2 (CONT'D)

Date	% Cl	% SO_3 (Total S as)	% K_2O
10/12/75	0.041	0.54	0.91
11/12/75	0.039	0.52	0.91
12/12/75	0.050	0.55	0.91
13/12/75	0.042	0.58	0.90
14/12/75	0.048	0.54	0.91
31/12/75	0.059	0.48	0.90
1/ 1/76	0.042	0.46	0.91
2/ 1/76	0.045	0.46	0.92
3/ 1/76	0.043	0.46	0.91
4/ 1/76	0.046	0.46	0.92
5/ 1/76	0.038	0.46	0.91
6/ 1/76	0.038	0.46	0.91
7/ 1/76	0.048	0.47	0.91
8/ 1/76	0.039	0.46	0.89
9/ 1/76	0.048	0.45	0.92
10/ 1/76	0.048	0.46	0.91
11/ 1/76	0.048	0.44	0.91
12/ 1/76	0.040	0.44	0.91
13/ 1/76	0.041	0.44	0.92
14/ 1/76	0.044	0.46	0.91
15/ 1/76	0.042	0.47	0.91
16/ 1/76	0.048	0.50	0.91
17/ 1/76	0.041	0.47	0.90
18/ 1/76	0.054	0.46	0.91
19/ 1/76	0.039	0.44	0.91
20/ 1/76	0.040	0.43	0.91
21/ 1/76	0.041	0.43	0.92

ADM CCE212

TABLE C.3. RESULTS FROM ANALYSES OF DISCARD DUST

Date	% CL	% SO_3 (Total S as)	% K_2O
7/10/75	0.99	7.09	7.37
8/10/75	1.01	7.22	7.45
9/10/75	0.89	7.28	7.34
10/10/75	0.96	7.48	7.66
11/10/75	0.96	7.39	7.48
12/10/75	1.35	7.59	8.26
13/10/75	2.51	10.34	11.27
14/10/75	1.64	6.65	7.65
15/10/75	-	NO DUST DISCARDED	-
16/10/75	2.40	7.35	9.16
17/10/75	1.88	6.00	7.32
18/10/75	1.86	6.02	7.22
19/10/75	1.77	6.12	7.13
20/10/75	-	NO SAMPLE.	-
21/10/75	-	NO DUST DISCARDED	-
22/10/75	2.08	6.23	7.83
23/10/75	1.41	5.65	6.70
24/10/75	3.08	6.05	8.60
25/10/75	5.11	5.56	10.07
26/10/75	4.28	5.49	9.28
27/10/75	4.01	5.22	8.63
28/10/75	4.39	5.15	8.87
29/10/75	3.89	4.84	8.21
30/10/75	-	NO SAMPLE	-
31/10/75	-	NO SAMPLE	-
1/11/75	6.79	3.62	9.62
2/11/75	6.62	3.27	9.38
3/11/75	5.85	3.10	8.57
4/11/75	5.82	2.81	8.34
5/11/75	3.09	4.08	7.46
6/11/75	1.35	4.12	5.83
7/11/75	1.07	4.11	5.47
8/11/75	0.75	3.76	4.67
9/11/75	0.83	4.13	5.42
2/12/75	5.33	5.84	9.36
3/12/75	4.14	6.37	8.78
4/12/75	2.64	6.51	7.81
5/12/75	7.14	12.66	16.28
6/12/75	4.76	6.28	9.10
7/12/75	5.75	6.41	9.88
8/12/75	6.24	6.97	10.70
9/12/75	4.76	5.41	8.24

TABLE C.3 (CONT'D)

Date	% Cl	% SO_3 (Total S as)	% K_2O
10/12/75	5.35	5.51	8.27
11/12/75	5.52	4.90	8.20
12/12/75	5.53	5.62	8.46
13/12/75	-	NO SAMPLE	-
14/12/75	5.68	5.54	8.65
31/12/75	-	NO SAMPLE	-
1/ 1/76	1.98	6.19	6.88
2/ 1/76	-	NO SAMPLE	-
3/ 1/76	-	NO SAMPLE	-
4/ 1/76	4.55	4.62	7.37
5/ 1/76	4.58	4.62	7.38
6/ 1/76	4.03	4.70	6.89
7/ 1/76	-	NO SAMPLE	-
8/ 1/76	3.06	5.31	7.25
9/ 1/76	4.50	4.51	7.60
10/ 1/76	1.20	5.43	6.07
11/ 1/76	1.11	5.27	5.79
12/ 1/76	1.01	5.16	5.54
13/ 1/76	1.20	5.37	6.10
14/ 1/76	0.76	4.94	5.16
15/ 1/76	0.92	4.89	5.15
16/ 1/76	0.80	4.41	4.62
17/ 1/76	0.78	4.50	4.68
18/ 1/76	0.69	4.28	4.49
19/ 1/76	0.72	5.01	5.32
20/ 1/76	0.76	4.81	5.19
21/ 1/76	0.86	4.28	4.84

TABLE C.4. RESULTS FROM ANALYSES OF RETURN DUST

Date	% Cl	% SO_3 (Total S as)	% K_2O
7/10/75	0.80	6.25	6.22
8/10/75	0.73	6.28	6.25
9/10/75	0.54	5.36	5.15
10/10/75	0.73	7.26	7.54
11/10/75	1.59	7.05	8.20
12/10/75	1.36	7.79	8.90
13/10/75	1.29	6.21	7.02
14/10/75	2.46	8.16	9.83
15/10/75	2.29	6.91	8.54
16/10/75	2.15	6.80	8.32
17/10/75	2.33	7.20	8.73
18/10/75	1.81	5.61	6.71
19/10/75	1.86	6.51	7.73
20/10/75	1.76	5.86	7.08
21/10/75	2.56	6.54	8.44
22/10/75	1.53	6.00	6.92
23/10/75	1.52	5.37	6.60
24/10/75	3.82	5.36	8.63
25/10/75	3.41	4.87	7.75
26/10/75	3.87	4.84	8.21
27/10/75	3.48	4.48	7.47
28/10/75	3.02	4.75	6.91
29/10/75	3.51	4.24	7.23
30/10/75	-	NO SAMPLE	-
31/10/75	4.22	2.58	6.49
1/11/75	4.66	2.84	7.07
2/11/75	6.37	3.22	9.05
3/11/75	3.96	2.47	6.28
4/11/75	4.00	2.70	6.69
5/11/75	1.27	3.60	5.20
6/11/75	1.00	3.67	4.91
7/11/75	0.79	3.77	4.92
8/11/75	0.54	3.54	4.50
9/11/75	0.44	3.30	3.89
10/11/75	-	NO SAMPLE	-
2/12/75	4.00	5.65	10.70
3/12/75	2.52	5.97	9.63
4/12/75	2.49	6.51	8.58
5/12/75	2.58	6.96	8.33
6/12/75	1.00	3.69	4.94
7/12/75	0.79	3.81	4.93
8/12/75	0.58	3.57	4.61
9/12/75	3.68	4.68	6.59

TABLE C.4 (CONT'D)

Date	% Cl	% SO_3 (Total S as)	% K_2O
10/12/75	2.51	3.68	4.60
11/12/75	2.36	3.45	4.22
12/12/75	3.69	4.22	5.94
13/12/75	4.04	4.07	6.05
14/12/75	3.02	4.06	5.16
31/12/75	1.56	5.09	5.60
1/ 1/76	1.78	5.14	5.99
2/ 1/76	1.77	4.70	5.65
3/ 1/76	2.42	4.62	5.82
4/ 1/76	3.55	4.48	6.33
5/ 1/76	2.37	3.36	4.29
6/ 1/76	2.56	3.43	4.64
7/ 1/76	1.35	3.23	3.58
8/ 1/76	1.76	4.91	5.56
9/ 1/76	2.30	3.71	4.91
10/ 1/76	1.06	4.74	5.05
11/ 1/76	0.93	5.05	5.46
12/ 1/76	0.80	5.14	5.37
13/ 1/76	0.79	4.82	5.10
14/ 1/76	0.78	4.85	4.93
15/ 1/76	0.78	4.41	4.59
16/ 1/76	0.65	4.27	4.38
17/ 1/76	0.58	4.11	4.10
18/ 1/76	0.69	4.19	4.22
19/ 1/76	0.58	4.56	4.70
20/ 1/76	0.72	4.47	4.62
21/ 1/76	0.87	4.24	4.83

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TABLE C.5. Btu AND CHLORINE CONTENT OF CHLORINATED HYDROCARBONS (SAMPLES FROM LIME TO KILN)

Material	Date	Btu/lb	% Chlorine	Viscosity (Centipoise @ 23°C)	Specific Gravity
Aliphatic	24/10/75	13400	21.52		
	27/10/75	11390	32.76		
	28/10/75	10750	39.40		
	3/11/75	8900	42.23		
	4/11/75	8590	43.52		
	13/11/75	8340	42.38		
	18/11/75	8410	43.38		
	Average	9970	37.88	-	1.13
Aromatic + Complex	10/12/75	9530	40.56		
	11/12/75	9500	45.91		
	12/12/75	8820	44.16		
	13/13/75	9320	41.80		
	15/12/75	9310	40.48		
	Average	9300	42.58	40.8	1.27
Polychlorinated Biphenyl	3/ 1/76	11380	36.16		
	4/ 1/76	11590	37.75		
	5/ 1/76	11880	34.90		
	6/ 1/76	12170	33.90		
	7/ 1/76	12070	33.19		
	8/ 1/76	12050	34.93		
	9/ 1/76	12000	33.90		
	Average	11880	34.97	17.0	1.18

TABLE C.6. Btu, S AND Cl ANALYSES FROM NO. 6 FUEL OIL

Date	Btu/lb	% S	% Cl
7/10/75	17809	2.40	
8/10/75	17222	2.42	
9/10/75	17978	2.34	
10/10/75	17942	2.26	Average
14/10/75	18106	2.26	7/10/75 - 22/10/75
15/10/75	18008	2.28	% Chlorine = 0.028%
16/10/75	17920	2.31	
17/10/75	17988	2.30	
20/10/75	17924	2.24	
21/10/75	17877	2.24	
22/10/75	17984	2.09	
23/10/75	18189	2.23	
24/10/75	17701	2.22	
27/10/75	17901	2.24	
28/10/75	17862	2.22	
29/10/75	17970	1.95	
30/10/75	17917	2.29	
31/10/75	17889	1.77	
3/11/75	18135	1.62	
4/11/75	18077	1.57	
5/11/75	18047	1.55	
6/11/75	18079	1.51	Average
7/11/75	18036	1.56	23/10/75-12/11/75
10/11/75	17979	1.26	% Chlorine = 0.064
11/11/75	17782	1.89	
12/11/75	17719	2.06	
2/12/75	17700	2.54	
3/12/75	17676	2.28	
4/12/75	17714	2.56	
5/12/75	17648	2.58	
8/12/75	17679	2.55	Average
9/12/75	17732	2.52	2/12/75-15/12/75
10/12/75	17695	2.58	% Chlorine = 0.047
11/12/75	17596	2.50	
12/12/75	17655	2.56	
15/12/75	17504	2.64	
30/12/75	17678	2.59	
2/ 1/76	17565	2.41	
5/ 1/76	17498	1.61	Average
6/ 1/76	17433	2.07	30/12/75-9/1/76
7/ 1/76	17630	2.28	% Chlorine = 0.030
8/ 1/76	17900	2.47	
9/ 1/76	17719	2.42	
12/ 1/76	17990	1.96	
13/ 1/76	17896	1.95	

TABLE C.6 (CONT'D)

Date	Btu/lb	% S	% Cl
14/ 1/76	17935	1.54	
15/ 1/76	17952	2.00	
16/ 1/76	18025	1.98	Average
19/ 1/76	17762	1.92	12/1/76-22/1/76
20/ 1/76	17846	1.89	% Chlorine = 0.038
21/ 1/76	18005	1.54	
22/ 1/76	18160	1.42	

TABLE C.7. DAILY RECORD OF PRODUCTION AND MATERIALS CONSUMPTION

Date	SLURRY FEED (tons/24 hr)	CHLORIN. HC (gal/24 hr)	CLINKER (tons/24 hr)	DISCARD DUST (tons/24 hr)
7/10/75	1653	0	1043	40.44
8/10/75	1676	0	1041	63.44
9/10/75	1681	0	1073	24.84
10/10/75	1658	0	1027	65.66
11/10/75	1585	0	1029	0
12/10/75	1325	0	845	18.94
13/10/75	1632	0	1036	6.96
14/10/75	1604	0	1047	23.00
15/10/75	1639	0	1064	0
16/10/75	1646	0	1058	12.90
17/10/75	1661	0	1065	17.86
18/10/75	1682	0	1081	15.32
19/10/75	1669	0	1079	4.93
20/10/75	1669	0	1071	15.97
21/10/75	1661	0	1078	0
22/10/75	1664	0	1046	45.36
23/10/75	1681	1170	1082	11.96
24/10/75	1686	1440	1079	19.72
25/10/75	1669	1440	1067	20.96
26/10/75	1732	1440	1112	16.42
27/10/75	1656	1440	1061	18.32
28/10/75	1652	1440	1040	42.58
29/10/75	1621	1440	1021	41.36
30/10/75	1633	2670	1032	37.17
31/10/75	1647	2880	1027	56.52
1/11/75	1658	2880	1029	63.32
2/11/75	1673	2880	1057	38.92
3/11/75	1679	2880	1030	80.66
4/11/75	1679	930	1010	107.72
5/11/75	1692	0	1044	72.82
6/11/75	1693	0	1054	60.46
7/11/75	1698	0	1058	59.90
8/11/75	1670	0	1030	73.50
9/11/75	1701	0	1056	64.26
2/12/75	1622	430	1038	20.58
3/12/75	1627	0	1042	18.30
4/12/75	1644	0	1039	37.72
5/12/75	1653	1640	1028	61.40
6/12/75	1670	2187	1056	38.26
7/12/75	1655	1351	1074	0
8/12/75	1666	1117	1043	51.36
9/12/75	1664	2121	984	129.78

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TABLE C.7. (CONT'D)

Date	SLURRY FEED (tons/24 hr)	CHLORIN. HC (gal/24 hr)	CLINKER (tons/24 hr)	DISCARD DUST (tons/24 hr)
10/12/75	1676	1997	994	127.66
11/12/75	1669	1308	999	113.76
12/12/75	1669	1821	1024	79.12
13/12/75	1661	1691	985	125.96
14/12/75	1653	1869	956	157.68
15/12/75	1658	1909	980	130.30
31/12/75	1606	0	1024	24.72
1/ 1/76	1595	0	1035	0
2/ 1/76	1608	0	1039	6.11
3/ 1/76	1630	2029	1017	55.43
4/ 1/76	1629	2210	1005	70.90
5/ 1/76	1627	2168	970	116.98
6/ 1/76	1616	1985	1034	19.86
7/ 1/76	1612	604	944	137.39
8/ 1/76	1615	1230	1045	4.54
9/ 1/76	1619	1367	1027	32.10
10/ 1/76	1621	0	1020	43.92
11/ 1/76	1627	0	1011	61.20
12/ 1/76	1636	0	1032	40.52
13/ 1/76	1639	0	1040	32.36
14/ 1/76	1618	0	1028	42.80
15/ 1/76	1633	0	1046	19.10
16/ 1/76	1596	0	1026	13.38
17/ 1/76	1606	0	979	85.76
18/ 1/76	1635	0	1026	47.62
19/ 1/76	1608	0	1020	32.22
20/ 1/76	1602	0	991	66.56
21/ 1/76	1629	0	1016	55.75

TABLE C.8. MATERIAL BAL

DATE	CHLORINE INPUT (lb/24 hr) SLURRY FEED	#6 OIL	CHLORINATED HYDROCARBON	TOTAL
7/10/75	2,645	81	0	2,726
8/10/75	1,877	81	0	1,958
9/10/75	1,748	82	0	1,830
10/10/75	1,923	81	0	2,004
11/10/75	1,902	78	0	1,980
12/10/75	1,801	67	0	1,868
13/10/75	1,632	81	0	1,713
14/10/75	1,412	80	0	1,492
15/10/75	1,508	81	0	1,589
16/10/75	1,416	81	0	1,497
17/10/75	1,694	81	0	1,775
18/10/75	1,850	81	0	1,931
19/10/75	1,535	81	0	1,616
20/10/75	1,435	81	0	1,516
21/10/75	1,262	80	0	1,342
22/10/75	1,331	81	0	1,412
23/10/75	1,345	185	2,845	4,375
24/10/75	1,686	183	3,502	5,371
25/10/75	1,435	183	3,959	5,577
26/10/75	1,905	190	4,416	6,511
27/10/75	1,391	182	4,873	6,446
28/10/75	1,553	182	6,411	8,146
29/10/75	1,783	183	6,642	8,608
30/10/75	1,502*	181	12,316	13,999
31/10/75	1,647	186	13,284	15,117
1/11/75	1,558	179	13,284	15,021
2/11/75	1,439	179	13,284	14,902
3/11/75	1,444	178	13,284	14,906
4/11/75	1,478	179	13,743	15,400
5/11/75	1,421	184	4,574	6,179
6/11/75	1,422	182	0	1,604

* Calculated from average data.

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ANCE FOR CHLORINE

CHLORINE RETAINED (lb/24 hr)			TOTAL % RETAINED
CLINKER	DISCARD DUST	TOTAL	
688	801	1,489	54.6
666	1,281	1,947	99.4
730	442	1,172	64.0
836	1,261	2,097	104.6
658	0	658	33.2
490	511	1,001	53.6
622	349	971	56.7
649	754	1,403	94.0
660	0	660	41.5
656	619	1,275	85.2
746	672	1,418	79.9
627	570	1,197	62.0
690	174	864	53.5
900	575	1,475	97.3
647	0	647	48.2
607	1,887	2,494	176.6
649	337	986	22.5
647	1,215	1,862	34.7
619	2,142	2,761	49.5
689	1,406	2,095	32.2
658	1,469	2,127	33.0
707	3,738	4,445	54.6
653	3,218	3,871	45.0
805	3,970*	4,775	34.1
698	6,036*	6,734	44.5
803	8,599	9,402	62.6
676	5,153	5,829	39.1
659	9,437	10,096	67.7
566	12,539	13,105	85.1
647	4,500	5,147	83.3
653	1,632	2,285	142.4

TABLE C.8 (CONT'D)

DATE	CHLORINE INPUT (lb/24 hr) SLURRY FEED	#6 OIL	CHLORINATED HYDROCARBON	TOTAL	CHLORINE RETAINED (lb/24 hr) CLINKER	DISCARD DUST	TOTAL	TOTAL % RETAINED
7/11/75	1,494	183	0	1,677	783	1,282	2,065	123.1
8/11/75	1,403	181	0	1,584	597	1,102	1,699	107.3
9/11/75	1,701	182	0	1,883	739	1,067	1,806	95.9
2/12/75	1,492	124	2,325	3,941	644	2,194	2,838	72.0
3/12/75	1,367	133	0	1,500	604	1,515	2,119	141.3
4/12/75	1,348	133	0	1,481	708	1,992	2,700	182.3
5/12/75	1,322	132	8,868	10,322	678	8,768	9,446	91.5
6/12/75	1,336	131	11,826	13,293	612	3,642	4,254	32.0
7/12/75	1,721	131	7,306	9,158	601	0	601	6.6
8/12/75	1,366	142	6,040	7,548	793	6,410	7,203	95.4
9/12/75	1,331	132	11,470	12,933	787	12,355	13,142	101.6
10/12/75	1,374	130	10,287	11,791	676	13,660	14,336	121.6
11/12/75	1,302	134	7,626	9,062	699	12,559	13,258	146.3
12/12/75	1,669	134	10,213	12,016	655	8,751	9,406	78.3
13/12/75	1,395	133	8,977	10,505	630	14,208	14,838	141.2
14/12/75	1,587	131	10,107	11,825	593	17,906	18,499	156.4
31/12/75	1,895	85	0	1,980	594	979	1,573	79.4
1/ 1/76	1,340	87	0	1,427	600	0	600	42.0
2/ 1/76	1,447	87	0	1,534	603	242	845	55.1
3/ 1/76	1,402	83	8,657	10,142	671	4,434	5,105	50.3
4/ 1/76	1,499	82	9,844	11,425	603	6,452	7,055	61.8
5/ 1/76	1,236	83	8,928	10,247	679	10,715	11,394	111.2
6/ 1/76	1,228	83	7,950	9,261	641	1,601	2,242	24.2
7/ 1/76	1,548	85	2,366	3,999	548	10,991	11,539	288.5
8/ 1/76	1,260	83	5,070	6,413	627	278	905	14.1
9/ 1/76	1,554	81	5,468	7,103	575	2,889	3,464	48.8
10/ 1/76	1,556	109	0	1,665	571	1,054	1,625	97.6
11/ 1/76	1,562	109	0	1,671	607	1,359	1,966	117.6
12/ 1/76	1,309	109	0	1,418	619	818	1,437	101.3
13/ 1/76	1,344	108	0	1,452	603	777	1,380	95.0

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TABLE C.8 (CONT'D)

DATE	CHLORINE INPUT (lb/24 hr) SLURRY FEED	#6 OIL	CHLORINATED HYDROCARBON	TOTAL	CHLORINE RETAINED (lb/24 hr) CLINKER	DISCARD DUST	TOTAL	TOTAL % RETAINED
14/ 1/76	1,424	108	0	1,532	617	650	1,267	82.7
15/ 1/76	1,372	108	0	1,480	607	351	958	64.7
16/ 1/76	1,532	107	0	1,639	616	214	830	50.6
17/ 1/76	1,317	108	0	1,425	724	1,338	2,062	144.7
18/ 1/76	1,776	108	0	1,874	575	657	1,232	65.7
19/ 1/76	1,254	107	0	1,361	571	464	1,035	76.0
20/ 1/76	1,282	107	0	1,389	575	1,012	1,587	114.2
21/ 1/76	1,336	109	0	1,445	589	959	1,548	107.1

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TABLE C.9. MATERIAL BALANCE FOR K_2O

DATE	K_2O INPUT (tons/24 hr) SLURRY FEED	K_2O RETAINED (tons/24 hr) CLINKER	DUST	TOTAL	TOTAL % RETAINED
7/10/75	15.21	11.78	2.98	14.76	97.0
8/10/75	15.25	11.66	4.73	16.39	107.5
9/10/75	15.30	12.23	1.82	14.05	91.8
10/10/75	15.09	9.04	5.03	14.07	93.2
11/10/75	14.58	13.07	0	13.07	89.6
12/10/75	12.18	9.13	1.56	0.69	87.8
13/10/75	15.18	11.29	0.78	2.07	79.5
14/10/75	14.76	12.04	1.76	13.80	93.5
15/10/75	15.24	15.64	0	15.64	102.6
16/10/75	15.31	12.27	1.18	13.45	87.8
17/10/75	15.45	13.95	1.31	15.26	98.8
18/10/75	15.64	13.40	1.11	14.51	92.8
19/10/75	15.52	13.06	0.35	13.41	86.4
20/10/75	15.52	13.71	1.27*	14.98	96.5
21/10/75	15.28	16.28	0	16.28	106.5
22/10/75	15.48	13.39	3.55	16.94	109.4
23/10/75	15.63	11.47	0.80	12.27	78.5
24/10/75	15.68	12.95	1.70	14.65	93.4
25/10/75	15.35	8.86	2.11	10.97	71.5
26/10/75	16.11	3.79	1.52	15.31	95.0
27/10/75	15.07	10.61	1.58	12.19	80.9
28/10/75	15.20	13.62	3.78	17.40	114.5
29/10/75	15.08	13.99	3.40	17.39	115.3
30/10/75	15.02*	9.91	2.91*	12.82	85.4
31/10/75	14.99	5.03	4.42*	9.45	63.0
1/11/75	15:09	3.70	6.09	9.79	64.9
2/11/75	15.39	4.44*	3.65	8.09	52.6
3/11/75	15.61	4.94	6.91	11.85	75.9
4/11/75	15.45	5.66	8.88	14.54	94.1
5/11/75	15.74	10.44	5.43	15.87	100.8
6/11/75	15.58	12.44	3.52	15.96	102.4
7/11/75	15.62	12.70	3.28	15.98	102.3
8/11/75	15.20	11.84	3.43	15.27	100.5
9/11/75	15.99	12.57	3.48	16.05	100.4
2/12/75	14.60	9.76	1.93	11.69	80.1
3/12/75	14.64	13.34	1.61	14.95	102.1
4/12/75	14.63	10.49	2.94	13.43	91.8
5/12/75	15.04	11.92	10.00	21.92	145.7
6/12/75	15.03	9.50	3.48	12.98	86.4
7/12/75	15.06	9.02	0	9.02	59.9
8/12/75	15.16	7.72	5.50	3.22	87.2
9/12/75	14.81	5.51	0.69	16.20	109.4
10/12/75	15.25	3.58	10.56	14.14	92.7
11/12/75	15.19	4.80	9.33	14.13	93.0

* Calculated from average data.

TABLE C.9 (CONT'D)

DATE	K_2O INPUT (tons/24 hr) SLURRY FEED	K_2O RETAINED (tons/24 hr) CLINKER	DUST	TOTAL	TOTAL % RETAINED
12/12/75	15.19	5.53	6.69	12.22	80.4
13/12/75	14.95	3.94	10.71*	14.55	97.3
14/12/75	15.04	4.59	13.64	18.23	121.2
31/12/75	14.45	12.29	1.70*	13.99	96.8
1/ 1/76	14.51	13.87	0	13.87	95.6
2/ 1/76	14.79	14.23	0.42*	14.65	99.0
3/ 1/76	14.83	7.83	4.01	11.84	79.8
4/ 1/76	14.99	14.27	5.22	19.49	130.0
5/ 1/76	14.80	7.57	8.63	16.20	109.4
6/ 1/76	14.70	6.00	1.37	7.37	50.1
7/ 1/76	14.67	11.89	0.93*	21.82	148.7
8/ 1/76	14.37	8.67	0.33	9.00	62.6
9/ 1/76	14.89	4.72	2.44	7.16	48.1
10/ 1/76	14.75	10.71	2.66	13.37	90.6
11/ 1/76	14.80	11.32	3.54	14.87	100.4
12/ 1/76	14.89	11.87	2.24	14.11	94.8
13/ 1/76	15.08	14.04	1.97	16.01	106.2
14/ 1/76	14.72	13.16	2.21	15.37	104.4
15/ 1/76	14.86	12.76	0.98	13.74	92.5
16/ 1/76	14.52	14.88	0.62	15.50	106.7
17/ 1/76	14.45	13.90	4.01	17.91	123.9
18/ 1/76	14.88	13.03	2.14	15.17	101.9
19/ 1/76	14.63	11.73	1.71	13.44	91.9
20/ 1/76	14.58	14.47	3.45	17.92	122.9
21/ 1/76	14.99	11.38	2.70	14.08	93.9

* Calculated from average data.

APPENDIX D

QUALITY OF CEMENT PRODUCED

APPENDIX D

QUALITY OF CEMENT PRODUCED

While remote, the possibility of non-volatile chlorinated hydrocarbons not being destroyed and remaining with the clinker was considered. It is common knowledge that excessive quantities of organic materials can detrimentally affect setting, air entraining and compressive strength characteristics of cement.

After preparing the daily composite clinker sample for analysis, the quantity of sample which had not undergone size reduction was retained. These were combined into a composite of several days, three such composites being prepared for each of the aromatic plus complex chlorinated hydrocarbon burn, the PCB burn and the final baseline burn. Each composite, after being crushed to approximately one-half inch, was blended with the correct amount of the normal production gypsum used at St. Lawrence Cement. The clinker-gypsum blends were ground in a laboratory ball mill. The grinding was timed and samples were taken at suitable intervals during grinding to determine surface area.

The cements were produced to conform to the requirements of Symbol 10 cement as designated in the Canadian Standards Association (CSA) Standard A5 "Portland Cements", and Type I cement as defined in the American Society for Testing and Materials (ASTM) designation C150, "Standard Specification for Portland Cement".

Each cement was tested in conformance to the following ASTM methods:

C185, Test for Air Content of Hydraulic Cement Mortar;
C109, Test for Compressive Strength of Hydraulic Cement Mortars (using 2-in. cube specimens);
C359, Test for False Set of Portland Cement (Mortar Method);
C204, Test for Fineness of Portland Cement by Air Permeability Apparatus;
C151, Test for Autoclave Expansion of Portland Cement;
C191, Test for Time of Setting of Hydraulic Cement by Vicat Needle.

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To ensure that differences in quality were not due to unexpected differences in cement composition, a chemical analysis was performed on each cement tested. Procedures followed were those normally used for control purposes at St. Lawrence Cement.

The technique used for determination of the concentration of each oxide was fusion with lithium tetraborate followed by x-ray fluorescence analysis. This method is commonly used for cement analyses. With the exception of lower K_2O content in the cements from clinkers produced while burning chlorinated hydrocarbons, there were no significant differences in their chemical compositions (Tables D.1, D.2 and D.3).

Differences in physical characteristics found by testing these cements were:

Setting Time - The water required to obtain normal consistency was greater and setting time shorter for baseline clinker cements. Shorter time of set and higher water requirement were attributed to the higher alkali content of the baseline clinker.

False Set - False set was severe on the cements from clinker produced during baseline burning. There was no indication of false set in cements from clinker produced while burning chlorinated hydrocarbons. The improvement was due to lower alkali content of the cement. In this regard, the determination of false set by ASTM Method C451, "Test for False Set of Portland Cement (Paste Method)" would not have shown as dramatic an improvement. This latter test takes into account the water requirement of cements, and therefore compensates for the greater quantity of water required by the higher alkali cements.

Compressive Strength - Higher initial and lower ultimate strengths are characteristics of higher alkali content cements. The only apparent differences in cements from clinkers produced with and without burning of chlorinated hydrocarbons were those expected because of the differences in alkali content.

TABLE D.1. CEMENTS FROM CLINKER PRODUCED DURING BASELINE BURN

Sample Number	7	8	9	Aver.
Chemical Tests				
Loss on Ignition (%)	1.52	1.51	1.43	1.49
SiO_2 (%)	20.69	20.59	20.53	20.60
Al_2O_3 "	5.93	5.90	6.00	5.94
Fe_2O_3 "	2.20	2.22	2.24	2.22
CaO "	63.42	63.39	63.35	63.39
MgO "	2.52	2.52	2.52	2.52
SO_3 "	2.74	2.79	2.89	2.81
K_2O "	1.15	1.23	1.22	1.20
Free CaO (%)	0.44	0.52	0.54	0.50
C_3S (%)	50.1	50.8	50.0	50.3
C_2S "	21.6	20.8	21.2	21.2
C_3A "	12.0	11.9	12.1	12.0
C_4AF "	6.7	6.7	6.8	6.7
Physical Tests				
Fineness				
Blaine (cm^2/g)	3406	3579	3607	3530
Passing 200 mesh (%)	96.4	97.6	98.8	97.6
Setting Time				
N.C. Penetration (mm)	10.0	9.5	9.0	9.5
N.C. Water (%)	22.5	23.0	23.0	22.8
Initial (minutes)	115	106	106	109
Final (minutes)	225	216	221	221
False Set				
Temperature °F	70	73	73	72
Penetration (mm)				
3 minutes	50	37	34	40
5 minutes	50	7	8	22
8 minutes	21	4	4	10
11 minutes	16	4	3	8
Remix	50	50	50	50
Compressive Strength				
1 day (psi)	2050	2010	1910	1990
3 day (psi)	2910	2990	3210	3040
7 day (psi)	3480	3610	3880	3660
28 day (psi)	4130	4470	4530	4380
Air Content				
Water (%)	73.0	73.0	73.0	73.0
Flow (%)	80.6	86.8	86.0	84.5
Air (%)	7.2	7.6	8.3	7.7
Autoclave Expansion (%)	0.07	0.09	0.05	0.07

TABLE D.2. CEMENTS FROM CLINKER PRODUCED DURING AROMATIC PLUS COMPLEX CHLORINATED HYDROCARBON BURN

Sample Number	4	5	6	Aver.
Chemical Tests				
Loss on Ignition (%)	1.63	1.86	1.63	1.71
SiO_2 (%)	20.37	20.51	20.83	20.57
Al_2O_3 (%)	5.85	5.79	5.89	5.84
Fe_2O_3 (%)	2.26	2.23	2.22	2.24
CaO (%)	63.19	62.99	63.56	63.25
MgO (%)	2.51	2.49	2.52	2.51
SO_3 (%)	2.81	2.69	2.89	2.80
K_2O (%)	0.66	0.53	0.69	0.63
Free CaO (%)	0.50	0.59	0.48	0.52
C_3S (%)	51.8	50.8	49.4	50.7
C_2S (%)	19.4	20.6	22.5	20.8
C_3A (%)	11.7	11.6	11.9	11.7
C_4AF (%)	6.9	6.8	6.7	6.8
Physical Tests				
Fineness				
Blaine (cm^2/g)	3626	3562	3561	3583
Passing 200 mesh (%)	98.0	97.4	97.2	97.5
Setting Time				
N.C. Penetration (mm)	10.0	10.0	9.5	9.8
N.C. Water (%)	22.0	22.0	22.0	22.0
Initial (minutes)	118	135	135	129
Final (minutes)	238	250	250	246
False Set				
Temperature °F	70	72	73	72
Penetration (mm)				
3 minutes	50	50	50	50
5 minutes	50	50	50	50
8 minutes	50	50	50	50
11 minutes	50	50	50	50
Remix	50	50	50	50
Compressive Strength				
1 day (psi)	1900	1640	1890	1810
3 day (psi)	3520	3200	3180	3300
7 day (psi)	4590	4360	4160	4370
28 day (psi)	5900	6050	5460	5800
Air Content				
Water (%)	71.0	72.0	72.0	71.6
Flow (%)	80.0	90.5	81.3	83.9
Air (%)	9.2	9.0	6.7	8.3
Autoclave Expansion (%)	0.03	0.04	0.02	0.03

TABLE D.3. CEMENTS FROM CLINKER PRODUCED DURING POLYCHLORINATED BIPHENYL BURN.

Sample Number	1	2	3	Aver.
Chemical Tests				
Loss on Ignition (%)	1.46	1.58	1.48	1.51
SiO_2 (%)	20.51	20.72	20.87	20.70
Al_2O_3 (%)	5.91	5.86	5.89	5.89
Fe_2O_3 (%)	2.16	2.18	2.16	2.17
CaO (%)	63.24	63.27	63.65	63.39
MgO (%)	2.53	2.56	2.58	2.56
SO_3 (%)	2.94	2.64	2.61	2.73
K_2O (%)	1.01	0.74	0.96	0.90
Free CaO (%)	0.53	0.57	0.69	0.60
C_3S (%)	50.4	50.0	50.3	50.2
C_2S (%)	20.9	21.8	22.0	21.6
C_3A (%)	12.0	11.9	12.0	12.0
C_4AF (%)	6.6	6.6	6.6	6.6
Physical Tests				
Fineness				
Blaine (cm^2/g)	3388	3579	3593	3520
Passing 200 mesh (%)	96.0	97.0	96.8	96.6
Setting Time				
N.C. Penetration (mm)	10.0	11.0	9.0	10.0
N.C. Water (%)	22.0	22.0	22.0	22.0
Initial (minutes)	153	125	112	130
Final (minutes)	273	250	235	253
False Set				
Temperature ^oF	70	71	71	71
Penetration (mm)				
3 minutes	50	50	50	50
5 minutes	50	50	50	50
8 minutes	50	50	50	50
11 minutes	50	50	50	50
Remix	50	50	50	50
Compressive Strength				
1 day (psi)	1980	1800	1990	1920
3 day (psi)	3080	3000	3260	3110
7 day (psi)	3770	4000	4090	3950
28 day (psi)	4620	5110	5080	4940
Air Content				
Water (%)	71.0	71.0	71.0	71.0
Flow (%)	88.0	84.5	82.2	84.9
Air (%)	7.7	7.9	9.2	8.3
Autoclave Expansion (%)	0.05	0.06	0.08	0.06

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APPENDIX E

EQUIPMENT DESCRIPTION AND ASSOCIATED ECONOMICS

APPENDIX E

EQUIPMENT DESCRIPTION AND ASSOCIATED ECONOMICS

In order to burn waste chlorinated hydrocarbons in a cement kiln, they must be blended to be compatible with the handling and storage system and to achieve uniform feed to the kiln. A storage tank and feed system with associated control devices must be installed at the kiln site.

For the program to be economically viable, the price structure must be favourable to the originator of the wastes and to the cement producer. The waste disposal company must be able to generate sufficient revenue to cover shipping, handling, blending, disposal of non-fuel fractions and receive some profit. The economics from the point of view of the cement producer are discussed in Section E.2.

E.1 Equipment Description

The system installed at the cement plant can vary. A simple inflexible installation with manual controls and a used rail car for storage would cost approximately $25,000. At the other extreme, a sophisticated system with large storage capacity, corrosion resistant construction, well instrumented could cost $200,000.

Although there are general similarities between cement kilns, the flow rate of waste chlorinated hydrocarbon depends on the percentage of chlorine in the waste, the decrease desired in the potassium and sodium levels of the finished product and the production capacity of the kiln. Thus, for the optimum system, the design, engineering, installation and operation must be compatible with these parameters.

Two systems are described herein; one is the actual system installed at the St. Lawrence Cement Co. kiln and the other has been somewhat arbitrarily selected as a basic system. This basic system assumes that a quality controlled blend of chemical wastes will be used. The fuel product would be a low viscosity, single-phase liquid, non-corrosive or mildly corrosive to carbon steel, not highly volatile, having an approximate composition of: 60,000 Btu/gallon, 40% Cl, and specific gravity of 1.2. Fuels with higher or lower Btu and chlorine can be prepared for those applications where other compositions are optimum.

At these compositional values, a feed rate of 1 lgpm into a 1000 ton per day kiln would provide an alkali reduction of 0.45% as K_2O. The Btu's provided would be a small percentage of the total heat requirement of the kiln. With waste streams with a lower chlorine level, larger volumes can be used to make up a greater fraction of the heat requirements, in practice up to 10-15% of total Btu input.

Other than capacity and the provision that the kiln be rotary, it makes little difference what the primary fuel or fuels are. Wet or dry fuels can burn waste chlorinated hydrocarbons, with consideration given to the increase in dust loading to the dust handling equipment.

E.1.1 Cost of basic system

The basic system with minimum component cost estimates would entail:

Equipment Cost:

Tank, 10,000 gal carbon steel	$ 8,000
Feed Pump, Centrifugal, 7.5 hp	1,200
Flame Arrestor	100
Vent Scrubber, Activated Carbon	1,000
Tank Level Indicator	2,500
Grounding	400
Tank Berming	1,000
Unloading Piping	500
Piping, Tank to Kiln, 100'	1,000
Electrical-Combination Starter	1,500
Concrete Pad, Site Preparation	2,500
Miscellaneous, Hardware	
Painting and NFPA Code Marking	2,500
Instrumentation	400
Nozzle Assembly	200
	$22,800
Installation:	4,000
Total System Cost, Installed	$26,800

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A schematic representation of the system is shown in Figure E.1.

Operating Cost:

Maintenance, 4% of investment/year	$1,080
Operating Labour, Based on 330 days/year	
Operating 24 hr/day	
1 hr per shift @ $8.00	8,000
Electricity, 7.5 hp, 8000 hr	
@ 3¢/kwh	1,800

Startup of the system should be achieved with minimum effort once the system is installed and tested for leaks. Allowance of $1,500 for initial startup should be adequate. Safety equipment for personnel protection and a fire exinguisher at the unloading/pumping station can be provided for about $250.

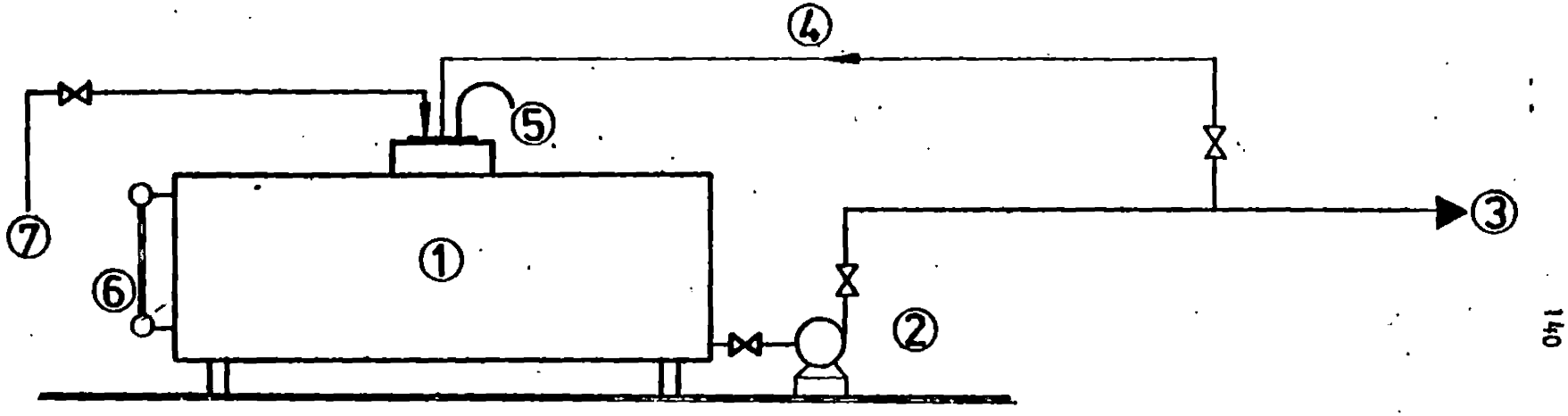
E.2.2 System at the St. Lawrence Cement Co. plant

The actual system used for the test (Figure E.2) was designed to contain corrosive materials as well as those with low flash points. Sophisticated equipment is used to control the feed to the kiln and the system includes traps to avoid vapours being emitted to the atmosphere. The storage tank received two liners of "Furoglass" membrane and one liner of 2½" acid proof brick.

Trucks were unloaded via a centrifugal pump through filters into a 55,000 gal storage tank. Fumes exhausted from the storage tank while unloading trucks were returned to the truck by a return vent line. Fumes emanating from the tanks by normal vapour diffusion or expansion due to temperature were removed by sodium hydroxide and charcoal filters.

Either of two centrifugal pumps was used to feed the kilns at a pressure of approximately 120 psi, the pressure maintained by returning an amount of material through a suitable orifice to the storage tank. Each kiln was controlled separately using an electro-pneumatic control valve, magnetic flow meter and transmitter.

The tubing inserted inside the pipe sleeve located on top of the burners was made from tantalum. The tubing was threaded so that a titanium nozzle, of correct size to atomize the quantity of liquid input to the kiln, up to a maximum capacity of 4 gallons per minute, could be attached.



1 CHEMTROL STORAGE TANK
2 PUMP
3 TO KILN
4 RETURN LINE
5 VENT PIPE
6 LEVEL GAUGE
7 FILLER PIPE

FIGURE E.1 SCHEMATIC DIAGRAM OF BASIC CHLORINATED HYDROCARBON FEED SYSTEM

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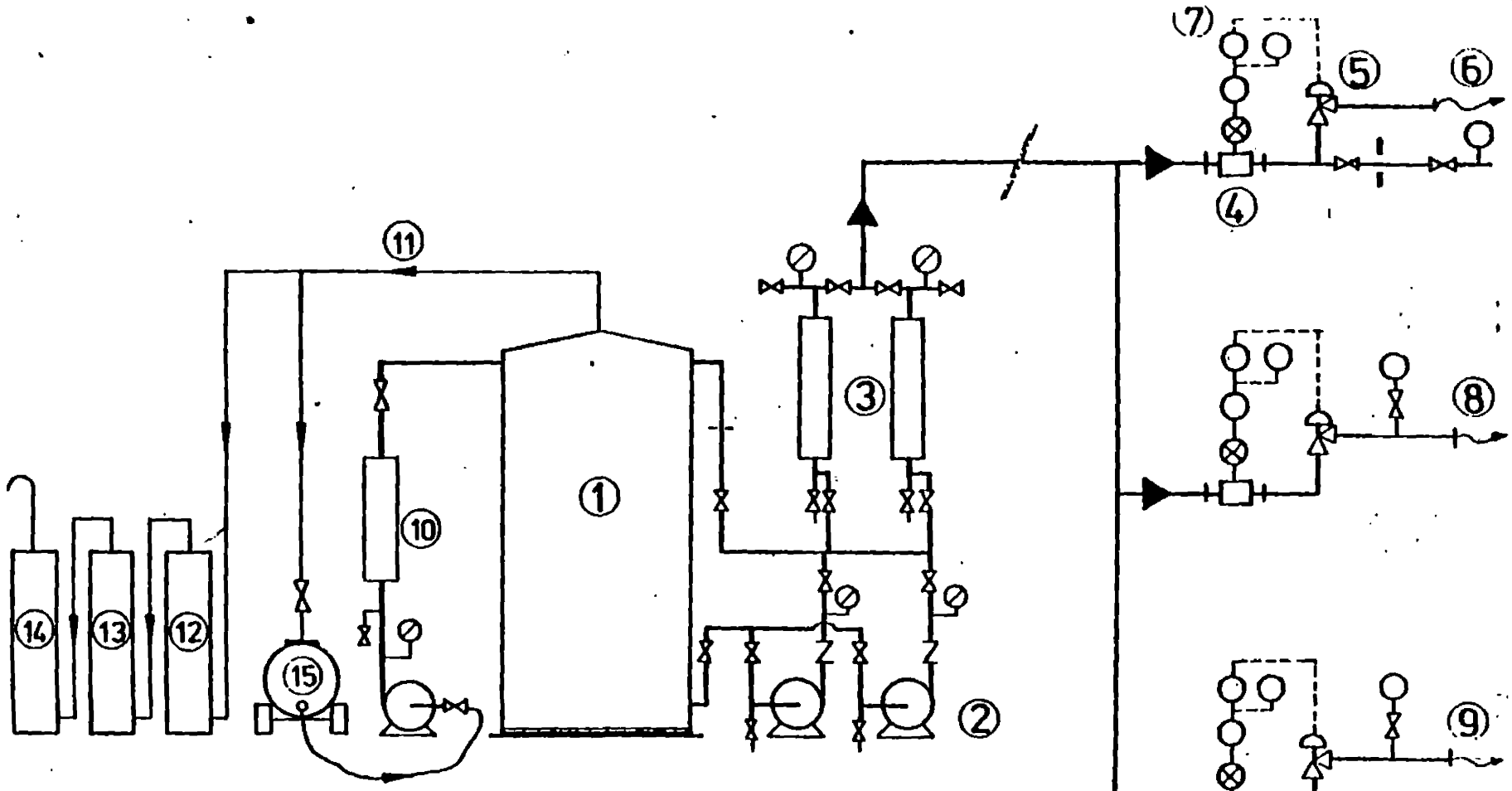

1 STORAGE TANK
2 KILN FEED PUMPS
3 FILTERS
4 FLOW METER
5 CONTROL VALVE
6 TO KILN III
7 FLOW RECORDING CONTROLLER
8 TO KILN II
9 TO KILN I
10 FILTER
11 TO ODOR CONTROL SYSTEM
12 BACK TRAP
13 CAUSTIC SCRUBBER
14 CHARCOAL FILTER
15 TRUCK

FIGURE E.2 SCHEMATIC DIAGRAM OF CHLORINATED HYDROCARBON FACILITIES

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The total installed cost of this system was over $200,000, comprising the following items:

Equipment and Installation:

Tank	$25,000
Acid Brick Tank Lining	35,000
Teflon* Lined Pumps and Filters	12,000
Teflon* Lined Piping	45,000
Odour Control Equipment	5,000
Foundations	10,000
Dike	1,000
Pump House	10,000
Site Clearing and Leveling	3,000
Instrumentation	20,000
Painting	5,000
Sales Tax	5,000
Engineering	18,000
Consultant	8,000
Travel Expense	10,000
TOTAL	$212,000

Operating Cost:

Maintenance and Operating Labour (cost per year)	$25,450
Electricity (23¢/hour for 8,000 hours)	1,840
TOTAL	$27,290

Due to the potentially dangerous nature of these fuels, both with regard to personnel safety and environmental considerations, an extensive training and instruction program was carried out.

E.2 Economics of Burning Waste Chlorinated Hydrocarbons

It is not possible to give a definite statement on the economics of burning chlorinated wastes for all circumstances. Some cement plants

*Trademark, E.I. du Pont de Nemours.

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require a reduction in the alkali oxide ($K_2O + Na_2O$) content of the finished product. In this case, chlorine must be added to the process materials, and is available from different sources in different geographical areas. Waste hydrochloric acid from the steel industry may be used where available; in other areas cement plants purchase calcium chloride. If reduction of alkali is not required, then addition of chloride would cause the generation of greater quantities of dust, thereby increasing dust disposal costs.

Another factor making economic comparisons difficult is the different waste streams available. In some cases, the chlorinated waste streams may be suitable for purifying and further use. Other waste streams, such as PCB's and insecticides banned for environmental reasons, present a serious disposal problem. Obviously, these different materials would not all cost the same for use in a cement kiln. However, to present some models, the price structure used by Chemtrol Pollution Services, Inc. for blended noncorrosive wastes suitable for use in the basic system described above has been adopted. At present, Chemtrol plans to charge 80 percent of the fuel value and, where applicable, 30 percent of the chlorine value for these blended "fuels". In the examples, the following assumptions have been made: The kiln is a wet process type producing 1,000 tons per day with a fuel requirement equivalent to 5,150,000 Btu per ton of production.

E.2.1 Process requiring addition of chlorine

Assume in this case that the fuel cost is $1 per million Btu and that it is necessary to reduce the K_2O content of the clinker by 0.45 percent. This would require approximately 6,800 pounds of chlorine per day. A 32 percent solution of calcium chloride weighing 13 pounds and costing $0.14 per Imperial gallon ($0.053 per pound of chlorine) is used. In this case, 2,565 gallons would be required at a total cost of $359.

This could be replaced by 'Trol Fuel*" containing a nominal 70 percent chlorine and 65,000 Btu per Imperial gallon. At a weight of 13 pounds per gallon, 750 gallons would be required each day. Using the

*Trademark, Chemtrol Pollution Services Inc.

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above mentioned price structure, the cost per gallon would be:

$$9.1 \text{ lb } Cl_2 \times \frac{\$0.053}{\text{lb } Cl_2} \times \frac{30}{100} = \$0.145$$

$$65{,}000 \text{ Btu} \times \frac{\$1.00}{1{,}000{,}000 \text{ Btu}} \times \frac{80}{100} = \$0.052$$

TOTAL $0.20

Thus, the 750 gallons would cost $150 and would supply 48.8 million Btu.

The total daily tangible savings then become:

Cost of Calcium Chloride	$359
Cost of Normal Fuel Replaced	$ 49
Less Cost of "Trol Fuel"	$150
Net Savings Per Day	$258

E.2.2 Process not requiring addition of chlorine

The 1,000 ton per kiln and a specific heat consumption of 5,150,000 Btu per ton of clinker produced and a fuel cost equivalent to $1.00 per million Btu is again taken as the model. In this case, however, no chlorine is required and the waste stream contains less than 5 percent chlorine. This material is available at $0.80 per million Btu and is used at a replacement rate of 10 percent of the Btu requirement or 515,000 Btu per ton of clinker.

The fuel normally used on the kiln but replaced by this waste stream would cost $0.515 per ton of clinker or $515 per day. The daily savings can be calculated as:

Cost of Normal Fuel Replaced	$515
Cost of "Trol Fuel"	412
Net Daily Savings	$103

This saving can be negated by the cost of discarding the additional dust collected in the precipitators (See Section 6.1), a factor which will vary with each cement plant.

E.2.3 Total economic considerations

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The above models are not intended to be all inclusive. Due to the many variables involved, each possible application must be assessed based upon economic factors existing in the locale. At the time the system

was installed at the St. Lawrence Cement Co., it was necessary to use chlorine in two wet kilns each having a capacity of 1,000 tons per year. For the period January through September 1976, maintenance on the system amounted to $18,760. Thus, the figure of $27,290 for yearly operating and maintenance cost is considered accurate. Under these circumstances, the economic picture over the period of a year becomes:

Total Savings Using "Trol Fuel" (600 kiln operating days @ $258 per day)	$154,800
Maintenance and Operating Cost	27,290
Interest on $212,000 @ 11%/year	23,320
Net	$104,190

This estimated saving, which would have given excellent payback on the system, has not been realized. Low alkali requirements have been falling into disfavour because such requirements are not compatible with the goal of energy conservation. With the requirement for chlorine addition, savings must be based only on fuel costs which, if all factors are favourable, would total for the two kilns:

Total Savings Using "Trol Fuel" (600 kiln operating days @ $103/day)	$61,800
Maintenance and Operating Costs	27,290
Interest on $212,000 @ 11%/yr	23,320
Net	$11,190

Even this modest sum has not been realized, for two reasons: the cost of discarding additional dust, and the unsteady supply of these wastes.

It is obvious from this discussion that plants requiring the addition of chlorine are in a better position to make burning of chlorinated wastes attractive than those plants not requiring chlorine. Also, a less sophisticated system than that installed at St. Lawrence Cement Co. is necessary if the only consideration is the fuel value of these wastes.

APPENDIX F

ONTARIO MINISTRY OF THE ENVIRONMENT EMISSION GUIDELINES AND ANALYTICAL SUPPORT

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APPENDIX F

ONTARIO MINISTRY OF THE ENVIRONMENT EMISSION GUIDELINES AND ANALYTICAL SUPPORT

F.1 Emission Guidelines

All industrial sources of potentially significant emissions to the atmosphere in Ontario come under the jurisdiction of the Province's Environmental Protection Act. The Act requires such sources to operate under a Certificate of Approval which specifies the acceptable operating conditions and emission rates for potential air contaminants. The Ministry of the Environment required that the experimental waste chlorinated hydrocarbon burn at St. Lawrence Cement Co., Mississauga meet certain conditions specified in a Certificate of Approval. Conditional approval was granted for each of the three stages of the waste burn (A, B, C) under the terms of the tentative guidelines for the allowable emission rates of organic chloride.

Pasquill-Gifford dispersion calculations based on the guideline emission rates from the wet kiln were used to predict the worst-case ground level concentration of residual organic chloride (½-hour average).

Table F.1 shows the specifications which were applied to each stage of the waste burn, along with the measured emission rates.

The less stringent guideline for the first two waste burns was met easily. Because of the large percentage of highly persistent polychlorinated biphenyls anticipated in the fuel for the third waste burn, a much more stringent guideline was given.

In the most critical case, the third burn, the calculated approximate flue gas concentration of residual chloride, 50 $\mu g/m^3$ (as Cl), based on the stated guideline, corresponds to roughly 5 ppb (v/v) of Aroclor 1242 or 17 ppb (v/v) of dichloromethane (at ambient temperature), the predominant individually identified component of the flue gas. These values compare with the detection limit for PCB's of 3 $\mu g/m^3$ or 0.3 ppb in the flue gas (ambient temperature).

Since no PCB was found in the flue gas samples and the methylene chloride concentration only slightly exceeded the very stringent guideline for organic chloride in this stage, the guideline should be considered to have been met without question.

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TABLE F.1. MOE SPECIFICATIONS APPLIED TO WASTE BURNS

Waste Burn	1	2	3	4	5*	6	7
A	0.5	99.5	99.990	5000	23-150	0.2	0.001-0.006
B	0.5	99.5	99.989	5000	16-150	0.2	0.001-0.006
C	0.005	99.995	99.986	50	88-150	0.002	0.004-0.006

Column Identification:

1. Guideline emission rate for residual organic chloride (g Cl/sec).
2. Estimated required percent destruction or retention of chlorinated fuel.
3. Estimated minimum percent combustion of chlorinated fuel from test data (Table 6, Section 5.3).
4. Approximate calculated flue gas residual chloride concentration based on guideline emission rate (µg Cl/m^3).
5. Approximate measured flue gas organic chloride concentration based on dichloromethane and data from Table 5, Section 5.3 (µg Cl/m^3). The upper limit of the range corresponds to 50 ppb organic Cl as CH_2Cl_2.
6. Calculated point of impingement ½-hour average chloride concentration based on guideline emission rate (µg Cl/m^3).
7. Approximate calculated point of impingement ½-hour average chloride concentration based on dichloromethane and data from Tables 5 and 6, Section 5.3 (µg Cl/m^3).

*Since no PCB's were detected in the flue gas samples, none of the residual organic chloride values in column 5 should be attributed to PCB's in any of these stages.

If the concentration of residual organic chloride in the flue gas (column 7, Table F.1) were taken to represent PCB's in a "worst case" (recall that no PCB's were detected), the calculated point of impingement concentration by the Pasquill-Gifford method is approximately equal to typical measured ambient air concentrations of PCB's in urban areas. There would appear to be little cause for concern when the emission guidelines are met in this process configuration.

The above discussion relates only to the wet-kiln tests at St. Lawrence Cement. If the same guidelines were applied to another kiln, for example the lower-level, multi-stack dry kiln at St. Lawrence Cement, the same emission rate as measured in the wet kiln tests would lead to a significant ground level concentration. For example, even if the stringent guideline for PCB emissions were met in this hypothetical case, the maximum ground level concentration is calculated by virtual source methods (applied to the dry kiln stack configuration) to be 0.07 $\mu g/m^3$ (as Aroclor 1242) which is 7 to 70 times the typical measured ambient air concentration of 0.001 to 0.01 $\mu g/m^3$. The point is that some caution should be exercised in applying the results of these tests to another stack configuration.

In the case of the third waste burn, it was estimated that the total organic vapour concentration in the flue gas during the tests was about 50 ppb, of which about 30 ppb was found to be dichloromethane. Since none of the components of the original fuel mixture were detected, however, the maximum residual concentration of Aroclor 1242, for example, could be only about 1 ppb or less (noting the approximate detection limit of 0.3 ppb). For speculation purposes only, in this worst case, 1 ppb Aroclor 1242 in the flue gas (at ambient temperature) would correspond to about 11 $\mu g/m^3$ PCB (or about 5 $\mu g/m^3$ as chloride) and about 0.1 kg of Aroclor 1242 emitted per day (24 hours of continuous operation). In reality, this quantity is an overestimate of the total emissions and is probably not significant.

F.2 Gas Chromatographic Analysis of Process and Emission Test Samples

F.2.1 Chromosorb 102 adsorption tube analysis

Duplicate Chromosorb adsorption tubes for each of the waste burns were analyzed by the Air Quality Laboratory, Laboratory Services

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Branch, Ontario Ministry of the Environment for support and cross-check of analytical results obtained by the Ontario Research Foundation. Each adsorption tube sample represented 60 litres of emission gas. Analysis was done after desorption at 120°C into an evacuated glass vessel by injecting a 1 ml gas sample into a gas chromatograph. This instrument was equipped with a 9 foot x 1/8 inch Chromosorb 102 column held at a temperature of 180°C, and a Sc^3H electron capture detector.

The results from these analyses are summarized in Tables F.2 to F.4. All Chromosorb tube samples, including those from "Baseline B", were found to contain small but measurable amounts of six or seven compounds and traces of a further six to eight compounds. These "measurable" compounds were almost certainly chlorinated, low-molecular weight compounds which, in the tables, have been designated "major" and "minor", according to the size of their gas-chromatographic peaks. Of these compounds, only chloroform had been tentatively identifled and quantitatively determined. All other compounds separated from each sample were estimated together by relating the sum of the gas chromatographic peak areas with those obtained from a chloroform standard. Their concentrations are listed under "Other Compounds".

The results shown in Tables F.2 to F.4 indicate that the total of all chlorinated compounds in the Chromosorb adsorption tube samples corresponds to concentrations only in the low parts per billion range in the stack emission gases.

The agreement between these results and those of the Ontario Research Foundation and TRW is only qualitative. The generally small amounts (ppb range) of organic chloride vapours found by ORF are confirmed but trends from stage to stage are not reproduced. Such disagreement is merely indicative that the limits of sensitivity of the combined sampling and analytical methods are being approached.

F.2.2 Fuel feedstock analysis

Samples of the waste chlorinated hydrocarbon fuels used in waste burns B and C were analyzed in the laboratory of Professor F.W. Karasek, Department of Chemistry, University of Waterloo under a research grant from the Air Resources Branch, Ontario Ministry of the Environment.

TABLE F.2. ST. LAWRENCE CEMENT WASTE BURN EXPERIMENTS - TEST 1
CHROMOSORB ADSORPTION TUBE ANALYSIS

Waste Burn Experiment	"Major" Compounds	"Minor" Compounds	Chloroform	Other Compounds	Total Compounds
			ppb	ppb	ppb
A	3	4	1.192	7.121	8.313
B	1	5	0.058	0.646	0.704
C	2	4	0.329	2.909	3.238
Baseline B	2	5	0.055	2.487	2.542
Blank (Chromosorb)	0	0	-	-	-

TABLE F.3. ST. LAWRENCE CEMENT WASTE BURN EXPERIMENTS - TEST 2
CHROMOSORB ADSORPTION TUBE ANALYSIS

Waste Burn Experiment	"Major" Compounds	"Minor" Compounds	Chloroform	Other Compounds	Total Compounds
			ppb	ppb	ppb
A	4	3	1.462	8.827	10.289
B	4	1	1.464	5.270	6.734
C	3	4	0.924	12.089	13.013
Baseline B	0	7	0.022	0.443	0.465
Blank (Chromosorb)	0	0	-	-	-

TABLE F.4. ST. LAWRENCE CEMENT WASTE BURN EXPERIMENTS - TEST 3
CHROMOSORB ADSORPTION TUBE ANALYSIS

Waste Burn Experiment	"Major" Compounds	"Minor" Compounds	Chloroform	Other Compounds	Total Compounds
			ppb	ppb	ppb
A	5	0	2.356	15.773	18.129
B	3	3	0.481	1.916	2.397
C	3	8	0.560	2.089	2.649
Baseline B	3	4	0.030	5.077	5.107
Blank (Chromosorb)	0	0	-	-	-

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F.2.2.1 Preparation of fuel samples. All samples were diluted ten times with Burdick and Jackson "Distilled in Glass" methylene chloride. A 0.1 ml aliquot of the fuel was made up to 1.0 ml with the methylene chloride.

Methylene chloride was chosen for the solvent based on previous fuel samples analyzed in this laboratory.

F.2.2.2 Analysis of fuel samples. All samples were surveyed by gas chromatography using a 10' x 2 mm i.d. glass column with a specially prepared, high resolution column packing, referred to as Ap-20M. A similarly prepared solution of Aroclor 1242 was also chromatographed for comparison.

The GC conditions used are shown in Table F.6 and were closely monitored by the use of a HP 5830 A Digital Gas Chromatograph using a flame ionization detector. The area of the solvent peak was rejected to facilitate comparison of GC data.

Mass spectral data were obtained using a Perkin-Elmer 900 GC interfaced to a HITACHI RMU-6 magnetic mass spectrometer via a Biemann - Watson effusion separator. The spectra were initiated and counted manually. All spectra were obtained with 70 eV ionizing voltage at 250°C.

Samples 1 and 9 were analyzed using GC/MS techniques as above.

F.2.3 Results and Discussion

Samples 8 to 10, the aromatic chlorinated fuels, displayed only seven compounds with individual integrated area percentages greater than 1% and only nine with similar area percentages greater than 0.5%. There appear to be only three major components: one with ca. 73% area, one with ca. 4.5%, and one with ca. 6.8%. This appeared to be the case for all the aromatic fuels. A representative bar chromatogram is shown in Figure F.1. The peak at four minutes in the aromatic fuel was ca. 73%.

Samples 1 to 7, the PCB fuels, displayed several peaks in addition to those of the aromatic fuels, samples 8 to 12. Comparison of the additional peaks with a chromatogram of Aroclor 1242 indicates that these peaks are due almost entirely to PCB compounds (see Figure F.1).

To illustrate this observation, the GC data from the aromatic fuel was added to the GC data from Aroclor 1242 and the computer program

TABLE F.5. FUEL SAMPLE IDENTIFICATION

Sample No.	Comments
1	Chemtrol Line Sample (PCB's), Jan. 3/76, 10:00 AM
2	" " " " , Jan. 4/76, 12:00
3	" " " " , Jan. 5/76
4	" " " " , Jan. 6/76
5	" " " " , Jan. 7/76, 9:00 AM
6	" " " " , Jan. 8/76, 8:45
7	" " " " , Jan. 9/76*
8	Chemtrol Line Sample (Aromatics), Dec. 10/75**
9	" " " " , Dec. 11/75**
10	" " " " , Dec. 12/75**
11	" " " " , Dec. 13/75**
12	" " " " , Dec. 15/75**

*Sample appeared to have water in it.

**Sample had reacted with liner of sample vial cap.

TABLE F.6. GAS CHROMATOGRAPH CONDITIONS
HP 5830-A GC

TEMP 1	50°
TIME	4 min
RATE	4°/min
TEMP 2	240°
TIME 2	50 min
INJ TEMP	280°
FID TEMP	300°
FLOW RATE	28 ml/min
CARRIER GAS	HELIUM
ATTENUATION	2^8 256

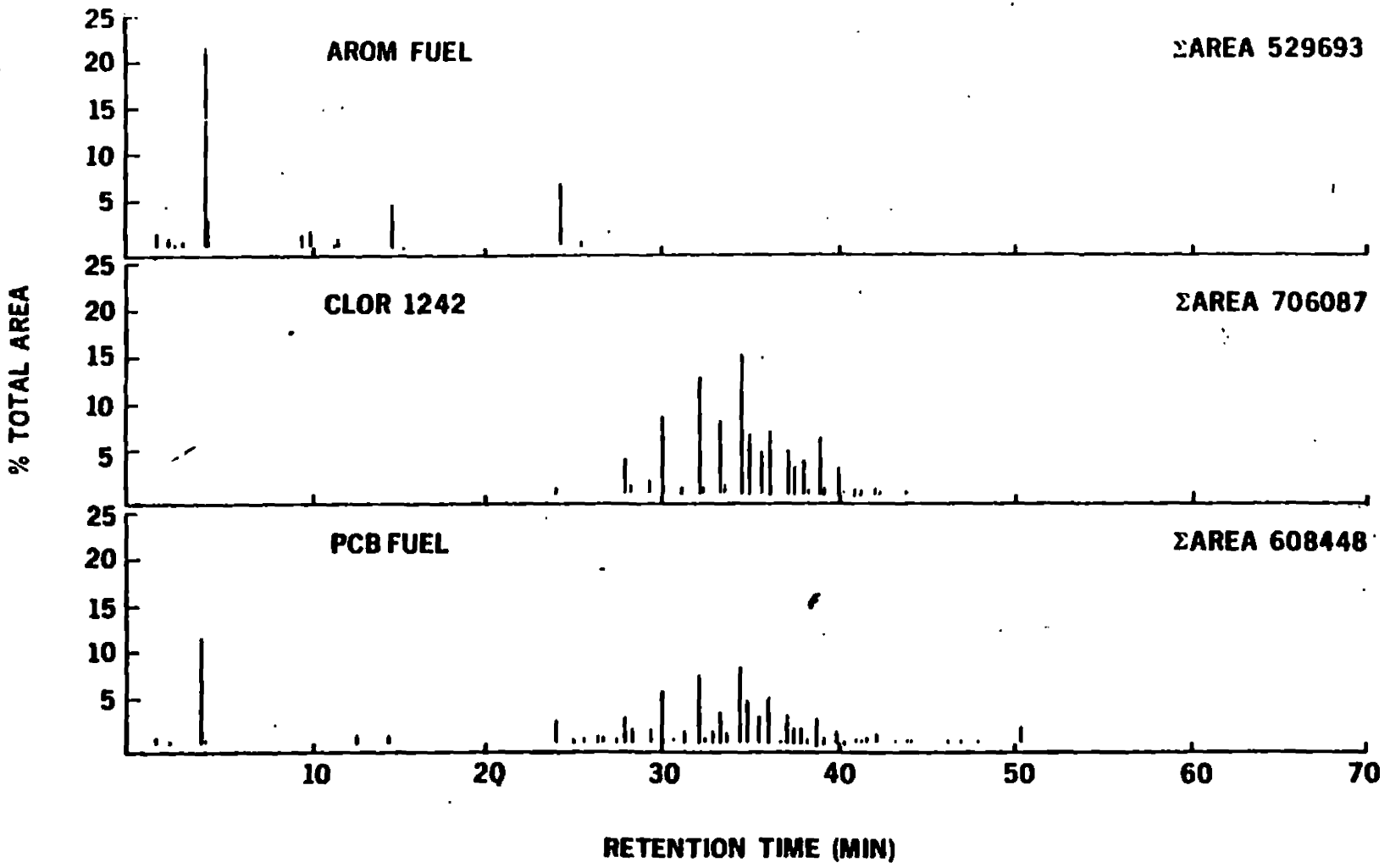

FIGURE F1 REPRESENTATIVE BAR CHROMATOGRAM

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treated the data as though it originated from a single sample. This computer-produced bar chromatogram, titled "AROM + CLOR", was then plotted in comparison with the bar chromatogram of the PCB fuel sample as shown in Figure F.2. The data were not subjected to any manipulation other than straight combination of the data. Inspection of the two plots shows such a close correspondence of GC peaks between the computer reconstructed mixture and the actual PCB fuel mixture that there is a reasonable assurance they are the same.

A GC/MS analysis was conducted on sample 1, one of the PCB fuels. A representative gas chromatogram with numerically identified peaks is shown in Figure F.3. Mass spectra were obtained for these numerically identified peaks. The probable identity, molecular weight and/or degree of chlorination is shown in Table F.7.

Since all of the peaks are found in the PCB fuel and only some of the peaks are found in the aromatic fuel, an estimate of the dilution or mixing of these compounds can be derived. During the gas chromatograph analysis, all variables were held constant; thus, absolute integrated area counts are indicative of changes in relative concentrations. These results are shown in Table F.8. The units are area counts and the values shown are $1/10^4$ of output values.

Peak #3 is absent in the aromatic fuel and in Aroclor 1242 but present in the PCB fuel. The mass spectrum of peak #3 suggests trichlorobenzene.

Peak #19 is present in small amounts in the chlorinated aromatic fuels, absent in Aroclor 1242 but present in increased concentrations in the PCB fuels. A definitive mass spectrum of this peak was not obtained but was suggestive of lack of halogenation and is most likely an unsaturated hydrocarbon of high molecular weight.

F.2.4 Conclusions

The aromatic fuel is primarily o-chlorotoluene and the PCB fuel is a mixture of Aroclor 1242 and the aromatic fuel. Area data for peak #1 indicated an initial dilution of approximately one-third (by comparison of area counts for aromatic fuels to area counts for sample 1) which increased to approximately four-fifths by the end of sampling data.

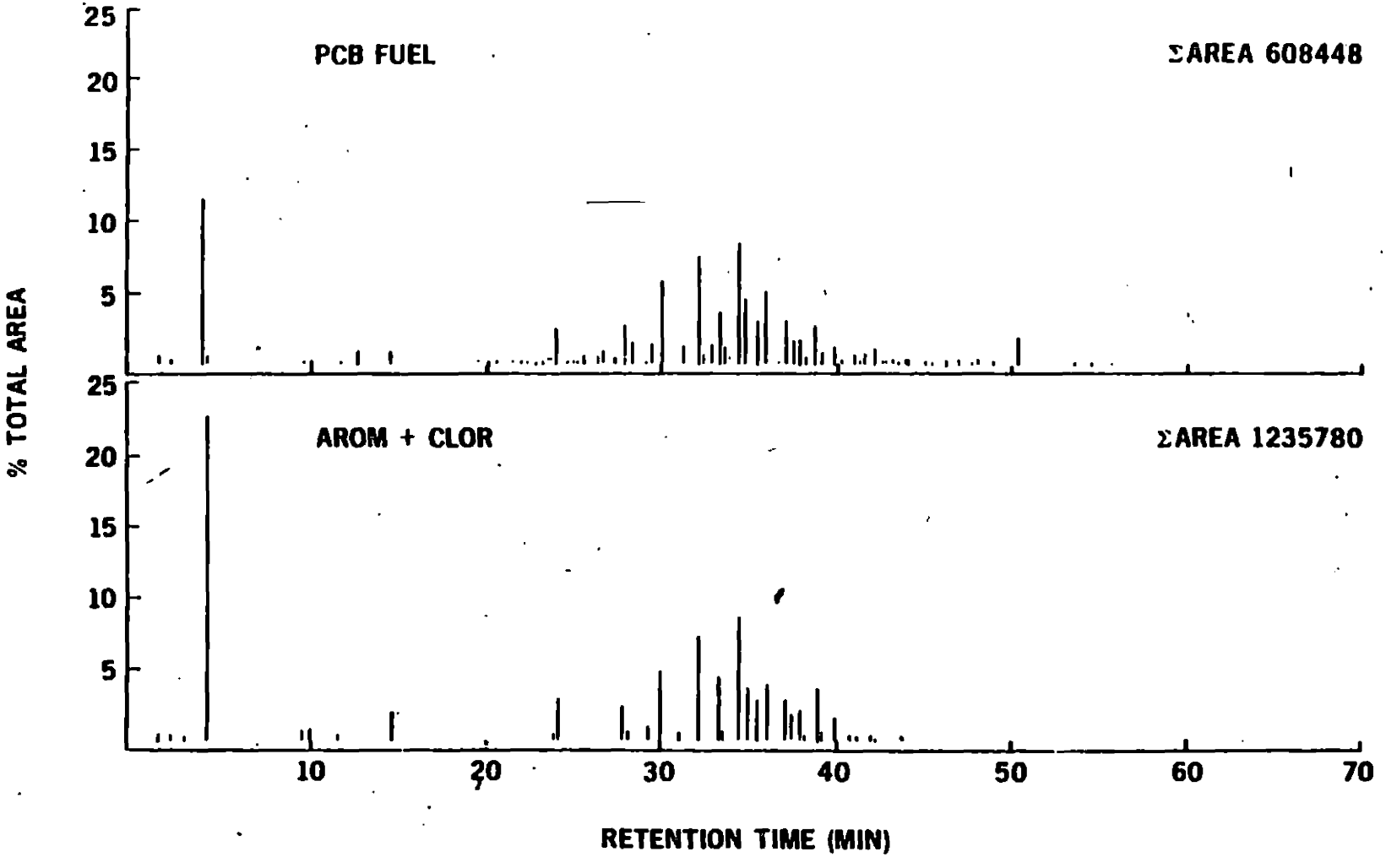

FIGURE F2 COMPUTER RECONSTRUCTED BAR CHROMATOGRAMS FOR PCB FUEL AND AROMATIC FUEL PLUS AROCHLOR 1242

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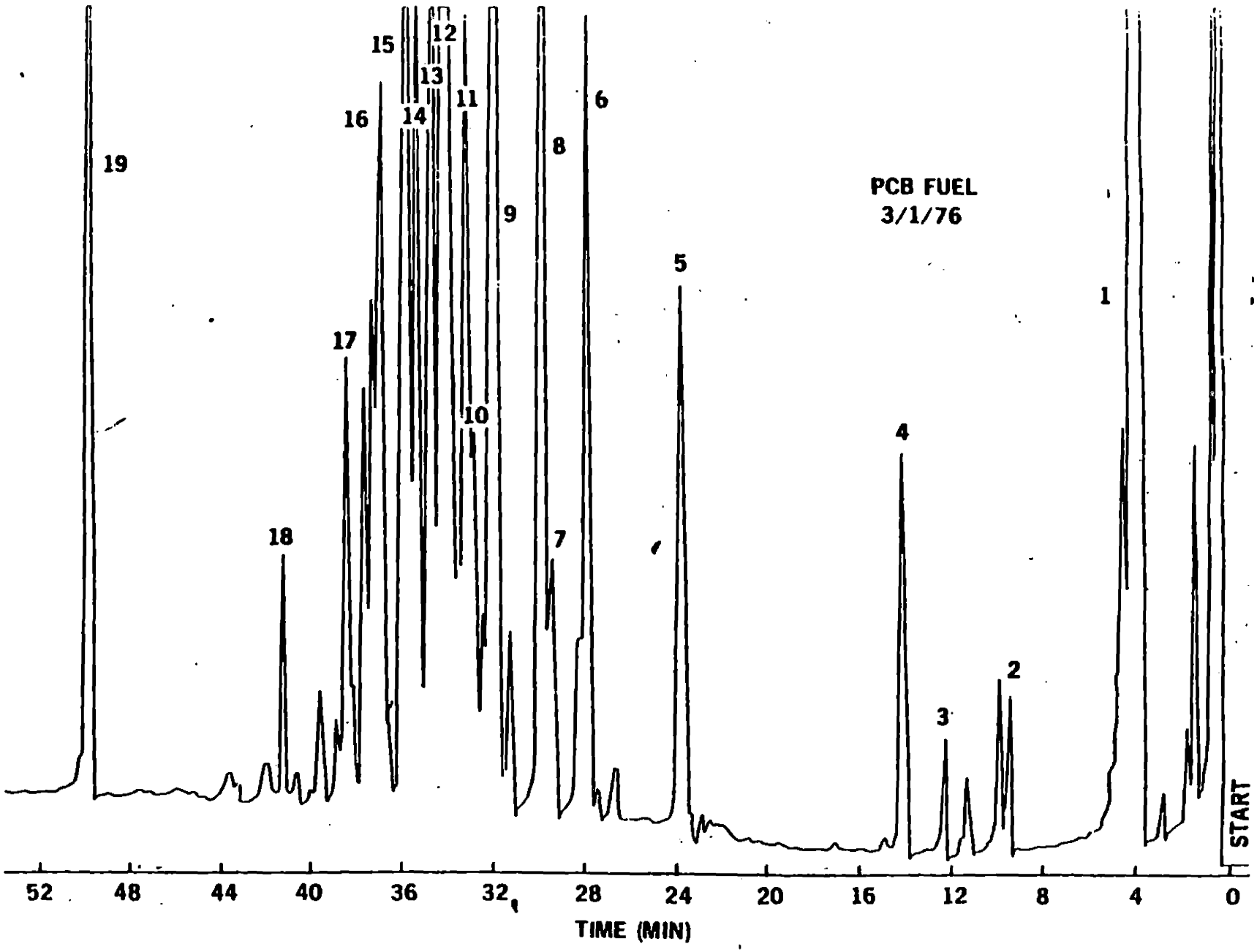

FIGURE F3 GAS CHROMATOGRAM FROM GC/MS ANALYSIS OF SAMPLE PCB FUEL

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The results of the University of Waterloo group with respect to identification of components of the waste burn B and waste burn C fuels are in agreement with those of ORF and TRW.

TABLE F.7. MS DATA FROM GC ANALYSIS OF SAMPLE PCB FUEL
(Reference to Figure F.3.)

Peak No.	Comments
1	MW 126, 1 chlorine - spectra suggest o-chlorotoluene
2	MW 160, 2 chlorines - spectra suggest aromatic compound - dichlorotoluene
3	MW 180, 3 chlorines - spectra suggest trichlorobenzene
4	MW appears to be 216 with 4 chlorines - possible identity $C_6H_4Cl_4$.
5	MW appears to be 216 with 4 chlorines - spectra very similar to peak #4
6-8	MW 222 2 chlorines - spectra suggest dichlorobiphenyls - PCB's
9-12	MW 256 3 chlorines - PCB's
13-16	MW 290 4 chlorines - PCB's
17 & 18	MW 324 5 chlorines - PCB's
19	MW uncertain - no suggestion of halogenation

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TABLE F.8. AREA COUNTS (x 10k)

Peak No.	8 10/12/75	9 11/12/75	10 12/12/75	11 13/12/75	12 15/12/75	1 3/1/76	2 4/1/76	3 5/1/76	4 6/1/76	5 7/1/76	6 8/1/76	7 9/1/76
1	3860	3976	3769	3994	3842	1200	1142	913.4	770.6	766.8	753.0	702.4
2	80.5	82.5	78.8	82.5	80.4	24.9	23.1	19.0	16.1	16.1	15.7	14.6
3	-	-	-	-	-	20.4	23.8	38.0	48.2	50.9	49.7	57.8
4	243.9	247.6	240.6	251.4	245.1	74.2	72.3	64.5	60.6	61.7	58.3	60.4
5	363.1	362.1	360.5	373.3	363.4	154.1	148.1	155.0	150.2	153.8	152.0	157.6
6	-	-	-	-	-	158.2	154.8	160.6	156.5	160.2	161.1	167.8
7	-	-	-	-	-	76.9	75.7	77.0	86.5	88.6	89.4	95.1
8	-	-	-	-	-	340.4	333.7	348.4	328.8	335.2	336.7	351.3
9	-	-	-	-	-	465.6	454.8	451.2	431.3	439.3	440.6	457.2
10	-	-	-	-	-	82.7	80.6	84.9	84.3	85.6	85.2	89.1
11	-	-	-	-	-	217.7	211.8	212.4	203.3	207.9	208.9	217.1
12	-	-	-	-	-	543.5	518.0	503.6	481.8	489.1	491.2	507.6
13	-	-	-	-	-	265.0	271.3	275.5	258.3	265.9	268.6	282.1
14	-	-	-	-	-	197.0	183.8	179.7	177.0	178.6	178.3	186.7
15	-	-	-	-	-	287.0	292.4	302.5	284.3	292.8	294.5	309.8
16	-	-	-	-	-	191.3	191.1	186.8	180.2	178.6	188.4	190.5
17	-	-	-	-	-	102.0	107.5	134.8	143.2	149.1	151.4	167.5
18	-	-	-	-	-	52.1	51.5	54.9	50.1	51.3	49.5	50.2
19	7.8	8.6	8.4	8.2	8.6	177.5	168.9	143.8	120.5	120.5	120.9	115.9

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APPENDIX G

LABORATORY ANALYSIS RESULTS FROM THE ST. LAWRENCE CEMENT FACILITY TEST

by

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TRW Systems Group

ACM C08257

APPENDIX G

LABORATORY ANALYSIS RESULTS FROM THE ST. LAWRENCE CEMENT FACILITY TEST

G.1 Summary

Analysis of the flue gas samples for organic composition gave the following results:

- Hydrocarbons were not detected in the samples of flue gas with detection limits ranging from 0.6 mg/m^3 to 0.009 mg/m^3.
- Low molecular weight chlorinated organic compounds such as methylene chloride, chloroform, and carbon tetrachloride were specifically searched for by gas chromatography with electron capture detection (ECD) and were generally not detected in most of the samples. Four samples indicated the possible presence of some of these compounds, but all at levels of less than 0.1 mg/m^3 of flue gas.
- Polychlorinated biphenyls were searched for by GC/ECD and GC/MS and were not found in any samples at the GC/MS detection limit of 3 $\mu g/m^3$ of flue gas.

Trace metal concentrations in the flue gases, as determined in the samples taken with the EPA sampling train, were all less than 10 $\mu g/m^3$, with the exception of lead in the WBC tests. The emission of lead during the WBC tests averaged 0.12 mg/m^3.

Analysis of the clinker product and discard dust samples for organic composition gave the following results:

- Hydrocarbons were not detected in solvent extracts of any of the clinker product or discard dust samples. The level of detection by GC/ECD was 5 $\mu g/g$ of sample or lower.
- Polychlorinated biphenyls were not detected in any of the clinker or dust samples by GC/ECD. Detection limits for PCB's in the samples were typically 0.04 $\mu g/g$ or better.

The inorganic character of the clinker products and electrostatic precipitator discard dusts was changed very little if at all by the addition

of the chlorinated wastes to the SLC wet kiln process. Trace metal levels in the WBB and WBC test samples did not differ significantly from the baseline samples.

Analytical techniques selected for analysis of flue gas constituents which include vapours, condensables and particulate matter were gravimetric, IR, LRMS, GC, GC/MS, SSMS, ICPOES, and AAS. These were selected on the basis of sensitivity and selectivity criteria to enable identification of species in the flue gas at concentrations on the order of 0.1 mg/m^3, representing the threshold level of the most toxic species as defined by OSHA and other occupational health and safety organizations. Detection limits for many of the techniques extend to $\mu g/m^3$ levels. However, specific analyses to identify compounds below the level of interest, 0.1 mg/m^3, were not routinely performed. The techniques used were both qualitative and quantitative in nature, with an intended accuracy range of plus or minus a factor of two to three.

G.2 Introduction

In cooperation with Environment Canada and the Ministry of Environment of Ontario, the United States Environmental Protection Agency supplemented the Canadian studies through participation in analyses of samples acquired from various streams during test burns of chlorinated hydrocarbons in the St. Lawrence Cement Co. wet process kiln. These analyses were performed by TRW Defense and Space Systems Group, Redondo Beach, California, under contract to the U.S. EPA. Samples were provided to TRW through the courtesy of the Ontario Research Foundation and St. Lawrence Cement Co., of Ontario, Canada.

Emphasis in the EPA sponsored work was directed toward analyzing for input waste residual compounds and by-products in the clinker (product), dust from the electrostatic precipitators, and the various component samples from the EPA Method 5 and ORF sorbent trap trains. These analyses were limited to the two test burns performed using chlorinated aromatic and polychlorinated biphenyl waste blends. In addition, background analytical work was accomplished on samples acquired during the two baseline tests in which the kiln was fired using only residual oil as a fuel. Analyses were also performed on the two waste blends. This work was done to supplement the Canadian laboratory results as well as to acquire

additional evaluation data in accordance with U.S. EPA protocol used for ongoing chemical waste incineration test programs in the United States.

A brief economic analysis was made by St. Lawrence Cement Co. using data from both their own operations and from Chemtrol Pollution Services Inc. (Appendix E).

G.3 Analysis Techniques

The purpose of the analyses performed on the samples from SLC was to identify and quantify:

- known hazardous species present from the waste as determined by pretest analysis of a sample of the waste material,
- secondary decomposition products (e.g., incomplete combustion products which are predictable), and
- other species found to be present but which are not predicted or otherwise expected.

A complete list of the samples received by TRW for analysis is given in Table G.1. This table shows what portion of the total sample collected by the trains was sent to TRW as well as the respective burns and test numbers for the received samples. The coding system used to uniquely identify each sample is shown in Figure G.1. These codes are used in subsequent tabulations of data and results.

The first step in the analytical approach involved various extraction and preparation procedures to separate the organic and inorganic constituents and/or to concentrate the samples in a suitable form for analysis. The extracts and concentrates were then analyzed by the techniques to be described in this section.

G.3.1 Extractions and sample preparation

G.3.1.1 Solvent extracts received from ORF. With a few exceptions, solvent extractions for organic species were performed by ORF using pentane or hexane. Subsequently, ½ aliquots were received by TRW and combined according to the plan shown in Figure G.2. These combinations were performed because:

1) the ½ aliquots represent relatively small gas sample volumes, thus making constituent concentrations very low and difficult to measure, and

TABLE G.1. SUMMARY OF SAMPLES RECEIVED FROM EACH WASTE BURN

Sample Description	Portion Received out of total Sample	Burn and Test No. of Samples Origin											
		BLA			MBB			MBC			BLB		
		1	2	3	1	2	3	1	2	3	1	2	3
EPA Train													
• Probe rinse													
Filtered insolubles	All				X	X	X	X	X	X	X	X	X
Solvent extract	1/4			X	X	X	X	X	X	X	X	X	X
Aqueous solution after filtration and extraction	All						X	X					X
• Filter													
Solvent extract	1/4			X	X	X	X	X	X	X	X	X	X
Filter with particulate	All				X	X	X	X	X	X	X	X	X
• Impingers													
Solvent extract	1/4			X	X	X	X	X	X	X	X	X	X
Aqueous solution after extraction	All						X	X					X
SRF Train													
• In-stack filter													
Solvent extract	1/4			X	X	X	X	X	X	X	X	X	X
Filter with particulate	All				X	X	X	X	X	X	X	X	X
• Probe rinse													
Filtered insolubles	All				X	X	X	X	X	X	X	X	X
Solvent extract	1/4			X	X	X	X	X	X	X	X	X	X
Aqueous solution after filtration and extraction	All						X	X					X
• [illegible] Impinger													
Solvent extract	1/4			X	X	X	X	X	X	X	X	X	X
Aqueous solution after extraction	All						X	X					X
• Distilled water impinger													
Solvent extract	1/4			X	X	X	X	X	X	X	X	X	X
Aqueous solution after extraction	All						X	X					X
• Chromosorb 102 sorbent tubes	1/4				X	X	X	X	X	X	X	X	X

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SAMPLE CODES CONSIST OF 3-5 SECTIONS

Burn	Sampling Train	Train Component Extracted	Any Special Preparation	Test No.
First Baseline on Primary Fuel - BLA Waste Burn on Chlorinated Aromatics - WBB Waste Burn on PCB Blend - WBC Second Baseline on Primary Fuel - BLB	Standard EPA Method 5 Train - EPA ORF Designed "Sorbent" Train - ORF	Filter/Insolubles - F Probe Rinse - PR Caustic Impinger - NAOH Water Impinger - H_2O Combined Impingers - I	Extracts of Acidified Solutions - AE	T1, T2, or T3 if sample is from only one test Blank if sample is a combination of all three tests

FOR EXAMPLE, ALL OF THE EXTRACTED SAMPLES FROM ONE WASTE BURN WOULD BE CODED AS FOLLOWS:

WBB-ORF-FE = Waste Burn B, ORF Train, Combined Filter Extracts from all three tests

WBB-ORF-PRE & NAOHE = Waste Burn B, ORF Train, Combined Probe Rinse and Caustic Impinger Extracts from all three tests

WBB-ORF-NAOH-AE-T3 = Waste Burn B, ORF Train, Extract of the acidified caustic impinger solution from Test 3

WBB-ORF-H_2OE = Waste Burn B, ORF Train, Combined Water Impinger Extracts from all three tests

WBB-EPA-FE & PRE = Waste Burn B, EPA Train, Combined Filter and Probe Rinse Extracts from all three tests

WBB-EPA-IE = Waste Burn B, EPA Train, Combined Impinger Extracts from all three tests

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FIGURE G.1. TRW SAMPLE CODING SYSTEM

2) all three tests of each waste were performed at one nominal operating condition.

In general, following this plan, the organic concentrate obtained for each extracted sample type (e.g., filters, impingers, solids, etc.) from each of the two sampling trains were the combination of all three tests of each waste. Exceptions to this plan were the BLA and aqueous samples for which only one of the three test samples were received (see Table G.1). At no time were EPA train samples combined with ORF train samples.

Small aliquots (2-5 ml) were first taken of the "as received" extracts and set aside for analysis of volatile compounds that would be lost in the next step which was to concentrate the remaining solvent sample using Kuderna-Danish evaporators and a steam bath.

The solvent extracts of the probe rinses, in addition to being combined as in the plan shown in Figure G.2, were also combined with the sample (EPA train-filter, ORF train-first impinger) whose juxtaposition in the sampling train and similar physical characteristics permit the combination. The rinses of the EPA train were made of the glass probe liner in front of the filter. However, with the ORF train which only has a short nozzle in front of the in-stack filter, rinses were made of the 14 feet of probe and tubing between the filter and the first liquid impinger. The resulting solutions were filtered through standard filter paper and then extracted by ORF.

G.3.1.2 Solids, aqueous solutions, and filters. The solid samples were prepared for organic analyses by extraction in a Soxhlet apparatus for 24 hours with distilled-in-glass grade pentane. These extracts were concentrated with Kuderna-Danish evaporators to a 10 ml volume. Preparation of the solid samples for inorganic analyses consisted of a low-temperature plasma ashing to remove possible organic interferences.

Other samples for inorganic analysis also required some degree of preparation. Aliquots of the aqueous impinger and probe rinse samples were taken and acidified with nitric acid to stabilize any metals present. Each of the insoluble residues obtained by filtering the probe rinses was combined by ORF with its matching particulate filter for treatment as one sample. These insolubles/filter samples were plasma ashed and then

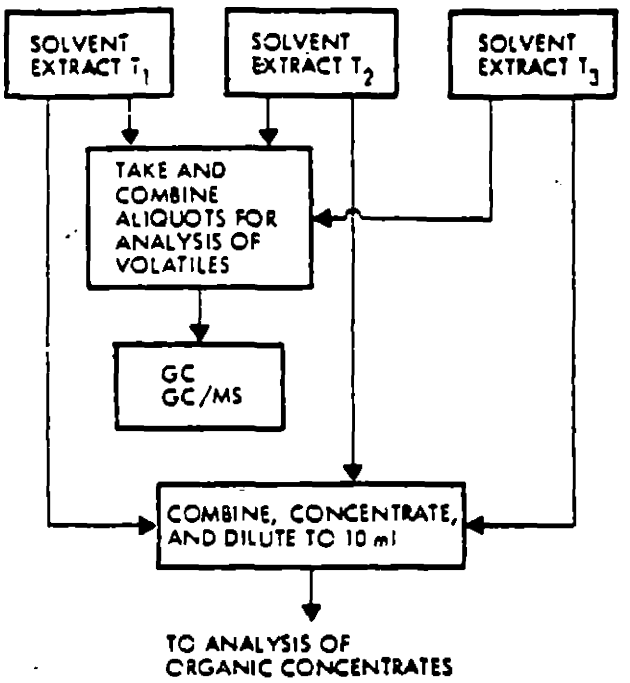

FIGURE G.2. PLAN FOR THE COMBINATION OF ORF SOLVENT EXTRACTS

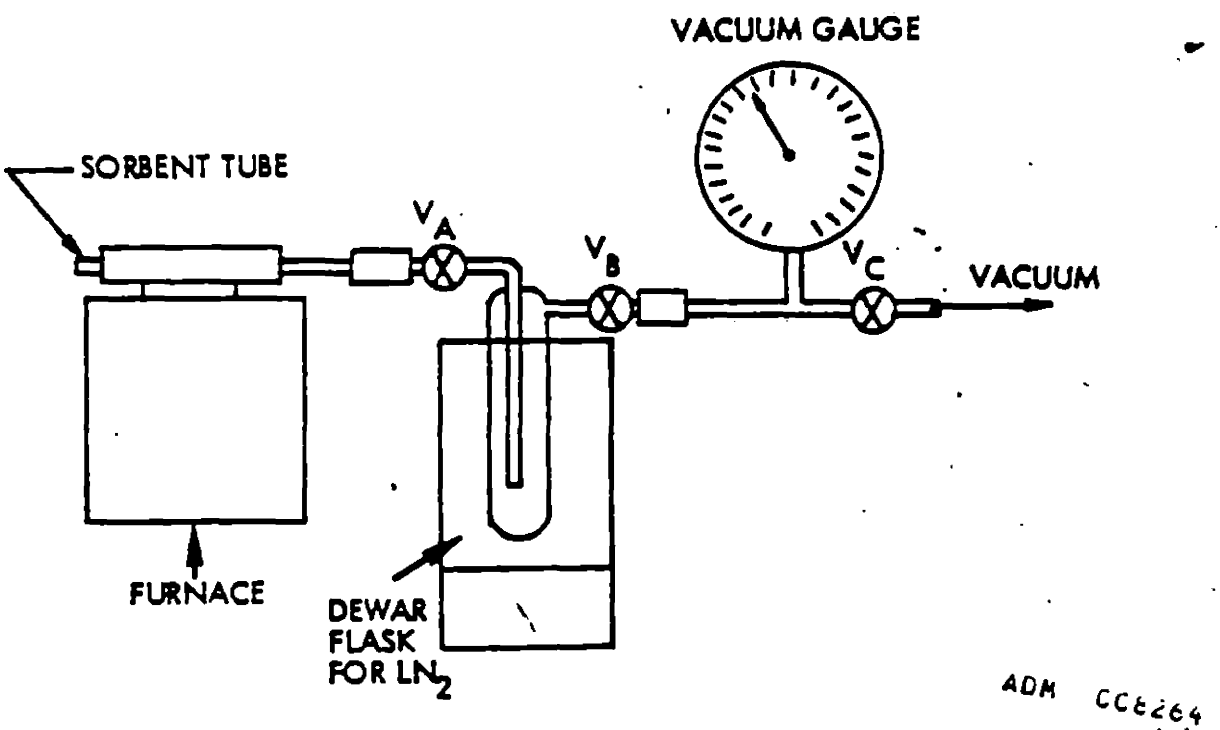

FIGURE G.3. DESORPTION SYSTEM FOR CHROMOSORB 102 TUBES

extracted by refluxing constant boiling aqua regia over the each sample for two hours. The resulting acid digests were made to 50 ml for analysis.-

G.3.1.3 Sorbent tubes. The Chromosorb 102 sorbent tubes from the ORF sampling train were prepared for analysis by a quantitative desorption technique. The apparatus used for the desorption is shown schematically in Figure G.3. The sorbent tube is attached with a minimum length of Tygon tubing to a 20 ml glass sample bulb and is then heated in a small furnace to 185° ±10°C.

With valve A closed and valves B and C open, the sample bulb was evacuated and immersed in liquid nitrogen. Valve A was then opened for 30 minutes to allow the contents of the sorbent tube to transfer to the sample bulb. Valves A and C were then closed, the LN_2 flask removed, the sample bulb allowed to equilibrate to room temperature, and the pressure recorded.

The volume of the entire manifold system, including each sample bulb, was carefully calibrated and on the average was 68.8 cc. With this information and the recorded pressure (assuming the temperature to be constant), the volume of the material desorbed was calculated according to the ideal gas law:

$$P_1V_1 = P_2V_2$$

where: P_1 = the pressure measured, in mm Hg
V_1 = the volume of the sample bulb and manifold, ~68.8 cc
P_2 = 760 mm Hg
V_2 = the calculated volume of desorbed material at 1 atm.

The desorbed material was recovered from the manifold by reimmersing the sample bulb in LN_2. Valve B was then closed and the sample bulb removed from the desorption system for analysis while still at negative pressure.

G.3.2 Analytical methods

The extracted and prepared samples were analyzed by various methods. The specific analyses selected depended to some extent on the samples' forms, which were:

For Inorganics

- Solids
- Aqueous and acid solutions

For Organics

- Aliquots of the neat solvent extracts
- Concentrates of the solvent extracts
- Desorbed materials from the sorbent tubes

G.3.2.1 Analyses for inorganics. The inorganic composition of the solid samples was determined by spark source mass spectrophotography (SSMS) with electronic detection, which will detect elements present down to a concentration of 1 ppm. This SSMS technique has an accuracy from 100-500% and will survey the sample for all the elements except gases (i.e., H, N, O, He, Ne, Ar, Kr, Xe, and Rn) and Hg because of its high volatility. Other elements with appreciable volatilities, such as Be and Se, have far reduced accuracies in this analysis.

The aqueous and acid solutions were first surveyed for metals by inductively coupled argon plasma optical emission spectroscopy (ICPOES). The ICPOES analysis determines 32 elements, including most of the toxic elements of interest in the program, down to ppb levels, with an accuracy of 100-200%. The purpose of this survey was primarily to check that the metals in the test samples were present in approximately the same amounts relative to each other as they were in the waste material. Those elements which, from the results either of the ICPOES survey or of the analysis of the waste material, seemed to be present at potentially toxic levels, were determined quantitatively by atomic absorption spectrometry (AAS). The sensitivity of this method varies from approximately 1.0-0.001 ppm for the elements which were determined, with an accuracy between 10-50%.

G.3.2.2 Analyses for organics. Organic constituents of the test samples were determined by a combination of the following techniques:

- infrared spectrometry (IR);
- gas chromatography (GC) with either an electron capture (EC) or flame ionization detector (FID);
- low resolution mass spectrometry (LRMS);
- combined gas chromatography/mass spectrometry (GC/MS).

The aliquots of the neat solvent extracts were analyzed only for volatile organochlorine compounds. EC/GC was used for this analysis and the samples were compared to standards of CH_2Cl_2, $CHCl_3$, and CCl_4 as well as the original waste material. The column was 183 cm x 0.635 cm o.d., glass, 1.5% OV 17 and 1.95% QF-1 on Chromosorb WHP.

The concentrates of the solvent extracts were analyzed to identify the less volatile compounds that would not be lost by evaporation of the extract. An aliquot of each sample was first taken and evaporated in a clean, 7 ml weighing bottle at ambient conditions to remove the solvent. The residue was then weighed on a micro balance to 0.001 mg and scanned by IR as an evaporated thin film. The sample was returned to the weighing bottle and stored for use in the LRMS analysis. To obtain an LRMS spectra, the sample was rinsed into the glass vessel for the solids probe inlet system and the solvent evaporated again at ambient conditions. The IR and LRMS analyses yield qualitative information about the classes or types of compounds (e.g., hydrocarbons, phenols, POM's, etc.) present as well as an idea of the complexity and toxic nature of the concentrated sample.

The sensitivity of the LRMS solids probe technique for specific compounds in an organic matrix can be estimated even though the mass spectrometer is not strictly considered a quantitative instrument. At typical mass spectrometer operating pressures of 10^{-6} torr, the relative volatility of organic materials at normal solids probe temperatures (100-250°C) is not an important factor. That is, the volatilities of materials of interest are sufficiently high for adequate detection. The solids probe of the mass spectrometer is in such close proximity to the ionizer that sample diffusion does not significantly reduce sensitivity. Previous experience and contacts with other laboratories using similar equipment indicate that if 10 micrograms of an organic compound is present in a solids probe along with other material, it will be detected to the extent that the ten or more strongest fragment peaks will be recorded. Since the typical weight of sample placed in the solids probe is 1 milligram, the required weight percentage of a given organic compound to be detected in an organic matrix is approximately one percent. Therefore, any compounds not detected by LRMS were assumed to be present at less than one percent levels.

The organic compounds in the extract concentrates were separated and quantified by GC using both flame ionization and electron capture detection. Columns and GC conditions are given below:

Flame ionization detection

- Varian 1860, dual differential FID
- Columns: dual, 183 cm x 2 mm i.d., stainless steel, 3.5% OV-17 on 100/120 mesh Chromosorb WHP
- Temperatures: column, ambient for 5 minutes, then ambient to 275°C at 10°C/min; detector, 275°C; injector, 250°C.
- Flow rate: helium carrier at 30 ml/min; hydrogen at 30 ml/min.; air, 300 ml/min.
- Attenuation: 1×10^{-10} a/mv

Electron capture detection

- Tracor MT-150, ^{63}Ni single ECD
- Column: 183 cm x 0.4 cm i.d., glass, 1.5% OV-17 and 1.95% QF-1 on 80/100 mesh Chromosorb WHP
- Temperatures: column, 200°C; detector, 225°C; injector 225°C.
- Flow rates: pre-purified N_2 carrier through column at 60 ml/min.; detector purge at 40 ml/min.
- Polarizing voltage: 14V; bucking range -2×10^{-8}; input attenuation, 10^2; output attenuation, X2 to X64.

G.4 Analytical Data

Data obtained from the various analyses performed will be presented in this section in the following order:

Chlorinated Hydrocarbon Wastes Tested

- Chlorinated Aromatics
- Polychlorinated Biphenyls (PCBs)

Samples Obtained from the EPA and ORF Sampling Trains

- Organic Constituents
- Inorganic Characterization

Solid Residues and Effluents from the SLC Kiln Process

- Clinker Products
- Electrostatic Precipitator Discard Dusts

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G.4.1 Chlorinated hydrocarbon wastes tested

Samples of the chlorinated wastes burned at St. Lawrence Cement were taken by ORF from the liquid waste feed tank on each day of testing. Composites of these were sent to TRW. The analyses used to characterize the wastes and determine the expected compounds of interest in the test burn samples were:

- thermal content - gross heat of combustion;
- viscosity;
- specific gravity;
- loss on ignition (LOI);
- C, H, N, S, and halogens;
- infrared spectroscopy (IR);
- gas chromatography/mass spectroscopy (GC/MS); and,
- spark source mass spectroscopy (SSMS).

G.4.1.1 Primary fuel. In addition to the two wastes, a sample of the primary fuel, bunker "C" oil, was also received. Of the analyses listed above only the gross elemental determination (C, H, N, S, and halogens) and a trace metal scan by X-ray fluorescence (XRF) were performed on the oil. Physical properties were not determined since they are fairly standard, and accurate compound identification was not necessary since the background of compounds contributed by burning the bunker "C" oil as fuel can best be determined by analysis of the combustion test samples from the baseline burn.

The elemental determination on the oil gave the following results:

- 86.87% C
- 9.89% H
- 0.36% N
- 2.62% S
- 0.05% Cl (total halogens as chlorine).

The XRF scan detected six elements at the levels listed below:

Element	Approximate Concentration (ppm)
Si	>500
P	50-500
Ni	5-50
V*	5-50
Ca	<25
Ti	<5

G.4.1.2 Chlorinated aromatics. The aromatic waste was a dark brown, low viscosity liquid that was visually free of sediment. The measured physical characteristics were:

- thermal content - 5170 kcal/kg (9310 Btu/lb);
- viscosity - 1.09 centistokes at 38°C (100°F);
- specific gravity - 1.281 at 16°C (60°F);
- LOI - 99.98%.

Elemental analyses performed showed the following composition:

- 44.00% C
- 3.48% H
- 0.028% N
- 0.019% S
- 49.10% Cl (total halogens as chlorine).

Analytical techniques used to determine the organic composition included IR and GC/MS.

IR

The IR spectrum indicated the waste to be composed primarily of aromatic hydrocarbons as well as aliphatic alkanes and alkenes with a strong response in the 600-800 cm^{-1} region which can correspond to C-Cl bonding. No indication of any other functional groups such as phenols, ethers, or amines was found. Comparison of the waste spectrum with spectra from the Sadtler indices for the compounds found by GC/MS, showed the principle

*Element is potentially toxic - OSHA TLV of <1 mg/m^3 for an eight-hour exposure.

constituent to be o-chlorotoluene, the most characteristic peak of which is a strong, sharp peak at 750 cm^{-1}.

GC/MS

Chromatographic separation was carried out on a Finnigan GC/MS system using two columns. One was Chromosorb 101, temperature programmed from 30° - 220°C at 10°C/min, and the other was OV-17 temperature programmed from 30° - 275°C at 10°C/min. The compounds shown in Table G.2 were identified and their concentrations calculated based on relative peak areas found from both columns and assuming equal response to the total ion monitor of the Finnigan instrument. These results reflect the fact that, in the course of performing the tests at SLC, the waste feed tank was not emptied between wastes. Thus, the material for the "aromatic" burns contains ~33% chlorinated aliphatics carried over from the previous burn (as a cost savings to the program, TRW did not plan to analyze samples from the chlorinated aliphatics burn). The primary constituent of the aromatic waste is chlorotoluene (52.5%) with the remainder made up of three other chlorinated aromatics: dichlorotoluene, octachlorocyclopentene, and octachloronaphthalene.

TABLE G.2. ORGANIC COMPOSITION OF AROMATIC WASTE BY GC/MS

Compound	Estimated Concentration (% w/w)
Acetone	1.6
Methylacetate	0.3
Dichloromethane	0.4
Chloroform	11.1
Carbon Tetrachloride	13.9
Dichloroethane	3.1
Trichloroethane	2.5
Tetrachloroethane	0.4
Trichloroethylene	1.0
Toluene	1.0
Chlorotoluene	52.5
Dichlorotoluene	4.6
Dimethyl Benzene (Xylene)	0.9
Octachlorocyclopentene	3.7
$C_{10}Cl_8$ (Octachloronaphthalene)	3.0

SSMS

Trace metals in the chlorinated aromatic waste were determined by spark source mass spectroscopy (SSMS). The waste was first ashed by a sulphated dry method. A very small amount of ash, 0.014%, was obtained of which the major elements were Ba, Fe, Na, P, S, Si, and Ti (the sulphur most likely represents the contribution from the H_2SO_4 added during ashing). Other elements detected by SSMS down to 1 ppb are shown in Table G.3. This analysis was performed to determine what potentially toxic elements might have been present in the waste at high enough concentrations to warrant quantitative examination of the flue gas test samples. Given the semi-quantitative nature of the data, the SSMS results should not be construed as a quantitative characterization of the waste material.

TABLE G.3. TRACE METALS IN THE CHLORINATED AROMATIC WASTE BY SSMS

Element	Approximate[a] Concentration (ppm)	Element	Approximate[a] Concentration (ppm)
Al	0.7-1.5	Sn	0.008
Ca	0.7-1.5	Zr	0.008
Cu	0.7-1.5	V[b]	0.007
Mg	0.7-1.5	As[b]	0.006
Zn	0.7-1.5	Ag	0.003
K	0.6	Cd[b]	0.002
Cr[b]	0.4	Ce	0.002
Pb[b]	0.3	La	0.002
Mn	0.07	Sb[b]	0.002
Hg[b,c]	0.07	Be[b]	0.001
Sr	0.06	Bi	0.001
Pt	0.05	Ge	0.001
B	0.05	Li	0.001
Co[b]	0.05	Rb	0.001
Ni	0.03	Se[b]	0.001
W	0.01	Sm	0.001
Mo	0.008	Yb	0.001

[a]The accuracy of this technique ranges from 100 to 500 percent.

[b]Potentially toxic metals - OSHA TLV of <1 mg/m^3 for an eight-hour exposure.

[c]Hg was determined by a highly quantitative atomic fluorescence technique.

G.4.1.3 Polychlorinated biphenyls (PCB's). The PCB waste was a medium brown, low viscosity liquid with fine suspended particulate that tended to float to the top and cake out on the sides of the container. The measured characteristics were:

- thermal content - 6,710 kcal/kg (12,083 Btu/lb);
- viscosity - 5.87 centistokes at 38°C (100°F);
- specific gravity - 1.196 at 16°C (60°F);
- LOI - 99.90%

Elemental analyses performed showed the following composition:

- 57.94% C
- 5.23% H
- 0.018% N
- 0.12% S
- 33.60% Cl (total halogens as chlorine).

The analytical techniques used to determine the organic composition of the waste were IR and GC/MS.

IR

The IR scan showed strong peaks at 1100 cm^{-1} and 1450 - 1480 cm^{-1} which are characteristic of biphenyls, and a peak at 750 cm^{-1} indicative of remaining o-chlorotoluene in the waste. Other small peaks in the spectrum matched those in the aromatic waste IR scan which substantiates the GC/MS results discussed below.

GC/MS

Analysis of the PCB waste was performed by the same GC/MS methods and conditions as for the aromatic waste, and the compounds that were identified are shown in Table G.4. The PCB waste composition showed the effect of previous waste material left in the feed tank. It was composed of 12% chlorinated aliphatics, 33% chlorinated aromatics, and 45% PCBs. There were 22 separate PCB compounds identified including several isomers of each of the multiple chlorinated biphenyls.

SSMS

Trace metals in the PCB waste were determined by SSMS. The waste was first ashed by a sulphated dry method. A small amount of ash, 0.15%,

TABLE G.4. ORGANIC COMPOSITION OF PCB WASTE BY GC/MS

Compound	Estimated Concentration (% w/w)
Water	0.7
Acetone	1.3
Methylacetate	0.5
Methanol	0.4
Chloroform	1.4
Carbon Tetrachloride	6.8
Ethanol	5.2
Dichloroethane	0.6
Trichloroethane	0.7
Hexachloroethane	0.2
Trichloroethylene	1.6
Tetrachloroethylene	0.2
Xylenes	2.3
Toluene	1.0
Chlorotoluene	17.2
Dichlorotoluenes	2.4
Trichlorotoluenes	3.3
Octachlorocyclopentene	4.0
Chlorobiphenyl	0.5
Dichlorobiphenyls	8.4
Trichlorobiphenyls	15.5
Tetrachlorobiphenyls	11-15
Pentachlorobiphenyls	2-6
Hexachlorobiphenyl-	1-2
Heptachlorobiphenyls	0.5
Octachlorobiphenyls	0.2
Di-n-octyl or Di-ethyl Hexyl Phthalate	4.0
$C_{10}Cl_8$ - Octachloronaphthalene	2.5

was obtained of which the major elements were Fe, Na, P, Pt, and Si. Other elements detected by SSMS down to 1 ppb are shown in Table G.5. This analysis was performed to determine what potentially toxic elements might have been present in the waste at high enough concentrations to warrent quantitative examination of the flue gas test samples. Given the semi-quantitative nature of the data, the SSMS results should not be construed as a quantitative characterization of the waste material.

G.4.2 Samples obtained from the EPA and ORF sampling trains

Samples obtained by the two trains from the WBB, WBC, and BLB tests were received for analysis. A list of the samples derived by ORF

TABLE G.5. TRACE METALS IN THE PCB WASTE BY SSMS

Element	Approximate[a] Concentration (ppm)	Element	Approximate[a] Concentration (ppm)
K	7-15	Se[b]	0.1
Zn	7-15	Sr[b,c]	0.07
Cu	7	Hg[b]	0.06
S	5	Cd[b]	0.05
Mg	5	Th	0.02
Al	4	La	0.01
Ni	4	Nb	0.01
Mo[b]	3	Bi	0.009
Ba[b]	2	Li	0.009
Ti	2	Rb	0.006
B	1	Ta	0.004
Ca	1	Au	0.003
W[b]	1	Nd	0.003
Cr[b]	0.8	Hf	0.002
Pb[b]	0.8	Sm[b]	0.002
V[b]	0.7	Be[b]	0.001
Ag	0.6	Dy	0.001
Mn[b]	0.5	Ga	0.001
Sb[b]	0.5	Ge	0.001
Sn[b]	0.5	Pr	0.001
As[b]	0.2	Sc	0.001
Zr[b]	0.2	U	0.001
Co[b]	0.1		

[a]The accuracy of this technique ranges from 100 to 500 percent.
[b]Potentially toxic metals - OSHA TLV of <1 mg/m^3 for an eight-hour exposure.
[c]Hg was determined by a highly quantitative atomic fluorescence technique.

from each train was presented in Table G.1. All of these samples were scheduled to be analyzed until, in early April, ORF's review of their analytical data brought them to conclude that the solvent extracts of the BLB samples had been contaminated with PCB waste material [G.1] which was confirmed by the analyses at TRW. The contamination appeared to have occurred before the split of the samples into 4 aliquots. In view of this development, analysis of the BLB solvent extract samples was discontinued and extracts from a BLA test were sent as replacements.

However, there was no evidence of a contamination problem with the remaining BLB samples. Thus, the filters, probe rinse insolubles,

aqueous solutions, and Chromosorb 102 sorbent tubes from the BLB tests were analyzed for a background reference to the corresponding WBB and WBC samples.

All of the test samples were coded for ease of reference. The coding used was presented in Figure G.1, which also showed the combination of the probe rinse samples with other appropriate samples. The reasons and methods for combining the probe rinses with either the filter (for the EPA train) or impinger (for the ORF train) samples, as well as the preparation and analytical techniques for all the samples were described in Section G.3.

Where constituents found in the test samples are reported as concentrations in the effluent gas, the sample gas volumes needed for the calculations were taken from Section 5.3 of the report. Volumes for the ORF train were taken from Table 4, and volumes for the EPA train from Table 7.

G.4.2.1 Organic constituents. Samples for the analysis of organic composition were in the form of:

- aliquots of the neat solvent extracts;
- concentrates of the solvent extracts;
- residues from the evaporation of the extract concentrates; and
- desorbed materials from the sorbent tubes.

These samples were first surveyed for their qualitative nature by gravimetric, infrared spectrometry (IR), and low resolution mass spectrometry (LRMS) techniques. Quantitative determinations and analysis for specific compounds, such as chlorinated hydrocarbons and PCB's, were then performed by gas chromatography (GC) and combined gas chromatography/mass spectrometry (GC/MS). The results obtained from all of these analyses are presented in the following paragraphs. The methods themselves are described in Section G.3.

Qualitative data. The purpose of the qualitative or survey analysis was to identify any material in the samples which were not present in the original waste, and therefore were not expected. In addition, this survey analysis searched for secondary or incomplete combustion products which would result from the waste being converted to compounds

other than CO_2, H_2O, and HCl. The qualitative data will be described in two groups: 1) Extract concentrate residues, and 2) material desorbed from the sorbent tubes.

1) Extract concentrate residues - The results of these qualitative analyses on the residues, obtained by evaporating aliquots of the solvent extract concentrates, are summarized and presented in Table G.6. This table includes:

- The identification of the extract samples according to the coding shown in Figure G.1. This coding shows how certain related samples have been combined.
- The Sample/Aliquot Ratio shows the total volume of extract prepared by ORF in the numerator and the volume received by TRW in the denominator. One-fourth of each extract was sent to TRW.
- The amount of residue found in TRW's portion of the total extract is expressed as milligrams (mg). Values have been corrected for appropriate blanks.
- The Total Residue is that amount (in mg) of residue found in TRW's portion, multiplied by the Sample/Aliquot Ratio. This value is indicative of what may be found in the total extract if analyzed by the same procedures.

Inspection of the IR and LRMS data revealed that the only materials detected in the evaporated residues of the various extracts (except for the contaminated BLB samples) were silicones, hydrocarbon oils, fatty acids or fatty acid esters, and phthalic acid esters.

These same materials were also present in the blank and control samples; their concentrations vary from sample to sample as estimated by LRMS. These materials, as classes of compounds, are not toxic and would not be considered an emissions hazard even if they were present in much higher concentrations. These materials are not believed to have come from the combustion gas. Samples from the EPA train did not show increased levels of these materials consistent with more than ten-fold sample volumes.

In the analysis of trace organics, it becomes very difficult to completely avoid these ubiquitous oils, plasticisers, lubricants, antioxidants,

TABLE G.6. SUMMARY OF ORGANIC QUALITATIVE SURVEY ANALYSES OF SAMPLE EXTRACTS

Sample Identification	Total Extract (ml) / TRW Aliquot (ml)	Survey Residue Found in TRW Aliquot (mg)	Total Residue (mg, corrected for Aliquot Factor)
Baseline Burn A			
BLA-ORF-FE-T3	200/50	3.23	12.92
BLA-ORF-PRE+NAOHE-T3	200/50	N/D[b]	N/D (<1.00)
BLA-ORF-H_2OE-T3	100/25	N/D[b]	N/D (<2.68)
BLA-EPA-PRE+FE-T3	300/75	0.12	0.48
BLA-EPA-IE-T3	100/25	2.09	8.36
Baseline Burn B			
BLB-ORF-FE	600/150	0.34	1.36
BLB-ORF-PRE+NAOHE	600/150	N/D[b]	N/D (<1.00)
BLB-ORF-H_2OE	300/75	0.50	2.00
BLB-EPA-PRE+FE	900/225	0.48	1.92
BLB-EPA-IE	300/75	0.04	0.16
Waste Burn B			
WBB-ORF-FE	600/150	0.07	0.28
WBB-ORF-PRE+NAOHE	400/100	N/D[b]	N/D (<1.00)
WBB-ORF-H_2OE	200/50	N/D[b]	N/D (<2.68)
WBB-ORF-NAOH-AE-T3	N/Ac	0.28	1.12
WBB-EPA-PRE+FE	900/225	1.50	6.00
WBB-EPA-IE	300/75	11.18	44.72
Waste Burn C			
WBC-ORF-FE	600/150	0.58	2.32
WBC-ORF-PRE+NAOHE	600/150	N/D[b]	N/D (<1.00)
WBC-ORF-H_2OE	300/75	14.83	59.32
WBC-ORF-NAOH-AE-T1	N/A[c]	0.23	0.92
WBC-EPA-PRE+FE	900/225	1.12	4.48
WBC-EPA-IE	300/75	6.25	25.00

[a]There is no significant difference in the results between test runs. The materials in the residues are not believed to have come from the combustion gas.

[b]N/D = Not detected at levels higher than the blank.

[c]N/A = Not applicable; the total caustic impinger contents from one test were used.

etc., that can enter the test matrix in very small amounts despite the most careful and extensive preparation of equipment and selection of reagents. One cannot be sure whether the source of these materials is the hardware, the reagents, the samples themselves, or a combination of these. A large number of blank and control samples might have distinguished the source, but due to the noncritical nature of the materials, such an examination was clearly not warranted.

It was pointed out that the survey analysis of the BLB samples known to contain PCB's [G.1] did, in fact, reveal their presence. Evidence of PCB,s was clearly shown in the LRMS data for the following BLB samples:

- ORF train, combined probe rinse extracts and caustic impinger extracts;
- ORF train, water impinger extracts;
- EPA train, combined probe rinse extract and filter extract.

Since these PCB's were found only as estimated minor constituents in samples whose total weights were less than one milligram, the ability of the mass spectrometer to detect these small quantities was clearly established. The LRMS procedures can usually detect 10 micrograms, or about one percent of a typical 1 milligram sample. The presence of a specific compound in an organic matrix is not normally detected by IR with adequate certainty unless present at 10 percent or higher. The sensitivity and detection limits of these techniques were discussed in Section G.3.2.

It is stressed that chlorinated species were specifically searched for in all of these residue samples and none were found except for in the contaminated BLB samples described above.

2) Materials desorbed from the sorbent tubes - The Chromosorb 102 sorbent tubes from the ORF sampling train were thermally desorbed to recover the collected sample according to the procedure described in Section G.3.1. The desorbed gases were then analyzed qualitatively by LRMS using a gas inlet system. The conclusions drawn from reduction and interpretation of the LRMS data were that all of the sorbent tubes contained essentially the same types of materials; however, the relative amounts of these constituents did appear to vary from sample to sample.

Although the LRMS is a qualitative technique, estimates can be made through inspection of the data to provide an indication as to whether a species is present as a trace, minor, moderate, or major component. Such a summary for the six selected sample sorbent traps that were analyzed is presented in Table G.7. An unused sorbent trap was also analyzed by the same procedure to estimate background contributions by the Chromosorb 102. Unfortunately a leak in the system resulted in the loss of sample and, therefore, usable data. Only carbon dioxide was seen in the mass spec data at greater than trace levels.

The volatile compounds removed from the sorbent traps and collected in the gas sample bulbs were largely the oxygen, nitrogen, carbon dioxide, and water that are the usual species found in combustion gases. The remainder of the compounds detected were those that could indicate incomplete combustion, or possibly the formation of other compounds. The levels at which these remaining compounds could be present were estimated on the basis of LRMS instrument response for key peaks attributed to these trace residual organics. These estimates indicated that the C_1 to C_5 hydrocarbons present as a major component of these trace residual organics could be present in the sampled combustion gases in the 1 to 10 ppm range. The minor or trace components of these trace organics were believed to be present at very much lower levels.

A summary of the LRMS peak patterns observed in the spectra of the desorbed gases and the compounds assigned to these patterns is given in Table G.8.

Quantitative data. Quantitation of the compounds detected and identified in the test samples was performed by GC and GC/MS techniques.

1) Extract concentrates - The chromatography with flame ionization detection was performed chiefly to analyze organic species. It should be noted that the FID is quite sensitive to chlorinated hydrocarbons as long as chlorination is not complete. At the electrometer settings used, the sensitivity, or the minimum detectable quantity, was 0.002 ng/µl as benzene, naphthalene, or Aroclor 1232.

The chief result of the analyses using the FID was that none of the concentrated samples showed peaks other than those found in the

TABLE G.7. APPROXIMATE CONSTITUENT LEVELS OF TRACE VAPOURS DESORBED FROM SORBENT TUBE SAMPLES BY LRMS

Sorbent Tube Sample	Constituent Level[a]						
	C_{1-5} Hydrocarbons	Nitromethane	NO, NO_2, and Possibly Ethanol	Benzene	Methyl Chloride	Substituted Benzene	Methyl Siloxane
WBB-T1	Minor	Trace	Trace	Trace	ND[b]	ND	Major
WBB-T2	Major	Minor	Major	Moderate	Moderate	Trace	Minor
WBC-T1	Major	Minor	Major	Minor	ND	Trace	Minor
WBC-T2	Major	Minor	Major	Moderate	ND	Trace	Trace
BLB-T1	Major	Moderate	Moderate	Major	ND	Trace	Trace
BLB-T2	Major	Minor	Moderate	Moderate	ND	Trace	Trace

[a]The range of trace to major levels represents 0.1-10 ppm concentrations in the flue gas.

[b]ND - Not Detected.

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TABLE G.8. SUMMARY OF THE INTERPRETATION OF LRMS SPECTRA FOR TRACE VAPOURS DESORBED FROM SORBENT TUBE SAMPLES

Peak Pattern (Peaks at Atomic Mass Units (AMU))	Assignment
15	Methyl group, CH_3
16	Methane, CH_4
17, 18	Water
27, 29, 41, 43, 55, 57	C_2-C_5 hydrocarbons
14, 16, 28, 32	Nitrogen/oxygen
44	CO_2
30, 46, 61	Possibly nitromethane CH_3NO_2*
30, 46	NO, NO_2* and/or ethanol
78, 50, 51, 52	Benzene
50, 52, 15	Methyl chloride CH_3Cl
91	Substituted benzene ring (e.g., toluene)
147, 207, 281	Methyl siloxane

*The 30 AMU peak was very large and it is believed that nitric oxide, nitrogen dioxide, ethanol and nitromethane may have all contributed to it.

solvent controls. Consequently, a "less than" value was assigned in terms of benzene for the analysis of hydrocarbons, or Aroclor 1232 for the analysis of chlorinated organics. The results are given in Table G.9.

The values presented in Table G.9 were derived in the following manner. The sample labeled WBB-EPA-FE+PRE, for example, totaled 225 ml as received. A 213 ml portion of this sample was concentrated to 10 ml in a Kuderna-Danish evaporator. The chromatogram of the concentrated sample showed no peaks other than solvent. Since the aromatic waste contained considerable chlorinated hydrocarbons, quantitation as Aroclor 1232 was considered appropriate.

Thus, WBB-EPA-FE+PRE contained <0.002 µg/µl of species as Aroclor 1232. The amount of material in the entire received sample volume of 225 ml was determined. This value was multiplied by four, since only one-quarter

TABLE G.9. RESULTS AND DETECTION LIMITS FROM GC/FID ANALYSIS OF THE CONCENTRATED EXTRACTS

Sample ID	ng/µl as Halocarbon[d]	Volume of Sample (ml)[a]	Aliquot Factor[b]	Fraction of Sample[c]	Volume of Sample Gas, Std. m^3	Concentration in Flue Gas (mg/m^3)
BLA-EPA-FE+PRE-T3	0.052	75	67/20	1/4	3.76	0.001
-IE-T3	0.26	25	21/10	1/4	3.76	0.003
-ORF-FE-T3	0.26	50	46/10	1/4	0.32	0.04
-H_2OE-T3	0.061	25	21/10	1/4	0.32	0.09
-PRE+NAOHE-T3	0.21	50	42/20	1/4	0.32	0.06
WBB-EPA-FE+PRE	ND(<0.0038)[e]	225	213/10	1/4	9.62	ND(<0.00002)
-IE	0.89	75	63/10	1/4	9.62	0.004
-ORF-FE	0.12	150	138/10	1/4	0.83	0.006
-H_2OE	0.26	50	42/10	1/4	0.83	0.02
-PRE+NAOHE	0.053	100	42/10	1/4	0.83	0.003
WBC-EPA-FE+PRE	0.019	225	213/10	1/4	9.97	0.00008
-IE	(lost)	75	63/10	1/4	9.97	(lost)
-ORF-FE	ND(<0.0038)	150	138/10	1/4	0.73	ND(<0.00002)
-H_2OE	ND(<0.0038)	75	63/10	1/4	0.73	ND(<0.00002)
-PRE+NAOHE	0.26	150	138/10	1/4	0.73	0.015

[a]Volume of sample received by TRW.

[b]Aliquot Factor: for example 67 ml of the 75 ml BLA-EPA-Fe+PRE sample received was concentrated to 20 ml for analysis.

[c]Fraction of Sample: All samples received by TRW were 25% of the total sample.

[d]The instrument was calibrated with Arpclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram. High sensitivity GC/MS ($3 µg/m^3$ of flue gas) did not detect any chlorinated species in samples WBC-ORF-FE and WBC-ORF-H2OE.

[e]ND = Not detected. Values in parentheses indicate the detection limits.

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of the whole sample was divided by the volume, in m^3, of gas sampled. A concentration value of <0.009 mg/m^3 in the flue gas was thus derived for the sample WBB-EPA-FE+PRE.

Since the minimum detectable quantity is constant and since both the volume of gas sampled and the volume of extract vary, this method of calculation gives different values of mg/m^3. It must be stressed that these analyses showed no species other than solvent.

Since the ECD is much more sensitive to polychlorinated species than the FID, the analyses using electron capture detection were performed to determine polychlorinated compounds below the level that could be detected by the FID analyses. At the electrometer setting used on the electron capture detector, the minimum detectable quantities for typical species of interest were:

- Aroclor 1232: 0.0038 ng/µl
- Naphthalene: 0.066 µg/µl
- Benzene: 0.11 µg/µl.

The most noteworthy result of the GC analyses using the ECD was that none of the concentrated extracts showed peak patterns corresponding to those given by Aroclor 1232 (the PCB mixture most similar to that burned in waste burn C) or Aroclor 1242. The quantified ECD results are given in Table G.10.

Some of the concentrated sample extracts, e.g., WBB-EPA-FE+PRE, showed no peaks other than solvent. Most of the extracts showed several very small peaks. After quantitation, all but one of the samples were below the level of interest, 0.1 mg/m^3, and no further effort was expended. One sample, WBC-ORF-FE, showed a number of peaks, some of which were large. Another sample, WBC-ORF-H_2OE, showed a large number of small peaks. Both of these samples were analyzed by GC/MS. The GC/MS analyses of the filter extract indicated one vanishing small hydrocarbon peak, a small phthalate ester peak, and 10 peaks which were various trimethylsilyl compounds (TMS). The GC/MS analyses of the water extract showed extremely small hydrocarbon peaks and 16 peaks that were trimethylsilyl compounds. Because these TMS compounds were most likely the result of some contamination, the peaks appearing in the chromatograms were considered spurious.

TABLE G.10. RESULTS AND DETECTION LIMITS FROM GC/ECD ANALSIS OF THE CONCENTRATED EXTRACTS

Sample ID	µg/µl as Benzene[d]	µg/µl as Halocarbon[d]	Volume of Sample, ml[a]	Aliquot Factor[b]	Fraction of Sample[c]	Volume of Sample Gas, Std. m^3	Detectable Limits of Concentration in Flue Gas, mg/m^3
BLA-EPA-FE+PRE-T3	ND(<0.002)[e]	-	75	67/20	1/4	3.76	ND(<0.05)
-IE-T3	ND(<0.002)	-	25	21/10	1/4	3.76	ND(<0.03)
-ORF-FE-T3	ND(<0.002)	-	50	46/10	1/4	0.32	ND(<0.3)
-H2OE-T3	ND(<0.002)	-	25	21/10	1/4	0.32	ND(<0.3)
-PRE+HAOHE-T3	ND(<0.002)	-	50	42/20	1/4	0.32	ND(<0.6)
MBB-EPA-FE+PRE	-	ND(<0.002)	225	213/10	1/4	9.62	ND(<0.009)
-IE	-	ND(<0.002)	75	63/10	1/4	9.62	ND(<0.01)
-ORF-FE	-	ND(<0.002)	150	138/10	1/4	0.83	ND(<0.1)
-H2OE	-	ND(<0.002)	50	42/10	1/4	0.83	ND(<0.1)
-PRE+HAOHE	-	ND(<0.002)	100	92/10	1/4	0.93	ND(<0.1)
MBC-EPA-FE+PRE	-	ND(<0.002)	225	213/10	1/4	9.97	ND(<0.009)
-IE	-	ND(<0.002)	75	63/10	1/4	9.97	ND(<0.01)
-ORF-FE	-	ND(<0.002)	150	138/10	1/4	0.73	ND(<0.1)
-H2OE	-	ND(<0.002)	75	63/10	1/4	0.73	ND(<0.1)
-PRE+HAOHE	-	ND(<0.002)	150	138/10	1/4	0.73	ND(<0.1)

[a]Volume of sample received by TRW.

[b]Aliquot Factor: for example 67 ml of the 75 ml BLA-EPA-Fe+PRE sample received was concentrated to 20 ml for analysis.

[c]Fraction of sample. All samples received by TRW were 25% of the total sample.

[d]The instrument was calibrated with benzene or Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram. High sensitivity GC/MS ($3 µg/m^3$ of flue gas) did not detect any chlorinated species in samples MBC-ORF-FE and MBC-ORF-H2OE.

[e]ND = Not detected, values in parentheses indicate the detection limits.

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These GC/MS analyses did not detect any chlorinated species in either sample (typical sensitivity of 3 $\mu g/m^3$ of the flue gas).

2) Aliquots of neat extracts - There was concern that the process of concentrating the sample extracts, as received in pentane and/or hexane, might cause the loss of relatively low boiling halocarbons such as chloroform which might be expected in the samples. Therefore, the retained portions of the as-received extract samples were chromatographed on the Tracor instrument. The column was operated isothermally at 70°C to increase resolution of low boiling compounds. The results are given in Table G.11.

Most of the samples showed no peaks other than solvent. Of those samples showing peaks other than solvent, all quantified below the level of interest (0.1 mg/m^3), and no compound identification by GC/MS was performed.

3) Materials desorbed from sorbent tubes - The sorbent traps were desorbed as discussed in Section G.3.1. Portions of the desorbed vapours contained in the sample bulbs were chromatographed isothermally at 70°C with electron capture detection. The samples were qualitatively similar to the sorbent trap blank (unused chromosorb 102) and the baseline B (fuel oil burn) samples. The waste burn B samples each contained a peak which might be CH_3Cl: WBB Test 1, 0.0001 mg/m^3; and WBB Test 2, 0.0002 mg/m^3. The waste burn C samples were essentially the same, qualitatively and quantitatively as the blank and baseline B samples.

G.4.2.2 Inorganic characterization. Inorganic elemental concentrations in the flue gas were determined by analysis of the particulate filters and the aqueous probe rinse and impinger samples. The filters (including the filtered probe rinse insolubles) were all acid digested. Out of these 20 digests (18 test samples and two blanks), three samples were prepared for a trace element survey analysis by combining equal aliquots from each of the three tests of WBB, WBC and BLB using the filter samples from only the EPA sampling train. The EPA train samples were selected on the basis of 1) representing larger sample gas volumes, and 2) having been taken by a method specific for accurate and representative particulate sampling. The results of the survey analysis are shown in Table G.12. The blank

TABLE G.11. RESULTS AND DETECTION LIMITS FROM GC/ECD ANALYSIS OF THE UNCONCENTRATED EXTRACTS

	ng/μl as Halocarbon[c]	Volume of Sample[a]	Fraction of Sample[b]	Volume of Sample Gas, Std. m^3	Concentration in Flue Gas, mg/m^3
BLA-EPA-FE+PRE-T3	ND(<0.0038)[d]	75	¼	3.76	ND(<0.0003)
-IE-T3	ND(<0.0038)	25	¼	3.76	ND(<0.0001)
-ORF-FE-T3	ND(<0.0038)	50	¼	0.32	ND(<0.002)
-H_2OE-T3	0.0051	25	¼	0.32	0.0016
-PRE-NAOHE-T3	ND(<0.0038)	50	¼	0.32	ND(<0.0024)
WBB-EPA-FE+PRE	ND(<0.0038)	225	¼	9.62	ND(<0.0004)
-IE	0.40	75	¼	9.62	0.012
-ORF-FE	ND(<0.0038)	150	¼	0.83	ND(<0.003)
-H_2OE	ND(<0.0038)	50	¼	0.83	ND(<0.0009)
-PRE+NAOHE	ND(<0.0038)	100	¼	0.83	ND(<0.0018)
WBC-EPA-FE+PRE	ND(<0.0038)	225	¼	9.97	ND(<0.0003)
-IE	0.10	75	¼	9.97	0.0030
-ORF-FE	ND(<0.0038)	150	¼	0.73	ND(<0.0031)
-H_2OE	0.15	75	¼	0.73	0.061
-PRE+NAOHE	ND(<0.0038)	150	¼	0.73	ND(<0.0031)

[a]Volume of sample received by TRW.

[b]Fraction of sample. All samples received by TRW were 25% of the total sample.

[c]The instrument was calibrated with Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram. High sensitivity GC/MS (3 $\mu g/m^3$ of flue gas) did not detect any chlorinated species in samples WBC-ORF-FE and WBC-ORF-H2OE.

[d]ND = Not detected. Values in parentheses indicate detection limits.

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TABLE G.12. TRACE METAL SEMI-QUANTITATIVE[a] SURVEY OF FILTER DIGESTS BY ICPOES

Element	Average Concentration[b] (mg/m^3)		
	WBB	WBC	BLB
Al	0.078	0.51	0.26
Ba	0.011	0.014	0.012
B	0.018	0.084	0.038
Ca	2.2	11.	6.5
Cd	0.0006	0.002	0.001
Cr	0.003	0.006	0.004
Co	ND[c]	0.001	ND[c]
Cu	0.003	0.007	0.003
Fe	0.18	1.1	0.73
Pb	0.047	0.12	0.044
Mg	0.076	0.38	0.21
Mn	0.003	0.018	0.013
Ni	0.003	0.006	0.002
P	0.014	0.055	0.044
K	14.	32.	6.7
Si	0.082	0.051	0.093
Ag	0.0003	0.003	0.0004
Na	1.8	5.5	2.4
Sr	0.004	0.013	0.0008
Ti	0.002	0.008	0.004
V	0.0006	0.002	0.001
Zn	0.014	0.042	0.027

[a]Accuracy estimated to be a factor of ±2 or better.

[b]Calculated based on average sample gas volumes of:

WBB - 3.2 m^3
WBC - 3.3 m^3
BLB - 3.4 m^3

Not corrected for filter contribution

[c]Not detected (<0.0003 ppm)

(an acid digest of unused filters) sample was not surveyed, so the values reported in this table are uncorrected for the filter background.

Of the 32 elements that can be determined by the ICPOES analysis, ten were not detected in the filter digest samples. These ten elements with their lower detection limits are listed in Table G.13, along with a calculation of the average detectable limit for each of these elements in the flue gas.

TABLE G.13. LIMITS OF DETECTION FOR UNDETECTED ELEMENTS BY ICPOES

Element	ICPOES Detection Limit (ppb)	Average Detectable[a] Limit in Flue Gas (mg/m^3)
Au	5	0.00008
As	40	0.0006
Be	1	0.00002
Eu	15	0.0002
Mo	11	0.0002
Se	60	0.0009
Te	65	0.0010
Sn	50	0.0008
W	90	0.0014
U	80	0.0012

[a]Based on an average sample gas volume of 3.3 cubic meters.

The results of this survey indicated only one element, lead, was present at potentially toxic levels in the stack. While not a problem with tne stack configuration in the present study, the concentration and the effect of thermal dispersion should be considered when extrapolating these results to other kilns. To be sure of an accurate measurement of the levels of lead and certain other toxic metals which the waste analysis indicated might be present at levels of interest, a quantitative determination by AAS was performed on five elements. The results from this analysis are presented in Table G.14.

The AAS results were corrected for background levels as determined by analysis of the filter blank sample. It should be noted that background contributions were not only from trace contaminants in the filter materials but also in some cases from matrix effects in the mixed acid solutions.

AAS was also used to analyze for selected elements in the aqueous probe rinse and impinger samples. Table G.15 lists the results from these analyses and shows that, in general, nothing significant was found. No background or blank solutions were available so the BLB results should be used to correct for background effects. The results for these aqueous samples were left in ppm because the total sample volumes were unknown.

TABLE G.14. CONCENTRATION OF TRACE METALS IN EFFLUENT GAS PARTICULATE MATTER BY AAS

Waste Burn	Train	Test	Concentration of Element (mg/m^3)				
			Ba	Cd	Co	Cr	Pb
WBB	EPA	1	≤0.008[a]	≤0.001	≤0.002	≤0.009	0.028
		2	≤0.008	≤0.001	≤0.001	≤0.002	0.012
		3	≤0.008	0.001	≤0.002	≤0.004	0.079
WBC	EPA	1	0.013	0.001	≤0.002	≤0.008	0.096
		2	≤0.008	0.002	≤0.002	≤0.008	0.103
		3	0.027	0.003	≤0.002	0.003	0.153
BLB	EPA	1	≤0.007	0.001	≤0.002	0.001	0.040
		2	≤0.008	0.002	≤0.003	≤0.007	0.062
		3	≤0.008	0.001	≤0.002	≤0.002	0.015

[a] "≤", a less than or equal to sign, indicates those elements which were detected but not significantly above background levels.

TABLE G.15. CONCENTRATION OF TRACE METALS IN AQUEOUS SAMPLES BY AAS

Train/Component	Waste Burn vs. Baseline	Concentration of Element (ppm)			
		Pb	Cr	Cd	Co
EPA-Probe Rinse	WBB	ND	1.9	ND	10.2
	WBC	ND	0.03	0.01	ND
	BLB	ND	ND	ND	ND
Impingers	WBB	ND	ND	ND	0.05
	WBC	ND	0.02	ND	ND
	BLB	ND	ND	ND	ND

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Analysis of the filter acid digest, probe rinse, and impinger samples from the ORF train by AAS confirmed the presence of those elements found in the EPA train samples. However, since the ORF train was not operated with the intent of collecting an accurate particulate sample (i.e., isokinetic, traverses, etc.) the AAS results for this train were not calculated out to concentrations in the flue gas.

G.4.3 Solid residues and effluents from the SLC kiln process

Of the four types of solid samples collected during the test program:

- clinker product;
- clinker fines;
- electrostatic precipitator discard dust; and
- cement mixes,

analyses were performed only on the clinker product and discard dusts for the following reasons. The clinker fines were recovered from air blown through the clinker product and were then returned to the clinker storage. The cement mixes were simply clinker product with gypsum added. Thus, neither of these materials represented unique samples. The following paragraphs describe the results of analyses performed on the clinker products (CP) and discard dust (DD) samples. If significant amounts of toxic materials were found in the analyzed samples, further tests on the remaining samples would have been conducted. However, this did not prove to be necessary.

G.4.3.1. Organic constituents. Portions of the clinker product and discard dust samples were extracted with pentane using a Soxhlet extractor and preextracted paper thimbles. A blank sample was prepared by running a pentane extraction on an empty, precleaned thimble. In addition, a doped control sample consisting of ~30 grams of clinker, to which 0.9 mg of a known PCB mixture had been added, was also extracted for analysis. This doped sample represented a PCB concentration ~30 ppm in the clinker product. These samples were all analyzed both qualitatively and quantitatively by the same techniques described in Section G.4.2.1.

Qualitative data. Aliquots of the pentane extracts were evaporated and the residue was weighed and scanned by both IR and LRMS. These results

TABLE G.16. RESULTS OF ORGANIC SURVEY ANALYSIS ON CLINKER PRODUCT AND DISPOSABLE DUST SAMPLES

Sample Identification	Weight of Extracted Sample (g)	Weight of Residue in Extract (mg)	Qualitative Nature of Residue
BLB-CP	30.270	<1.16*	Hydrocarbon oils, phthalate esters, traces of fatty acids and silicones*
BLB-DD	24.185	1.31	
WBB-CP	29.445	1.30	
WBB-DD	18.948	1.16	
WBC-CP	21.816	<1.16*	
WBC-DD	33.112	<1.16*	
PCB Doped Control	29.998	<1.16*	All of the above compounds plus polychlorinated biphenyls

*The residue obtained from the blank thimble and pentane sample was 1.16 mg. Sample values varied with some being less than 1.16 mg due to the variability of the background. Over this range, the differences in residue weights are not significant.

are summarized in Table G.16. In most cases, the amount of weighable residue found in the extracts did not exceed that found in the blank. The materials identified by IR and LRMS are indicative of the low level contamination by greases, oils, soaps, etc., that often accompanies trace organic analysis. Hydrocarbon oils, phthalate esters, fatty acids, and silicone compounds were found in all the extract residues including the blank. No indication of the chlorinated species was found in any of the test samples.

Polychlorinated biphenyls were clearly detected in the PCB doped control sample. The LRMS spectrum contained peaks at 220, 222, 290, 292, and 294 AMU. The PCB's present at 30 ppm in the doped clinker were easily found and it is certain that much lower levels could have been detected. It is estimated that the mass spectrometer can detect the strongest peaks from a specifically searched for compound when present at the 10 ng level in a 1 milligram organic residue from the clinker. This results in a lower limit of detection by this qualitative

survey technique of about 1 ppb in the clinker or dust. The IR survey data was not useful in detecting PCB's at this level.

Quantitative data. The clinker and dust extracts were analyzed by GC with both FID and ECD detection. The results are given in Tables G.17 and G.18, respectively. Using the FID, no peaks other than solvent were found, and the results are expressed as minimum detectable quantities. Three of the samples showed no peaks other than solvent when analyzed with the ECD. The three samples which had peaks other than solvent using the ECD were quantitated at well below the level of interest.

To ascertain the recovery of PCB's from the clinker and dust samples, a 30 gram sample of clinker was doped with 0.9 mg of Aroclor 1232, extracted and concentrated in the same fashion as the clinker and dust samples. The ECD chromatogram of this artificial sample matched the pattern of a neat sample of Aroclor 1232, and the recovery of PCB's from the doped sample was calculated as 25%. This recovery factor has been applied to the clinker and dust samples in Tables G.17 and G.18. (The recovery factor is the reason why the values for the samples in Table G.17 exceed several ppm. If the minimum detectable quantity using the FID is 0.002 µg/µl, then after applying the recovery factor, the concentration in the sample cannot exceed 0.008 µg/µl. For a 10 ml extract volume and a 30 g clinker sample, the composition is thus <2.7 µg/g.)

G.4.3.2 Inorganic characterization. The CP and DD samples were also examined for trace metal content by spark source mass spectrometry (SSMS). The major constituents of both types of material were determined to be aluminum, calcium, iron, magnesium, sodium, sulphur, and silicon. Other trace inorganic elements which were detected down to a 1 ppm concentration are listed in Table G.19. It should be remembered that SSMS data are semi-quantitative. The values reported should be considered as being accurate within 500% of the true value.

The trace metal character of the clinkers and dusts did not change significantly from one waste burn to the other. The relatively low feed rate of the wastes, compared to that of the precursor material and the primary fuel, appeared to make any contribution of trace metals from the wastes negligible.

TABLE G.17. RESULTS AND DETECTION LIMITS FROM GC/FID ANALYSIS

Sample ID	µg/µl as Halocarbon[a]	Volume of Sample (ml)	µg/g of Sample Material
BLB-CP	ND(<0.002)[b]	10	ND(<3.0)
WBB-CP	ND(<0.002)	10	ND(<3.3)
WBC-CP	ND(<0.002)	10	ND(<4.5)
BLB-DD	ND(<0.002)	10	ND(<3.9)
WBB-DD	ND(<0.002)	10	ND(<5.1)
WBC-DD	ND(<0.002)	10	ND(<2.9)

[a]The instrument was calibrated with Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram.

[b]ND = Not detected. Values in parentheses indicate detection limits.

TABLE G.18. RESULTS AND DETECTION LIMITS FROM GC/ECD ANALYSIS

Sample ID	ng/µl as Halocarbon[a]	Volume of Sample (ml)	µg/g of Sample Material
BLB-CP	0.059	10	0.02[c]
WBB-CP	0.11	10	0.04[c]
WBC-CP	ND(<0.004)[b]	10	ND(<0.002)
BLB-DD	ND(<0.004)	10	ND(<0.002)
WBB-DD	ND(<0.004)	10	ND(<0.002)
WSC-DD	0.060	10	0.02[c]
CP+PCB	22.4	10	7.5

[a]The instrument was calibrated with Aroclor 1232. However, the Aroclor peak pattern was not found in any sample chromatogram.

[b]ND = Not detected. Values in parentheses indicate detection limits.

[c]No chlorinated species were detected in the qualitative survey of these samples by LRMS.

TABLE G.19. SELECTED TRACE METALS IN SLC CLINKER PRODUCT AND DISCARD DUST SAMPLES BY SSMS

	Concentration (ppm)[a]					
	WBB		WBC		BLB	
Element	CP	DD	CP	DD	CP	DD
As	<1.5	3	<1.5	3	<2.9	1
B	30	30	30	10	30	30
Ba	70	70	300	100	70	30
Be	ND[b]	ND	1	ND	7	ND
Ce	10	30	70	30	10	10
Co	ND	ND	ND	3	1	ND
Cr	7	10	30	10	30	10
Cu	1	10	3	7	7	3
Cs	ND	10	ND	30	ND	10
Dy	1	ND	3	1	1	ND
Ga	1	1	3	1	3	10
Ge	ND	ND	ND	ND	1	3
La	7	7	30	10	10	7
Li	ND	~1000	30	100	100	100
Mn	100	100	300	300	300	100
Mo	1	1	1	1	3	1
Nb	3	3	7	3	3	3
Nd	10	10	10	10	10	7
Ni	7	3	7	7	10	3
Pb	ND	70	3	100	ND	30
Pr	3	3	10	3	3	1
Rb	7	100	10	300	10	70
Sc	ND	1	ND	ND	7	3
Se	ND	10	ND	3	1	1
Sm	ND	ND	1	1	1	ND
Sr	700	300	700	700	700	100
Th	1	7	7	7	3	1
Ti	700	700	700	700	700	700
U	ND	1	3	3	1	ND
V	30	30	30	30	70	30
Y	3	3	7	10	3	3
Zn	30	30	70	100	30	30
Zr	30	30	100	70	70	10

[a] SSMS data generally ranges within 500% accuracy.

[b] ND - Not Detected (<1 ppm).

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APPENDIX H

DEVELOPMENT, CONSTRUCTION AND EVALUATION OF A COLLECTION SYSTEM FOR LOW MOLECULAR WEIGHT HALOCARBONS

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APPENDIX H

DEVELOPMENT, CONSTRUCTION AND EVALUATION OF A COLLECTION SYSTEM FOR LOW MOLECULAR WEIGHT HALOCARBONS

H.1 Summary

Numerous experiments have been performed to determine the effectiveness of absorbents and adsorbents to remove and retain low molecular weight halocarbons from a flowing gas stream. Initial studies using a particulate sampling train, requiring a high gas flow rate of at least 0.5 cfm, indicated that neither absorbents nor adsorbents would efficiently collect compounds such as chloroform ($CHCl_3$) present in the gas stream at low concentrations of a few parts per billion. An inert adsorbent, e.g. Chromosorb 102, was found, however, to efficiently remove and retain $CHCl_3$ at much lower gas flow rates of 0.2 - 1.0 litres/minute. A collection system for low molecular weight halocarbons was constructed and evaluated at low flow rates over sampling periods of up to four hours duration. Results obtained from several tests indicated that the system had a collection efficiency of better than 90% over the longest time period. Desorption of adsorbed halocarbons was readily achieved by thermal treatment of the adsorbent.

H.2 Introduction

Late in 1975, an experimental program to burn waste chlorinated organic compounds in a rotary cement kiln was carried out at the St. Lawrence Cement Company (SLC) plant in Mississauga, Ontario. The program, sponsored by Environment Canada, was designed to obtain information on

- the use of waste chlorinated hydrocarbons as a supplemental fuel to the kiln;
- the reduction of alkali concentration of the clinker by the chlorine contained in the waste materials added; and,
- the effect of emissions from the kiln on air quality.

In order to collect the required information, process and emission samples were collected during periods when different composite wastes were burned in the kiln. The emission samples were analyzed for trace chlorinated organic compounds.

During preliminary discussions between members of the Ontario Ministry of the Environment (MOE), the Ontario Research Foundation (ORF) and SLC prior to initiating the study, some concern was expressed about the sampling methodology for trace chlorinated organic compounds. Since a major program requirement was to obtain the particulate emission rate during each burn, it was hoped that the EPA Method 5 sampling train, used to collect particulate material, could also be used for the collection of chlorinated organic compounds. However, it was not known whether absorbents or adsorbents were more efficient for collection of the organic compounds, or whether either collection medium would be efficient at the high gas flow rates required for particulate sampling.

MOE, therefore, requested that ORF complete a laboratory investigation to evaluate suggested procedures, and to develop an optimum method for the sampling and collection of trace chlorinated organic compounds which might be present in the kiln emissions. This report describes the test program carried out in the laboratory and presents the data obtained using specific chlorinated compounds as representative pollutants.

H.3 Background Information

Previous studies involving the incineration of chlorinated organic compounds [H.1] have indicated that, if complete combustion to CO_2, H_2O and Cl_2 or HCl is not realized, then trace amounts of volatile compounds such as CCl_4, $CHCl_3$ and CH_2Cl_2 may be present in the combustion gases. (Though it was unlikely that any HCl or Cl_2 produced would pass through a cement kiln without reacting to form alkali chlorides, it was necessary to consider these gases as possible pollutants for analysis also.)

The EPA Method 5 train for particulate sampling is also used to collect organic compounds in the impingers by condensation and scrubbing. The efficiency of collection for a particular substance is dependent on gas flow rate and volatility of the organic compound. For compounds more volatile than water, the collection efficiency is probably close to zero. To collect these volatile compounds, specific organic solvents have been used in the impingers, replacing the water normally present. There is, however, little data available on the collection efficiencies obtained.

In recent years, organic compounds in the ambient air have been collected using inert adsorbents [H.2]. These materials have tended to replace activated carbon for most applications since they are unaffected by water vapour, and recovery of adsorbed species is considered, in general, to be easier and more efficient. Recovery of adsorbed species may be accomplished either by thermal desorption or solvent extraction. An application of this technique has been to collect polycyclic organic compounds from combustion effluents [H.3].

Bearing in mind that, in the study to be carried out at SLC only trace amounts of more volatile organic compounds were expected to be in the kiln emissions, it was decided to evaluate both adsorbents and adsorbents in an EPA Method 5 sampling train for collection, retention and subsequent recovery of compounds such as $CHCl_3$ and CH_2Cl_2. If a collection method proved to be effective for capture of these compounds, then it would almost certainly be effective for the collection of higher molecular weight species, such as those chlorinated compounds present in the waste feed material.

H.4 Test Methodology

The normal gas flow rate through a particulate sampling train to maintain isokinetic sampling for most sources is 0.5 to 1.0 cfm. A flow rate of 0.5 to 0.7 cfm was, therefore, chosen for initial experiments using the EPA Method 5 train, which was illustrated in schematic form as Figure A.5 in Appendix A.

H.4.1 Retention and collection studies

H.4.1.1 Absorbents. Initially, tests were conducted to find a suitable high boiling solvent for use in an impinger system, in order to trap low molecular weight organochlorine compounds, e.g. $CHCl_3$, CCl_4, DCE and TCE.

The following solvents were tested for their suitability as an impinger solution for use in an EPA stack sampling train:

- reagent grade toluene;
- reagent grade xylene; and,
- reagent grade decane.

All solvents were redistilled prior to use in order to remove or limit to usable levels interfering peaks in the GC-EC chromatographic

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profiles which tended to obscure measurement of the components of interest.

- Tests were made to see if trace quantities of volatile chlorinated compounds could be retained in a solvent such as toluene with a high gas flow rate passing through the train for a period of four hours, a time anticipated for tests at SLC. A sampling train was, therefore, assembled in the laboratory with probe and oven temperature set above 250°F to warm incoming gas.

Toluene (100 ml) containing known amounts of 1,2-dichloroethane (EDC) and 1,1,2-trichloroethane (TCE) (main constituents of the first waste feed in the waste chloride study at SLC) was placed in impinger A (see Figure A.5). 100 ml of pure toluene was placed in impinger B, impinger C was empty and impinger D contained silica gel. Air was pulled through the sampling train after cooling the impingers to ice-water temperature, at a flow rate of 0.5 cfm. After running for four hours, the contents of each impinger were noted and analyses made for EDC and TCE. At specific times during each test, the parameters normally recorded during a source sampling test, such as impinger inlet and outlet temperatures and orifice Δp, were recorded. At the conclusion of each test, the total volume of gas sampled was determined.

This type of experiment was repeated, with 100 ml of water in impinger A, 100 ml of toluene containing EDC and TCE in impinger B, impinger C empty and impinger D containing silica gel. Both experiments were then repeated using xylene and decane as absorbents. Additional experiments were made using decane with known quantities of CCl_4, $CHCl_3$ and $CHCl_2$ in the standard impinger solution.

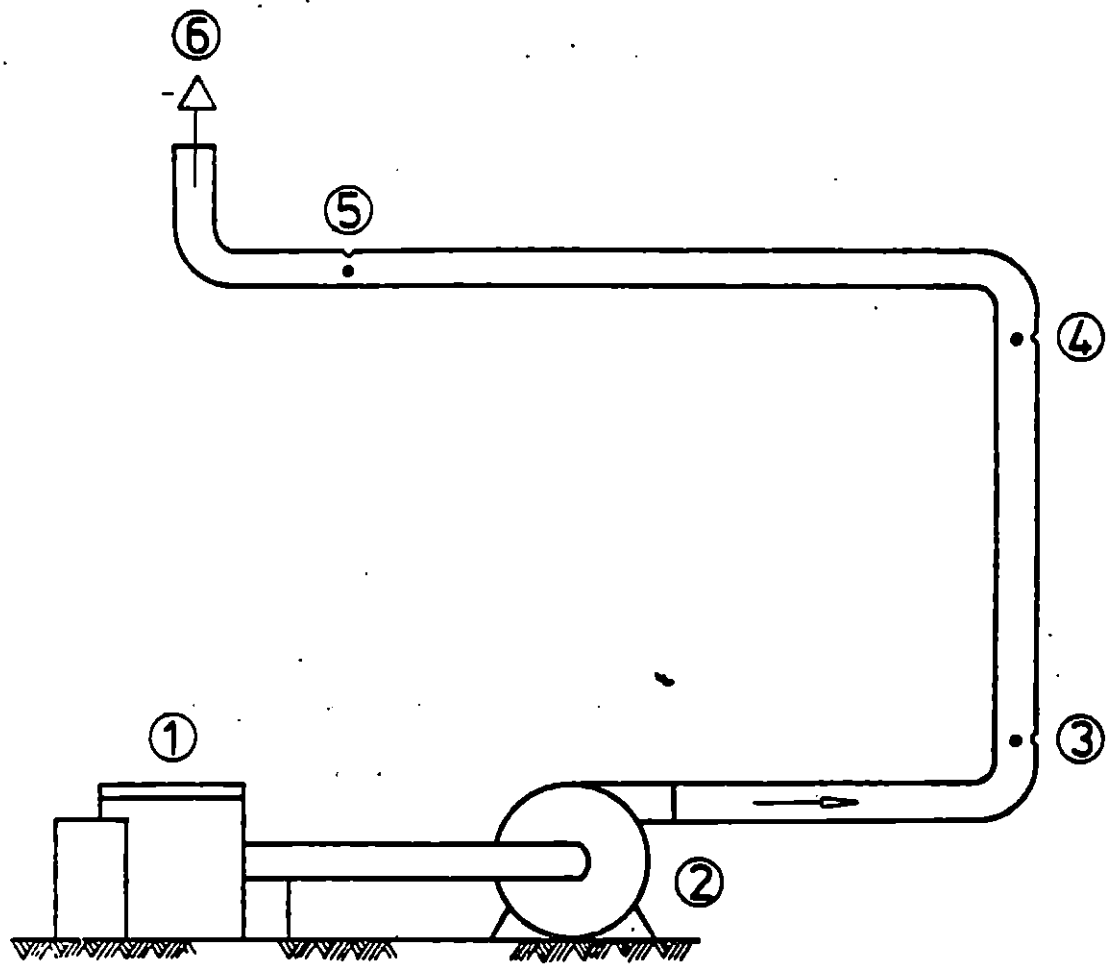
H.4.1.2 Adsorbents. Though a large number of adsorbents are capable of adsorbing a wide variety of organic compounds, Chromosorb 102 was used for the tests described below because it was readily available, and could be purchased without delay from various companies supplying chromatographic materials.

In order to determine fairly rapidly if Chromosorb 102 would adsorb volatile chlorinated compounds, the following experiment was performed. 100 ml of decane containing known quantities of CCl_4, $CHCl_3$ and TCE was placed in impinger B of the sampling train, and 25 gm of

Chromosorb 102 in impinger D. Impinger A contained 200 ml of distilled water and impinger C was empty. Room air at 0.5 cfm was then pulled through the system for one hour and at intervals of 10 minutes the decane solution was analyzed for chlorinated organic concentration. After one hour the Chromosorb was removed from the impinger, placed in a septum sealed container and heated to 100°C. Head-space samples were then analyzed for the respective chlorinated organic compounds. All three halocarbons present in the spike had been retained by the resin.

Following this experiment, a series of tests were carried out using the ORF test duct system, depicted in Figure H.1. This system allows dust or gaseous pollutants to be added at a controlled rate into an air stream flowing through a one-foot diameter duct at flow rates of 500 to 2500 cfm. Sampling ports are located at ideal and non-ideal positions in the system, to allow sampling of the air stream with an EPA type sampling train or other collection equipment. A low flow of air was allowed to bubble through $CHCl_3$ in a midget impinger and bleed into the main air flow in the duct. By varying the carrier flow through the $CHCl_3$, concentrations of 10 to 140 ppb of $CHCl_3$ were obtained in the duct air stream. These concentrations were determined both from weight loss of $CHCl_3$ with time and direct analysis of the air flowing in the duct. Tests were made with Chromosorb in impingers C and D but considerable carry over of the adsorbent occurred at flow rates of 0.5 - 0.7 cfm. This was minimized in further tests by placing a fine mesh screen on top of the Chromosorb layer in the impinger. At a $CHCl_3$ concentration of 13 ppb, breakthrough of this pollutant with 25 gm of Chromosorb in the third impinger occurred within 30 minutes.

It was recognised that high volume flow rates through the adsorbent caused not only contaminant problems with the material in the sampling train but saturated the bed fairly rapidly. This latter occurrence was proved by repeating the experiment with the Chromosorb packed tightly in a collector. A final series of tests were, therefore, completed, evaluating both Chromosorb and activated carbon in tube collectors at much lower air flow rates of 1-2 litres/minute. The $CHCl_3$ concentration in the air stream was analyzed before and after the collector at selected time intervals over a period of four hours. For both adsorbents collection of $CHCl_3$ was more than 90% efficient for the duration of each test. Since



1 DUST FEEDER
2 BLOWER
3 SAMPLING PORTS NON IDEAL LOCATION
4 SAMPLING PORTS IDEAL LOCATION
5 SAMPLING PORTS
6 TO ATMOSPHERE

FIGURE H.1 TEST DUCT SCHEMATIC

desorption of adsorbed species from Chromosorb was readily accomplished thermally and since, unlike activated carbon, the adsorption characteristics of Chromosorb are unaffected by moisture in the gas stream, Chromosorb 102 was selected as a suitable adsorbent for the SLC waste chloride program.

H.5 Collection System Evaluation

This section outlines the experimental protocol undertaken to verify the performance of Chromosorb 102 as a collection media for the concentration and analysis (by adsorption/desorption) of low molecular weight chlorinated hydrocarbons from an air stream under conditions relevant to field sampling. The concentration and analysis procedure is essentially an extension of the method used to concentrate organohalogen compounds present in potable water [H.4].

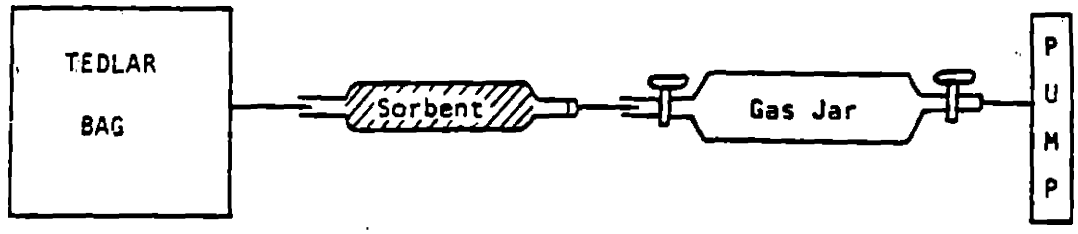
Adsorptive capacity values were determined. Adsorptive capacity is defined as the amount of solute vapour retained by a given weight of sorbent. In this study only low levels of chlorinated hydrocarbons (1 - 10 ppb) were examined since anticipated levels of organohalides in the sampling streams were expected to be low (i.e. ng/m^3).

The sampling cartridges consisted of glass tubes (11 mm i.d. x various lengths) containing various depths of sorbent bed supported by plugs of silanized glass wool. The tubes were conditioned by heating to 200°C and passing a stream of N_2 through them (40 ml/min) for four hours.

Known concentrations of air-solute vapour mixtures were prepared. The solutes examined were $CHCl_3$, CCl_4 and dichloroethane (DCE). The solutes were examined both individually and as mixtures. The air-solute vapour mixtures were prepared as follows.

Microlitre quantities of organic compounds were injected into gas jars of known volume. The gas jar was heated to ~ 50°C and, after cooling, aliquots were removed and added to Tedlar bags. The bags initially were evacuated and then half filled with air, at which stage the aliquot from the gas jar was injected into the bag. The bag was finally filled to the desired capacity (6, 20 and 40 litres).

A schematic diagram of the component parts of the test assembly is shown below.



The various parts of the assembly were connected to each other by means of Teflon tubing. Differing air-solute mixture concentrations of $CHCl_3$ were used to determine the adsorptive capacity of the Chromosorb 102. The $CHCl_3$ concentrations used were 5 ppb and 10 ppb. A flow rate of 250 ml/min was maintained throughout the run. For these conditions the collection efficiency of Chromosorb 102 for $CHCl_3$ was 100 percent. At various time intervals the pump was stopped and the gas jar disconnected. Aliquots (1 ml) were removed from the gas jar and analyzed for $CHCl_3$ by gas chromatography (GC). The first detection of $CHCl_3$ in the gas jar was taken as the stage in the test for the determination of breakthrough volume, i.e. the volume of air necessary to purge the adsorbed vapour through the cartridge.

From the breakthrough volume of the air-solute mixture of known concentration and the weight of sorbent in the cartridge it was possible to calculate the adsorptive capacity of Chromosorb 102 for $CHCl_3$ under the given experimental conditions.

From the data determined with respect to the adsorptive capacity of Chromosorb 102 for $CHCl_3$ and the knowledge that a four hour sampling period at a flow rate of 250 ml/min would be required in the field tests,

sampling cartridges of the following dimensions were constructed: 11 mm i.d. x 11.5 cm long containing 6 g of Chromosorb 102. These cartridges were used to determine desorption efficiency data.

$$\text{Desorption efficiency} = \frac{\text{quantity } CHCl_3 \text{ from Chromosorb 102}}{CHCl_3 \text{ concentration in air sampled} \times \text{Volume of air sampled}}$$

The same test assembly as described previously was used to collect $CHCl_3$ on the cartridge. The adsorbed $CHCl_3$ was thermally desorbed into an evacuated gas jar. The adsorbent tube and the gas jar were connected by Teflon tubing. The tube was heated to a fixed temperature by wrapping with heating tape controlled by a variable transformer (170°C). After reaching maximum temperature, the stopcock of the gas jar between the jar and the tube was opened. Heating of the sample tube was continued for a further 15 minutes, after which time the stopcock of the gas jar was closed, the gas jar removed from the sample tube, taken outside the laboratory and allowed to fill up with the cleanest possible air. The contents of the gas jar were then subjected to GC analysis. Aliquots (1 ml) were removed from the gas jar using an air-tight syringe and injected into a gas chromatograph.

Gas chromatography was conducted on a Varian 1200 series chromatograph equipped with an electron capture detector. The GC parameters used are shown below.

Column	- 2 m x 2 mm SS containing Chromosorb 102 (80/100 mesh)
Column temperature	- 180°C
Injector temperature	- 215°C
Detector temperature	- 215°C
Detector	- EC
Flow rate	- N_2 ~ 31 ml/min
Range and attenuation	- as required
Chart speed	- as required

The concentration of solutes present in the gas jars following desorption was determined by measuring peak areas of the vapours and comparing them with those of prepared standards. The initial concentration

in the Tedlar bag was known, and, from the volume of air drawn through the cartridge, the actual concentration contacting the cartridge was calculated. The desorption efficiency was then calculated.

H.6 Results and Discussion

Experiments using toluene and xylene as absorbents showed that a considerable loss of both solvent and chlorinated organic compounds occurred after a four hour test. The solvent was found in all impingers following the one in which the standard solution was placed. Estimated solvent losses were 40-60%. Losses of CCl_4, $CHCl_2$ and TCE ranged from 50 to 90%. With decane as the adsorbent, the solvent loss was less than 10%. However, the loss of chlorinated compounds was 60 to 100%. Due to time restraints and the obvious problem of solvent or pollutant loss at the high gas flow rate, this method of collection using absorbents was rejected.

As discussed in Section H.4.1.2, retention of volatile halocarbons by the adsorbent at high gas volume flow rates was poor and the breakthrough rapid. The results for the collection system finally selected (Section H.5) are summarized below.

Adsorptive Capacity

Component	µl/g (sorbent)
$CHCl_3$	0.1

Desorption Efficiency

Tedlar bag concentration of $CHCl_3$	Desorption Efficiency %
1.25 ppb	90
	96
	104
5.0 ppb	92
	110
10.0 ppb	94
	102

(The higher concentration samples required a second thermal desorption in order to remove all the solute from the sorbent. However, the first desorption was always better than 75%.)

Two additional experiments were performed. They were:

a) An air-solute mixture of CCl_4 and DCE (5.00 ppb level; 40 ℓ Tedlar bag) was run through the system using a back-up gas jar in order to test whether these solutes were retained by the Chromosorb 102. Regular checks of the gas jar using GC to analyze for the presence of CCl_4 and/or DCE failed to show any trace. Thermal desorption of the tube followed by GC analysis gave good recoveries for CCl_4 and DCE (>90%).

b) An air-solute mixture of $CHCl_3$, CCl_4 and DCE (2.5 ppb level; 40 ℓ Tedlar bag) was prepared. This mixture was drawn through the test system which contained two additional traps prior to the Chromosorb 102 cartridge. One trap contained water (50 ml) and the other 5% NaOH solution (80 ml). These traps were included in the ORF train in order to remove residual Cl_2 and/or HCl. Thermal desorption of the tube contents gave good recoveries of the solutes (>90%).

H.7 Conclusions

The laboratory study undertaken showed that low molecular weight halocarbons cannot be efficiently collected by absorbents or adsorbents from a gas stream at high flow rates (~ 0.5 cfm).

There are numerous literature references to the technique for collecting trace quantities of component vapours by drawing air through cartridges containing sorbent media such as polymer beads, activated carbons or stationary liquid phases chemically bonded to solid supports [H.5].

This report has demonstrated such a procedure for the collection of low molecular weight chlorinated hydrocarbons on Chromosorb 102. It has been shown to give quantitative collection together with quantitative recovery of the trapped species using a thermal desorption technique.

The sampling tube technique appears to give better results for sampling traces of low molecular weight organochlorine pollutants in air than impinger methods.

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APPENDIX I

GC/MS/COMPUTER DETERMINATION OF CHLORINATED HYDROCARBONS AND PCB'S

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ACM CC831C

APPENDIX I

GC/MS/COMPUTER DETERMINATION OF CHLORINATED HYDROCARBONS AND PCB's

In February 1970, 30 extracted samples were received from Dr. G. Thomas of the Ontario Research Foundation. These samples were taken from the burning of chlorinated hydrocarbon wastes in a cement kiln. Requests were made to determine the nature and quantity of any heavy chlorinated hydrocarbons, in particular PCB's, present in the samples.

Experiments were completed and the procedures are briefly described as follows:

Material: All apparatus and reagents used in the experiment were examined by gas chromatograph-flame ionization detector (GC-FID) analysis of a pure hexane extract to ensure freedom from organochlorine residue contamination. The chlorinated isomers (PCB's) and Aroclor mixtures were obtained from Analabs, North Haven, Conn., U.S.A.

GC-FID: A Perkin-Elmer 990 model GC-FID with a datasystem PGP-1 was used. The procedures for standard calibrations were given in a previous paper (to be published as a chapter in the book "Advances in Dynamic Mass Spectrometry" 1976). Chromatograph operating parameters were as follows:

Column 12' x 1/8" O.D.	stainless steel
Column packing	6% Apiezon L on chromosorb W 80/100 mesh
Column temperature	Initial 100°C programmed at 4°C/min. to final temp. 200°C and hold
Injection temperature	250°C
Manifold temperature	250°C
Carrier gas	Helium 40 ml/min.

GC/MS/Computer: A Finnigan 1015 D GC/MS system was used with a data system 6000 series. Its performance has been studied and documented in the same paper as mentioned above. It also includes standard PCB mass spectra and computed reconstructed Aroclor chromatograms. The instrumental data are as follows:

Finnigan 1015D GC-MS Instrumental Data

A

Instrumental Data GLC

Column	12' x ¼" all glass
Column packing	6% Apiezon L 80/100 mesh chromosorb W
Column temperature	225°C
Injection temperature	250°C
Carrier gas	helium 40 ml/min.
Sample size	5 to 7 microlitres per injection

B

Instrumental Data Ms

Filament current	180 microamperes
Electron energy	70 or 20 eV
Operating pressure	6.68×10^{-3} N/m^2 (5×10^{-6} torr)
Scanning speed	4 seconds
Standard deviation of spectra	maximum 570

After the quadruple MS operating parameters were adjusted the sample was injected into the GC. The ion abundance chromatogram of the GC effluent was acquired by scanning the mass range (40 to 400). The dialogue required for mass spectrometer control, data acquisition and obtaining the plot are given by software programs. At the end of the GC run the computer plots a reconstructed gas chromatogram (ion abundance chromatogram) of total ion amplitude versus the spectrum number. Identification of these chromatographic peaks can be accomplished by plotting the mass spectrum of a specified peak or by a limited mass plot chromatogram which is obtained under computer control by searching through the collected spectra and identifying spectra containing ions with a specific m/e value.

Result and Discussion

(All chromatograms and computer reconstructed chromatograms are kept on file at the Air Pollution Technology Centre, Department of the Environment, Ottawa, Canada.)

Computer reconstructed gas chromatograms of Aroclor 1242, 1254, and 1260 were made. By focusing on specific mass/charge ratio (m/e) peaks such as 290 (tetra-chloro biphenyls), 324 (penta-chloro) or 358 (hexa-chloro), an ion current plot for a particular PCB isomer versus the Aroclor spectrum is obtained.

Gas chromatograms on Perkin Elmer 990 GC were done for some blank solutions and concentrated samples (all samples were concentrated from about 25 ml to 1 ml). No chlorinated hydrocarbons nor PCB's were found in the samples. If they are present the concentrations are below the sensitivity limit of GC-FID of 1 ng or less.

Mass spectra for the GC peaks of spectrum numbers 365 and 487 from the reconstructed chromatogram plot of sample (WBC-T3, EPA train, impinger) reveals that only hydrocarbons are present in the sample. No evidence for chlorinated compounds was found. A limit mass searching technique has failed to give any indication of the presence of PCB's. The computer library search of standard Aroclors did not match those obtained from the sample.

It was concluded, therefore, that there were no heavy chlorinated hydrocarbons or PCB's in the samples. If they were present the weights were less than 1 ng.

LTC MAF JA RGM

2 file PCB Analysis

March 15, 1976

Dr. I. E. Wallen
Environmental Protection Agency
Office of Toxic Substances
401 M Street S.W.
Washington, DC 20460

Dear Dr. Wallen:

Monsanto has a concern over the validity of the perchlorination technique used by EPA and others to measure and/or confirm polychlorinated biphenyls in environmental materials.

In our investigation of the perchlorination method, we have found that such chemicals as biphenyl, alkylated biphenyl, and many other substituted biphenyls, interfere with the perchlorination technique. It also appears that various petroleum components may interfere. If these chemicals were present in environmental materials that were being tested for PCB's using the perchlorination method, erroneously high PCB concentrations would be reported.

A recent article in the Journal of the AOAC (Vol.58, No.3, 1975) points out two other limitations of the perchlorination procedure:

1. High and variable reagent blanks, which cause erroneously high findings.

2. Formation of bromononachlorobiphenyl, which causes low recoveries.

A copy of the article is attached.

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Since these limitations can lead to significant errors in determining trace levels of PCB's in environmental samples, we suggest that EPA carefully review the validity of the perchlorination technique. Results that have been obtained using this technique may not be valid.

If any other information is needed, please let us know.

Sincerely,

J. Coleman Weber
Manager, Product Acceptability

mah

cc: Dr. A. C. Trakowski
Environmental Protection Agency

bcc: W. C. Hammann - T3A
R. E. Keller - T1B
J. P. Mieure - T2F
D. Wood - B2SC
K. W. Easley - Washington 1920
R. G. Kaley - T2F

file PCB Soil Analysis

DEC 8 1975

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER AND HAZARDOUS MATERIALS

December 1, 1975

Mr. W.B. Papageorge
Manager, Product Acceptability
Specialty & Process Chemicals
Monsanto Industrial Chemicals Co.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Dear Mr. Papageorge:

Pursuant to your request attached is a copy of the paper "Environmental Levels of PCB's." Also attached, is a contractor's report describing PCB levels in soil samples taken from the area surrounding your facility in St. Louis.

If I can be of any further help, please contact me on 202-755-6956.

Sincerely yours,

Vincent J. DeCarlo, Chief
Monitoring & Information Systems Branch
Office of Toxic Substances (WH-557)

ADM CC8317

PLAINTIFF'S EXHIBIT 908

ENVIRONMENTAL LEVELS OF PCB's

Doris J. Kuopp
Vincent J. DeCarlo
U.S. Environmental Protection Agency
Washington, D.C. 20460

ABSTRACT

Since the 1966 discovery in Sweden that chlorinated biphenyls were widely dispersed in the environment their environmental levels have been the subject of many studies with the results indicating that PCB's can have adverse ecological and toxicological effects. However, a well planned national approach to environmental sampling has not been attempted thus hindering making a national assessment of the PCB problem. This paper reviews the levels that are currently being found in the environment.

INTRODUCTION

Since the 1966 discovery in Sweden that chlorinated biphenyls were widely dispersed in the environment, their levels have been the subject of many studies both abroad and in the United States. Extensive laboratory and environmental measurements indicate that PCB's can have adverse ecological and toxicological effects, are very resistant to environmental degradation and are being discharged by many different sources.

This paper will focus on the current PCB data base in an effort to assess the PCB levels in the environment on a national basis.

ENVIRONMENTAL PCB SOURCES

Before the PCB data base is examined, it would be of interest to review how these chemicals get into the environment. The major sources contributing to the environmental levels of PCB's are industrial effluents, manufacturing processes, consumer and industrial waste materials, sewage treatment facilities and accidental spills. Lacking extensive air and soil data from these sources, available water data are shown in Table 1. The 5 major PCB spills in 1973-75 all involved transformers. In 4 of those incidents, the PCB's were spilled on soil while in the fifth the transformer was dropped on a pier and the contents were spilled into the water. In the latter incident, 283 gallons were spilled and it was estimated that only 70-90 gallons were recovered. In all cases the material that could be recovered was drummed up and entombed at a cost approaching $2.3 million.

REVIEW OF THE PCB DATA BASE

To assess the scope and extent of PCB's in the environment, all national surveys and national data bases maintained by the U.S. Environmental Protection Agency (EPA) were examined, including STORET, the national water quality storage and retrieval system, the National Soils Monitoring Program for Pesticide Residues and the Human Monitoring Program. In addition, data from special data bases maintained by the United States Geological Survey and the open literature were also examined along with available unpublished reports. Using these data, maps were constructed showing the concentrations of PCB's in urban soils and the aquatic environment.

The data from the national surveys show that a great deal of effort has been expended and continues to be expended but that the data are very limited. On examination, all States are believed to show some level of PCB contamination. In Table 2 States which had significant levels in at least one medium are listed with their reported PCB levels for surface and ground water, bottom sediments and fish. In Table 3, a number of localized studies are listed along with the reported environmental data. In all these studies the most extensive measurements have been in fish.

TABLE 1

ENVIRONMENTAL SOURCES OF PCB's

SOURCE	EFFLUENT WATER CONCENTRATIONS (ppb)
PAPER MILLS	
Wisconsin[1]	0.1 - 18.5
WASTE PAPER MILLS	
Wisconsin[1]	18.5
INDUSTRIAL EFFLUENTS	
California[2]	0 - 76
Wisconsin[2]	.04 - 0.25
Ohio[2]	0 - 17
Michigan[3]	.1 - 7000
MUNICIPAL WASTE WATER TREATMENT PLANTS	
Michigan[3]	0.5
Wisconsin[1]	.05 - 17.0
Ohio[2]	.10 - 17
California[2]	0.16 - 76
CAPACITOR AND TRANSFORMER FACILITIES	
New York[4]	2600
Massachusetts[5]	42.5
PCB MANUFACTURING FACILITY	
East St. Louis[5]	.87
SPILLS	Variable

1. Kleinert, S. J., Environmental Status of PCB in Wisconsin, May 8, 1975, Wisconsin Department of Natural Resources.
2. PCB's and the Environmental, Report of the Interdepartmental Task Force on PCB's, National Technical Information Service, 1972.
3. Statement of Concerns of the Lake Michigan Toxic Substances Committee Related to Polychlorinated Biphenyls, June 1975. Prepared by Karl F. Bremer, USEPA, Chicago, Ill.
4. Unpublished Data - Royal J. Nadeau and Robert F. Davis, Investigation of Polychlorinated Biphenyls in the Hudson River, Hudson Falls-Ft. Edward Area, August 1974.
5. Field Sampling and Analysis of Toxic Pollutants Interim Report, Battelle, Pacific Northwest Laboratories, August 1974.

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WATER

On the basis of the national aquatic environmental data collected in 1971-1972 and in 1974, a continuing widespread accumulation of PCB's in water, sediment and fish appears to be occurring. However, no trend analysis is possible with the available measurements. For example, whole water measurements have been taken throughout most of the country but those states reporting non zero readings are few in relation to the number of states showing zero concentrations. This is due both to the low solubility of PCB's and to the usual analytical procedure that limits detectability to the 0.1 ppb level. More meaningful water concentrations were obtained in the Lake Ontario[1] and Orange County, California[2] studies where concentrations in water at the ppt (ng/l) level were measured. At these levels, changes in PCB concentrations could be found with distance and time and could be related to other measurable parameters such as PCB concentrations in sediment, flora and fauna.

SEDIMENTS

Since PCB's are relatively insoluble, it is not surprising that bottom deposits have shown significant concentrations. Although 30 states collected samples in the 1974 study, 15 had less than 4 stations reporting and showed zero readings. Of the remaining 15, with at least 4 reporting stations, 13 showed detectable concentrations. Since the 13 states involved were not necessarily the same in both studies, only a very broad comparison may be made, i.e., five states had lower concentrations, four states were higher and four did not sample again.[3] We may conclude, then, that in these states with any monitoring effort in the 1974 study, PCB's are present in bottom deposits and the levels are not any lower than in the 1971-72 study. Considering the persistence of PCB's, a significant proportion of the nation's waters are now affected and will continue to be.

SOILS

The National Soils Monitoring Program is a small sampling effort studying only 5 urban areas each year. However, PCB's were detected in three of the five cities sampled in each of the years for which data are available, 1971-73. Of the 22 positive readings 17 of them were below 1 ppm. Of the cities sampled in 1973, Pittsfield, Mass., was of particular interest because it has a large transformer and condenser plant using large quantities of PCB's. Six different sampling sites within one mile of the plant show no detectable PCB residues. In contrast, the soil surrounding another facility in Illinois using PCB's in the manufacture of investment casting waxes was recently measured for PCB content. Samples taken in an area one-quarter mile radius around the plant ranged in value from 0.77-5.2 ppm. The PCB's identified were mixtures of Aroclor 1260 and decachlorobiphenyl. Levels up to 1.8 ppm Aroclor 1260 were found at 1-1/4 miles from the plant. Samples were collected from this facility as part of a study being conducted for the Office of Toxic Substances at sites suspected to have PCB concentrations. Other sites sampled in March of 1975 were in the vicinity of an investment casting company in Michigan and the PCB manufacturer in Illinois. Surface soil samples were collected at each site up to a distance of approximately one mile from the plant boundary, at 1/4 mile intervals in all directions. PCB's were detected in soils at both sampling locations. Concentrations ranged from the detection limit of 0.001 ppm to over 20 ppm. The distribution of all PCB's analyzed appears higher near the plant site and generally decreases with distance from the site.[4] Details of the sampling sites and the concentration levels measured are shown in Figure 1.

TABLE 2

SELECTED STATE DATA ON ENVIRONMENTAL LEVELS OF PCB's

State	Surface and Ground Water[1] µg/l	Bottom Sediment[1] µg/kg	Fish[3] ppm
AL			1.53-5.48
AR		20-2,400	1.69-3.88
CA	0.1	20-190	
CO	0.3		
CT	0.1-0.2	5-350[2]	2.16-5.34
FL	0.1-2.1	5-3,200	0.10-1.25
GA		10-1,300	0.52-1.18
IL			1.21-11.3
IA			0.35-1.41
MD	0.1	10-1,200	0.56-1.31
MA	0.2		
MI			4.00-11.7
MN	0.1-0.3		0.44-1.09
MS		50-170	
NB			0.47-4.58
NJ	0.1	3-800[2]	0.10-4.00
NY	0.1-4.0	3-13,000[2]	2.68-9.50
OH			1.73-8.07
OR		1-5-140	0.71-3.62
PA	0.2	6-700[2]	1.94-2.48
PR	0.1		
SC		30-200	0.10-7.3
TX	0.1-3.0	7.9-290	0.10- .22
UT			0.15-2.14
VA	0.1	5-80	
WV		10	0.31-1.20
WI			1.24-14.8

1. All data in this column taken from Hans J. Crump-Wiesner, Herman R. Feltz and Harvin L. Yates, A Study of the Distribution of Polychlorinated Biphenyls in the Aquatic Environment, Jour. Research U.S. Geol. Survey 1, 603 (1972, unless otherwise noted.
2. USGS Sediment data, 1974.
3. All data in this column taken from Croswell Henderson, Anthony Inglis and Wendell L. Johnson, Organochlorine Insecticide Residues in Fish Fall 1969 National Pesticide Monitoring Program, Pesticide Monitoring Journal 5, 1(1971).

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TABLE 3
SELECTED PCB STUDIES

	Fish (ppm)	Water (ug/l)	Sediment (ug/kg)	Plankton (ppm)
LAKES				
Lake Ontario[1, 2]	0.14 - 9.17	0.035 - 0.097	43 - 245	3.4 - 11.8
Lake Erie[3, 4]	0.2 - 7.8			
Lake Superior[5]	0.3 - 5.6			
Lake Huron[6]	0.16 - 11.0			
Lake Michigan[6, 9]	0.1 - 165.3		3.72 - 636	
Cayuga Lake[10]	3.4 - 9.7			
Lake St. Clair[16]	tr - 3.8	0.1 - 0.2		
RIVERS				
Iowa				
Mississippi River[11]	0.9 - 5.5			
Texas				
Brazos River[12]		0.1 - 0.5		
Utah				
Green River[12]		0.1		
New York				
Hudson[13]	7 - 350	1.0 - 2800	6.6 - 6,700,000	
Michigan				
Saginaw River[6, 14]	6.9 - 165.3	0.1 - 0.21		
Kalamazoo River[7, 15]	<0.01 - 164.56	0.1 - 0.45	100 - 560	
Portage Creek[7]		0.1 - 0.48	10 - 475,400	
Wisconsin				
Milwaukee[8]		.02 - 2.17		
MARINE ENVIRONMENT				
Atlantic Ocean[17, 18]	0.038 - 0.190	0.0009 - 0.0036		
Bay of Fundy[19]	0.07 - 1.54			
Gulf of Mexico/Caribbean Sea[20, 21]	0.032 - 0.059			0.157 - 1.055
Southern California[22]	0.04 - 6.6	0.0015 - 0.019		

1. Clarence L. Haile, Gilman Veith, G. Fred Lee and William C. Boyle, Chlorinated Hydrocarbons in the Lake Ontario Ecosystem, EPA-660/3-75-002, June 1975, U.S. E.P.A., Corvallis, Oregon.
2. Klaus L. Kaiser, Mirex, An Unrecognized Contaminant of Fishes from Lake Ontario, Science 18, 523 (1974).
3. Richard L. Carr, Charles D. Finsterwalder and Michael J. Schibi, Pesticides Monitoring Journal 6:23 (1972).
4. John R. M. Kelso and Richard Frank, Organochlorine Residues, Mercury, Copper and Cadmium in Yellow Perch, White Bass and Smallmouth Bass, Long Point Bay, Lake Erie, Trans. Amer. Fish. Soc., 103:577 (1974).
5. Unpublished data. Gilman D. Veith and G. E. Glass, PCB's and DDT in Fish from Western Lake Superior, U.S. E.P.A., Duluth, Minnesota.
6. Unpublished Data - John L. Hesse, Bureau of Water Management, Michigan Department of Natural Resources, June 1973.
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8. Gilman D. Veith and Fred G. Lee, Chlorobiphenyls in the Milwaukee River, Water Research, 1971.
9. Unpublished data - Schacht 1974, EPA 600/3-74-002.
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12. Jean A. Schulze, Douglas B. Manigold and Freeman L. Andrews, Pesticides in Selected Western Streams 1968-1971, Pesticides Monitoring Journal 7:73 (1973).
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16. Michigan Department of Agriculture, Bureau of Consumer Protection, 1973 Great Lakes Environmental Contaminants Study.
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18. George R. Harvey, Helen P. Miklas, Vaughan T. Bowen and William G. Steinhauer, Observations on the Distribution of Chlorinated Hydrocarbons in Atlantic Ocean Organisms, Journal of Marine Research 32:103 (1973).
19. V. Zitko, O. Hitzinger and P.M.K. Choi, Contamination of the Bay of Fundy - Gulf of Maine Area with Polychlorinated Biphenyls, Polychlorinated Terphenyls, Chlorinated Dibenzodioxins and Dibenzofurans, Environmental Health Perspectives, 1:47 (1972).
20. C. S. Giam, A. R. Hanks, R. L. Richardson, W. M. Sackett and M. K. Wong, DDT, DDE, and Polychlorinated Biphenyls in Biota from the Gulf of Mexico and Caribbean Sea - 1971. Pesticides Monitoring Journal 6:139 (1972).
21. C. S. Giam, M. K. Wong, A. R. Hanks, W. M. Sackett and R. L. Richardson, Chlorinated Hydrocarbons in Plankton from the Gulf of Mexico and Northern California, Bulletin of Environmental Contamination and Toxicology 9:376 (1973).
22. The Ecology of the Southern California Bight: Implications for Water Quality Management, Southern California Coastal Water Research Project, 1500 East Imperial Highway, El Segundo, 1973.

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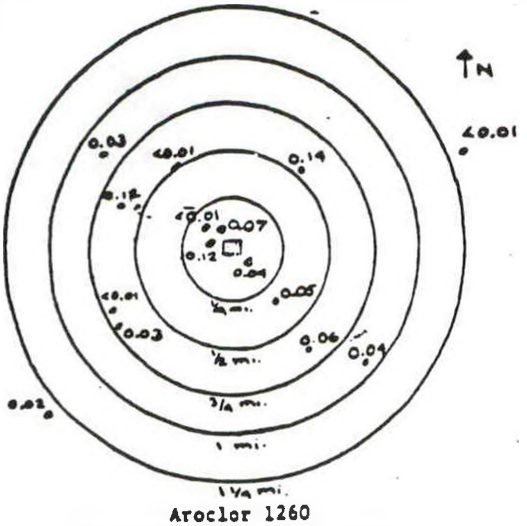
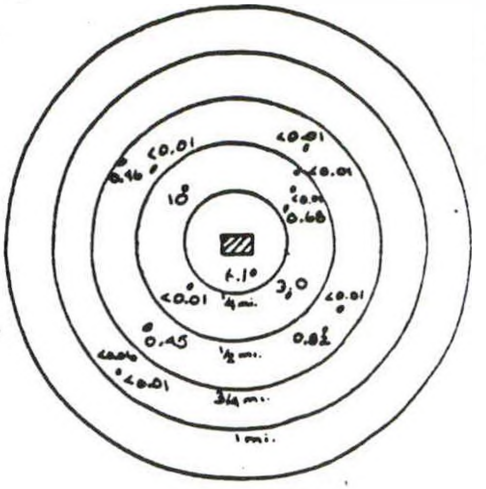
Figure 1

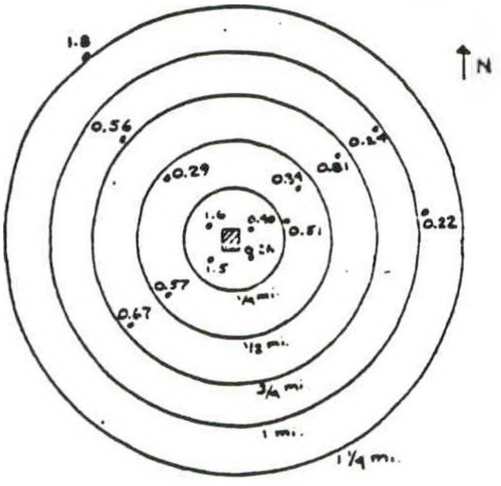
Concentration of PCB's in Soil with Distance
(ppm)



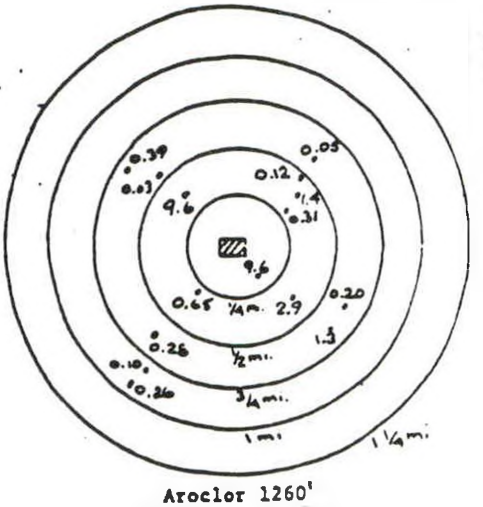
Aroclor 1260
Investment Casting Company



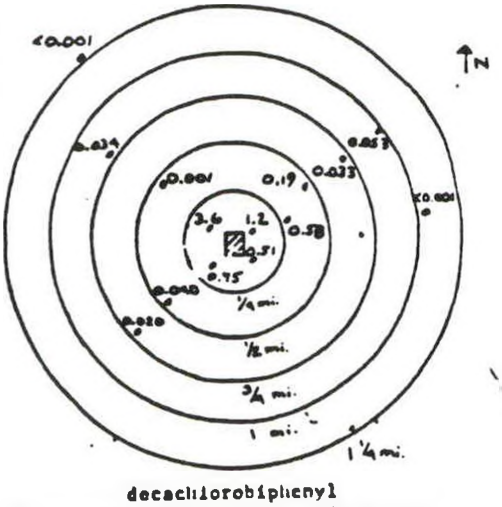
Aroclor 1242
PCB Manufacturer



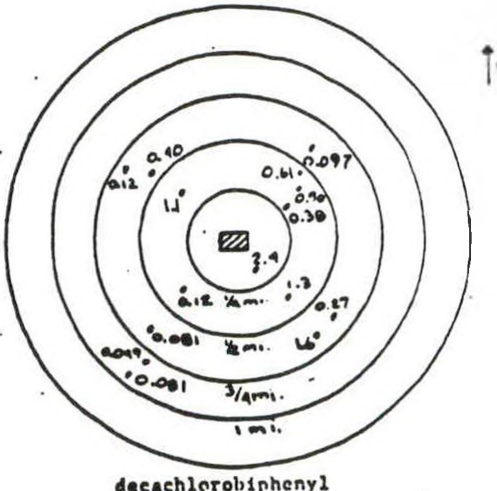
Aroclor 1260
Investment Casting Wax Manufacturer



Aroclor 1260'
PCB Manufacturer



decachlorobiphenyl
Investment Casting Wax Manufacturer



decachlorobiphenyl
PCB Manufacturer

ADM CC8321

AIR

PCB measurements in air along with the related transport studies are practically nonexistent. Harvey and Steinhauer[5] have reported levels ranging from 3.9 - 5.3 ng/m3. Air measurements by Bidleman and Olney for Rhode Island ranged from 2.1-9.4 ng/m3 and from 0.21 - 0.65 ng/m3 at Bermuda.[6] Snow melt water data from Wisconsin ranged from zero to 0.24 ppb. The suggestion has been made that atmospheric fallout may be the most significant source of PCB discharge to the waters of the state of Wisconsin.[7]

FISH

Fish have been studied on a nationwide basis by the Department of the Interior since 1967. In the 1969 study, PCB levels were identified in fish from 35 states.[8] Data from the nationwide sampling programs, 1970-1973, are currently being prepared but were not available for this report. Consequently, nationwide fish data are not available any more currently than 1969, with the exception of the isolated studies listed in Table 3. The 1969 national study showed PCB levels generally within the FDA 5 ppm guideline. In the Great Lakes area, PCB levels in fish from Lake Michigan were so high, 7.6-10.9 ppm, that FDA seized shipments of coho salmon in May 1975.[9]

Although transport mechanisms are not well known and would vary through different ecosystems, it is interesting to consider the Lake Ontario Ecosystem Study summarized in Table 4. From this study an estimate of biomagnification is possible giving a sediment to fish ratio of 1:120. The FDA guideline of 5 ppm in the edible portion of fish corresponds to a sediment concentration of 41 ppb - a figure exceeded in all 13 states reporting through USGS in 1974.

HUMANS

With PCB's as widespread across various media as they are, it is expected that levels would be identified in humans as well. The Human Monitoring Program, in 1972, found that 3035 out of 4102 samples from 31 States showed levels ranging from less than 1 ppm to more than 3 ppm. In 1973, 964 out of 1277 samples from 28 States again showed levels in the same range. In both years approximately 75% of the adipose tissue analyzed contained some polychlorinated biphenyls. Unfortunately we do not know age, occupation or residential histories of the cases involved so it is difficult to trace the levels back to the potential sources.

CONCLUSIONS

Although there are many national and state groups collecting environmental PCB data, limitations in the current data base prevent one from making a uniform national assessment of PCB environmental levels. It appears that if a well planned national approach to sampling were attempted, the data base could be improved in a very short period of time.

TABLE 4

LAKE ONTARIO ECOSYSTEM[1]

FISH, µg/g	
Alewife	.14 - 4.36
Smelt	1.40 - 3.49
Slimy Sculpin	1.58 - 9.17
WATER, ng/l	38 - 97
SEDIMENT, ng/g	43 - 245
WET PLANKTON, µg/g	3.4 - 11.8

1. Haile, C. L., Veith, G. D., Lee, G. F., Boyle, W. C., Chlorinated Hydrocarbons in the Lake Ontario Ecosystem (IFYGL) June, 1975.

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1. Haile, C.L., Veith, G.D., Lee, G.F., Boyle, W.C., Chlorinated Hydrocarbons in the Lake Ontario Ecosystem (IFYGL), June 1975.
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7. Kleinert, S.J., Environmental Status of PCB's in Wisconsin, May 8, 1975, Wisconsin Department of Natural Resources.
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9. Bremer, Karl E., Draft copy of "Statement of Concerns of the Lake Michigan Toxic Substances Committee related to PCB's," June 1975.

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Data from Vicinity of Monsanto Co., Sauget, IL.

Aroclors have been produced by Monsanto Co. at the Sauget, Illinois site since prior to 1957. PCB mixtures ranging from 16 percent chlorine to 68 percent chlorine have been produced over the years. Production of the higher percent chlorine mixtures has been voluntarily reduced since 1970 and lower substituted isomers have been introduced. Polychlorinated terphenyls and chlorinated benzenes have also been produced at this facility. It is reported (Papageorge, 1975) that terphenyl production was suspended in 1971.

A typical chromatogram of a soil sample taken in the vicinity of the Monsanto facility is shown in Figure 8 along with the chromatogram of several other PCBs run under the same instrument conditions. This particular soil sample contains 11 ppm Aroclor 1242, 9.3 ppm Aroclor 1260 and 1.0 ppm decachlorobiphenyl. Lighter chlorinated Aroclor mixtures are likely present as well. The instrument conditions employed, however, do not give adequate separation of these mixtures to permit accurate quantification. The presence of decachlorobiphenyl at the concentrations observed is interesting. Decachlorobiphenyl has been reported as a component of only one Aroclor mixture, Aroclor 1268 (Hutzinger, Safe and Zitko, 1974). Whether it may be a component of any of the terphenyl mixtures or biphenyl/terphenyl mixtures or a by-product is not known.

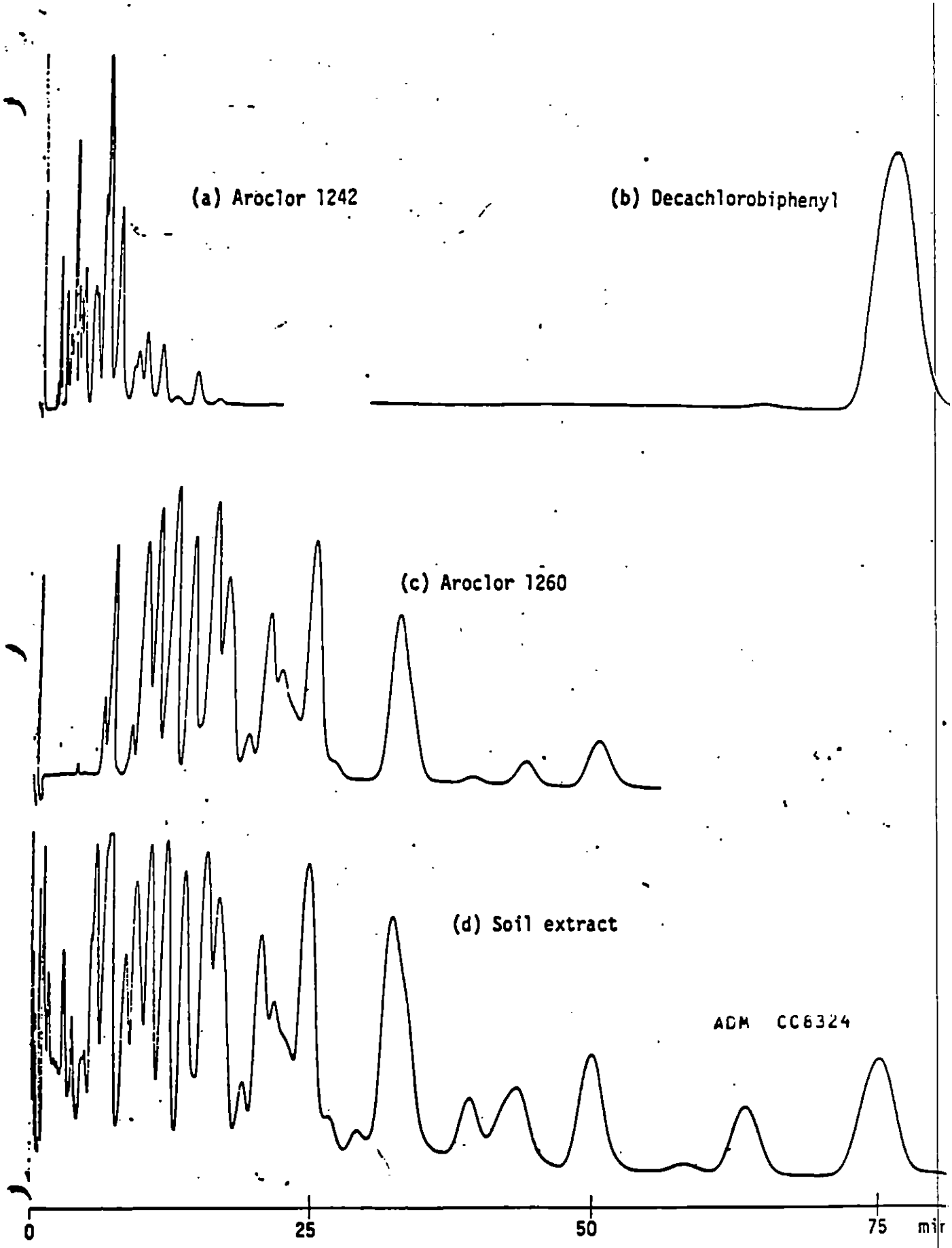

Figure 8. Typical chromatograms of standard Aroclors, decachlorobiphenyl and a soil sample taken in the vicinity of Monsanto Co., Sauget, Illinois.

The measured soil concentration of Aroclor 1242, Aroclor 1260 and decachlorobiphenyl in the vicinity of the Monsanto facility are depicted in Figures 9, 10 and 11, respectively. Figure 12 shows the long-term average wind direction in the area. The distribution of all PCBs analyzed appears to be higher near the plant site and generally decreasing with distance from the site. Furthermore, there is evidence that generally higher concentrations are present in the soils located to the southeast. This corresponds to the predominant wind direction and may suggest an airborne transport of the PCBs from the facility.

One 15 cm deep core sample was taken 1/2 mile southwest of the Monsanto site. Analysis of the bottom 11 cm of this soil yielded PCB concentrations basically equivalent to the top 4 cm.

A 24-hour composite sample from the influent and the effluent of the Sauget village sewage treatment plant taken beginning 0800 on February 17, 1975, was provided by plant personnel. The Monsanto Co. jointly owns this facility. Analysis of these samples were as follows:

	Aroclor 1242	Aroclor 1260	Decachlorobiphenyl
influent	6.8 µg/l	8.7 µg/l	<0.01 µg/l
effluent	4.5 µg/l	4.7 µg/l	<0.01 µg/l

The treatment plant effects a reduction of 34 percent Aroclor 1242 and 46 percent Aroclor 1260. No decachlorobiphenyl was detected.

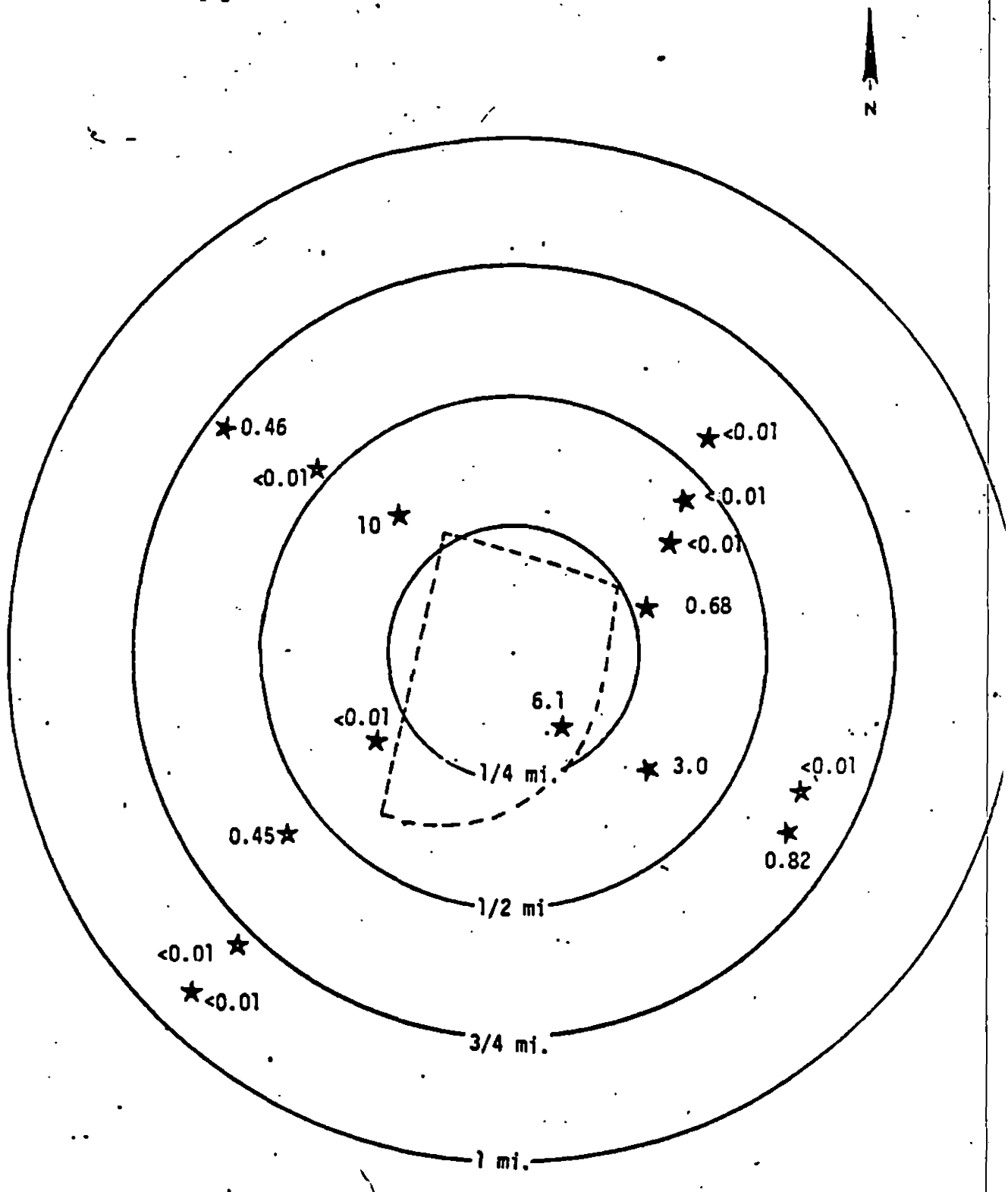

Figure 9. Concentration of Aroclor 1242 in soil as a function of distance from Monsanto Mfg. Co. Concentrations are expressed in ppm.

ADM CC8326

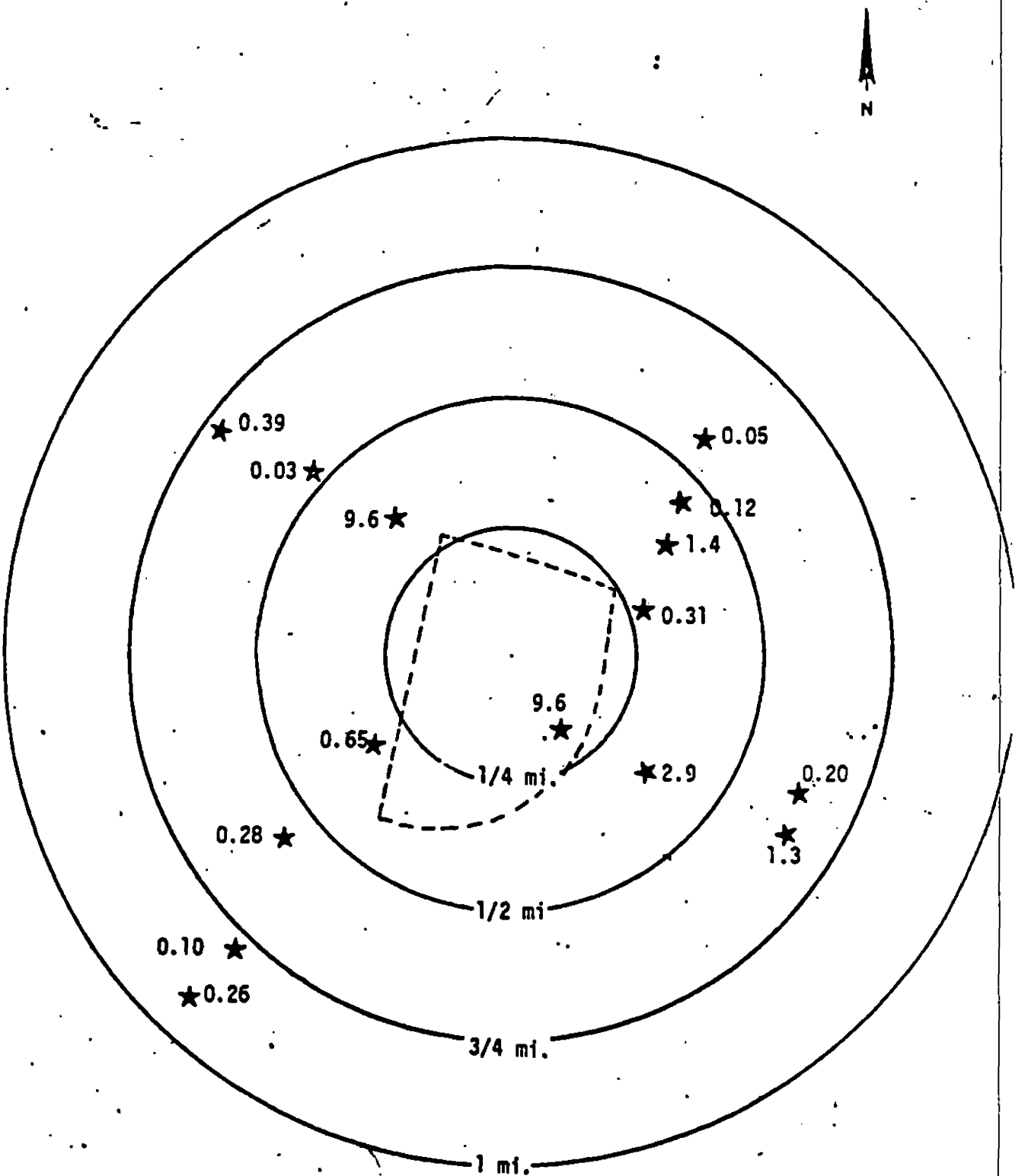

Figure 10. Concentration of Aroclor 1260 in soil as a function of distance from Monsanto Mfg. Co. Concentrations are expressed in ppm.

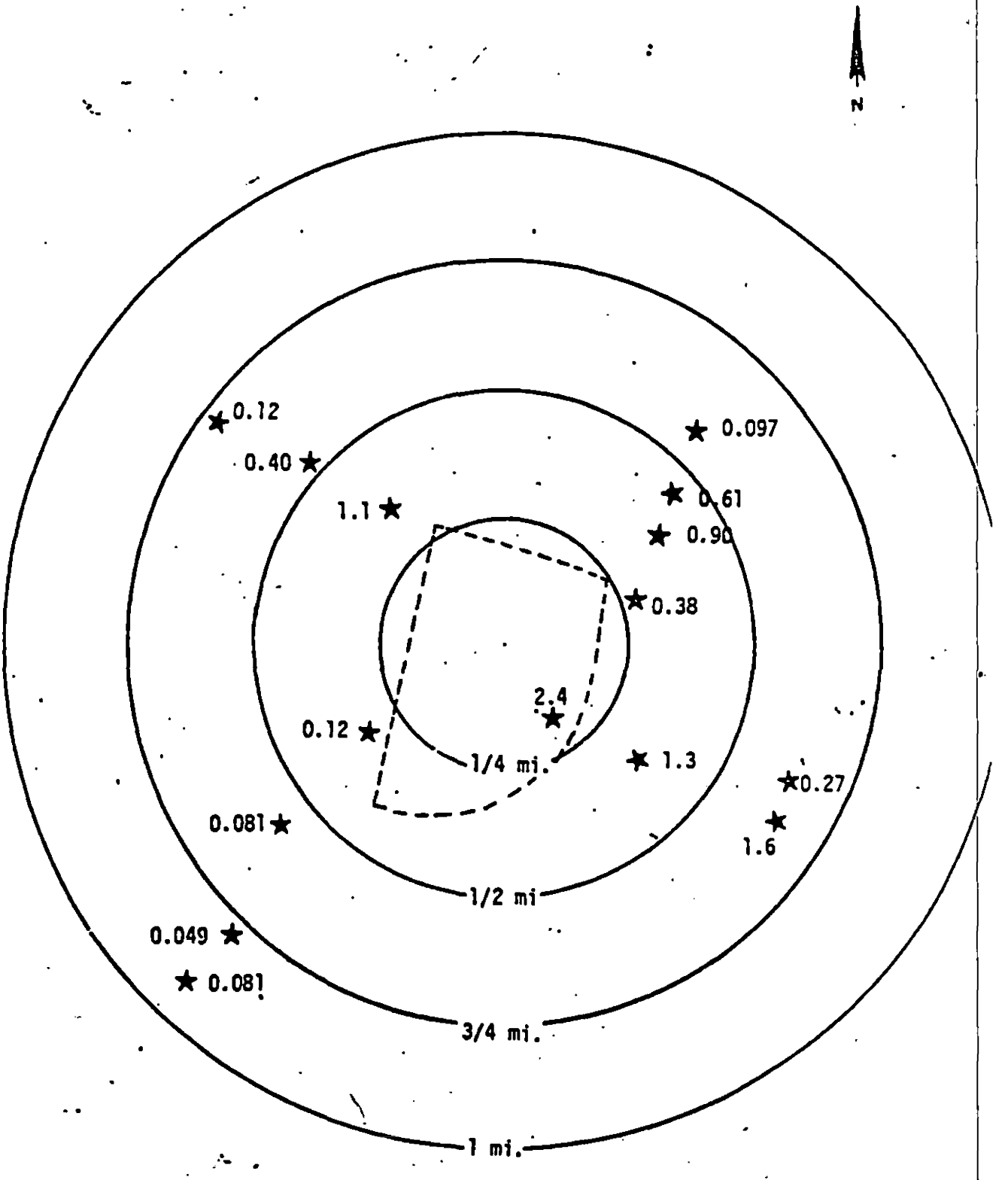

Figure 11. Concentration of decachlorobiphenyl in soil as a function of distance from Monsanto Mfg. Co. Concentrations are expressed in ppm.

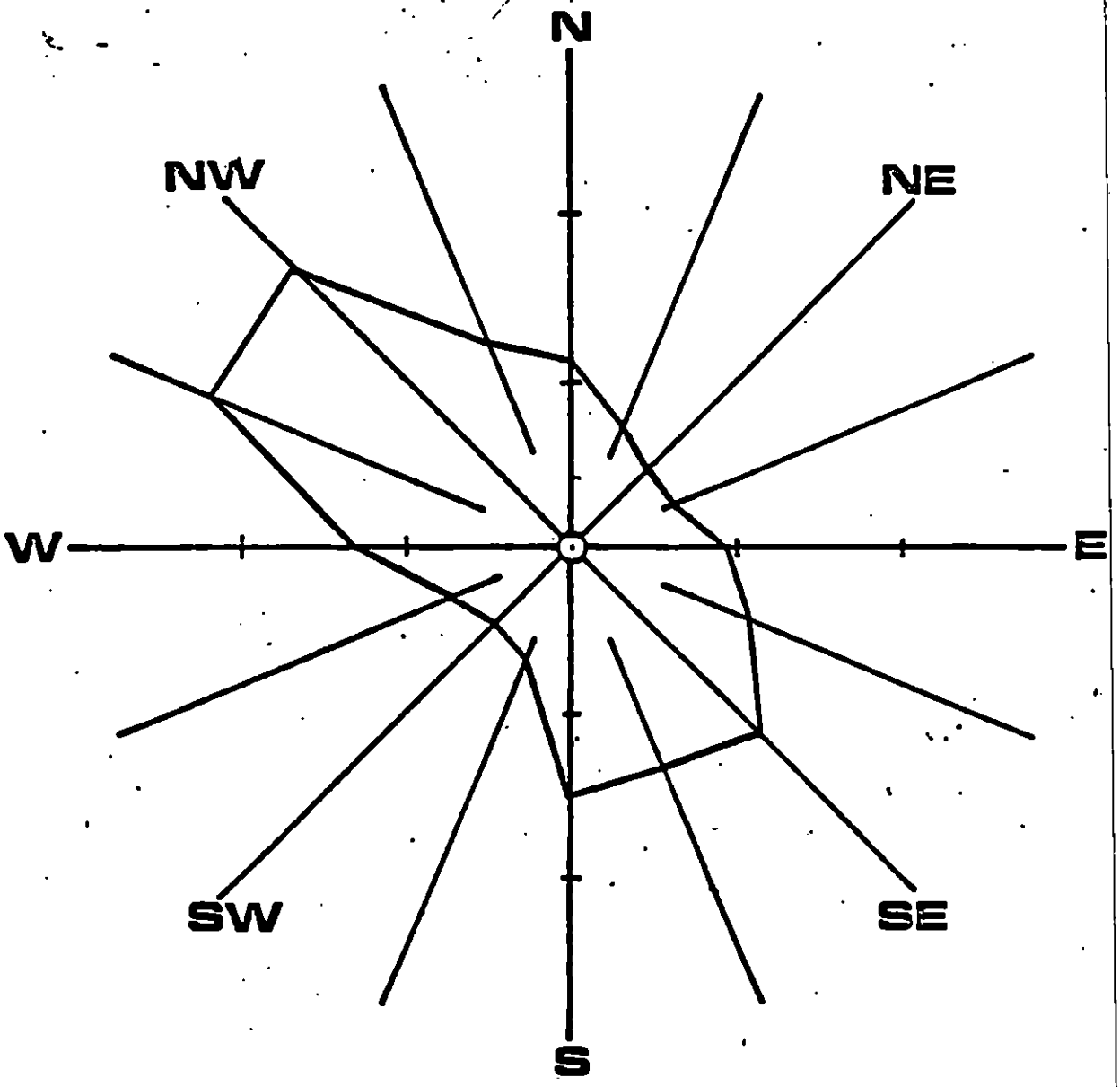

Figure 12. Ten Year Averaged Wind Rose for St. Louis, Missouri, January through March, 1951-1960.

Scale: 1" = 5% Calm Winds = 2.0%

ACM 008329

bcc C. R. Wilmore - NEMA
Tyler Nourse - EIA

bbcc D. Hosmer
A. Leisy
D. Wood

February 18, 1976

Mr. John P. Lehman, Director
Hazardous Waste Management Division
U.S. Environmental Protection Agency
Washington, D.C. 20460

Dear Mr. Lehman:

Enclosed are our comments and suggestions to your draft "Recommended Procedures for Disposal of PCB Containing Wastes".

We have made several changes on pages 1, 2, 5, 7 and have added Appendix B - Disposal Services and changed your Appendix B to C with a minor correction.

I would appreciate receiving a copy of your revised guidelines.

If we can be of any help, please let me know. My phone number is (314) 694-2027.

Also enclosed for your information is a Monsanto summary on PCBs.

Sincerely,

J. Coleman Weber
Manager, Product Acceptability

cs

cc K. W. Easley

Recommended Procedures for the Disposal of PCB-Containing Wastes (Industrial Facilities)

On December 22, 1975, the Administrator of the Environmental Protection Agency announced an action plan of regulatory and administrative actions to help ensure that polychlorinated biphenyls currently in service do not enter the environment. One portion of that program includes investigation and recommendation of appropriate disposal procedures for industrial users of this family of chemicals. The Agency is also evaluating the consumer waste disposal problem and may issue further guidance on that subject at a later time.

General Background

Polychlorinated biphenyls (PCBs) are chlorinated aromatic organic compounds which give rise to concern because of their toxicity coupled with their pervasiveness and persistence in the environment and their tendency to accumulate in food chains. It is this bioaccumulative characteristic which manifests itself by possible adverse effects on animals, including man, that causes the present and continuing concern over the disposition of PCBs to the environment. PCBs have been used both in "closed" systems, or sealed as dielectric fluids in transformers and capacitors, and in "open" applications, where the PCBs are used in and consumed with the product.

Uses of PCBs in "open" applications included impregnation of cotton and asbestos for braided insulation of electrical wiring; a plasticizer in wire and cable coatings; in plasticizers of

vinyl chloride polymer films; in high-pressure hydraulic fluids; specialized lubricants and gasket sealers; heat transfer agents; and machine tool cutting oils. Former open applications also include: formulation into some epoxy paints; protective coatings for wood, metal, and concrete; adhesives; and in carbonless reproducing paper. Today PCBs are supplied by Monsanto only to the electrical power distribution industry where they are marketed as dielectric fluids in "closed" or sealed systems such as transformers and capacitors.

The sole producer of PCBs in the United States is the Monsanto Company, under the trade name of Aroclor. PCBs have also been marketed and used by manufacturers in their products under various trade names. Appendix A provides a listing of the trade names used by domestic and foreign manufacturers. Cumulative sales in the U.S. since the introduction of PCBs are estimated to be 1.5 billion pounds. In 1970 Monsanto voluntarily restricted sales only to the electrical power distribution industry where they are marketed as dielectric fluids in "closed" or sealed systems such as transformers and capacitors. As a result, current production is down more than 50% from the peak years before 1970, but still amounts to about 30 million pounds per year. Monsanto has introduced Aroclor 1016 which is reported to have lower toxicity and higher biodegradation rates. Most capacitors

(using PCBs) produced in the past two years use Aroclor 1016.

Almost all of the PCBs ever produced still present a serious threat to the environment because of their toxicity, bioaccumulative characteristic in the food chain and slow degradation. An estimated 750 million pounds of PCBs produced are still in use; 300 million pounds are estimated to be present in landfills. It is estimated that less than half the PCBs ever produced have entered the environment; of this amount, only about 10% (50 million pounds) are estimated to have degraded or been incinerated. The recommendations of this document are directed only at the PCBs presently in service (or which will enter service as a result of future production).

Purpose

Pursuant to Section 204 (b)(1) of the Solid Waste Disposal Act, as amended, the Administrator may issue advisory guidance and recommendations related to the disposal of waste materials. These recommended procedures do not have standard-setting or regulatory status, but represent the best information available on preferable disposal options for PCB-contaminated waste materials. In addition, the Agency plans to conduct studies to determine other options for treatment and disposal of PCB-containing wastes (including incineration of capacitors containing PCB liquids) during calendar 1976. The Agency is also aware that the American National Standards Institute is in the process of revising its guideline for disposal of askarels containing PCBs

(ANSI C107.1-1974). As significant new information becomes available from these and other sources, this Federal Register issuance will be revised.

The purpose of this issuance is to provide guidance for the disposal of PCB-containing wastes. This guidance is addressed primarily to industrial users of PCBs, particularly those manufacturing and/or using capacitors and transformers containing PCBs, although the recommended procedures are appropriate to all PCB-containing wastes.

Technical Background

Polychlorinated biphenyls are a class of synthetic compounds which have no known counterpart in the natural environment. PCBs are manufactured by the chlorination of biphenyl with anhydrous chlorine using iron filings or ferric chloride as a catalyst. The three most important physical properties of PCBs are low vapor pressures, low water solubility, and high dielectric constants. They are miscible with most organic solvents. The chemical properties that make PCBs desirable industrial materials are their excellent thermal stability, their strong resistance to both acidic and basic hydrolysis, and their general inertness. They are quite resistant to oxidation.

In the process of replacing hydrogen atoms with chlorine atoms, a large number of substitution combinations arise.

Theoretically, there are 210 possible chlorinated biphenyl compounds but only about 100 are likely to occur in commercial products. In commercial preparation, PCB compounds contain from 12 to 68 percent chlorine; the typical product is a mixture of several compounds.

Monsanto, the sole U.S. producer of PCBs, has adopted a four-digit designation for its Aroclors; the last two digits represent the approximate chlorine content by percentage weight. The first two digits indicate the type of material: biphenyl, triphenyl, or mixture of the two. The higher chlorinated biphenyls are non-flammable and have extremely low volatilities. Unfortunately, some of the characteristics (stability, non-degradability) which make PCBs so valuable in industrial applications also make them highly persistent in the environment.

The chemical stability, low volatility, high dielectric constant, and compatibility with other chlorinated hydrocarbons have resulted in many and varied industrial applications for the PCBs. The solubility of PCBs in nonpolar solvents explains why they are readily absorbed into fatty tissue and into the liver. Their resistance to oxidation or other types of chemical degradation explains their persistence and accumulation in animal tissue. The latter effect is enhanced both by their insolubility in water and solubility in organic solvents. Their chemical inertness and resistance to metabolism account for their low acute toxicity. But as they

slowly build up in a living system, their concentration approaches toxicity levels, at which point chronic effects make themselves evident.

The low solubility of PCBs in water probably limits the rate at which they are dispersed by water systems, but does not seem to limit their range of dispersion. PCBs discharged into a river or lake will accumulate in the sediment in relatively high concentration. Plants and animals can concentrate PCBs above their level in water alone. Shrimp and oysters exposed to 10 ppb of Aroclor 1254 have been known to bioaccumulate from 130- to 3300-fold.

PCBs are not intended to get into the environment, but they do because their unique chemical properties prevent them from being destroyed by usual waste disposal methods. Thus, they inadvertently escape and become widely dispersed. Environmental transport models for PCBs have not been developed. Conclusions regarding their behavior, particularly their distribution and transport in the environment, are based largely upon the results of DDT research. Recent data indicates that aerial transport is the most efficient route, although dumping and river runoff will contribute more effectively to local contamination.

Disposition of PCBs

The persistence of PCBs necessitates extremely careful attention to final disposition of PCBs and PCB-contaminated

materials. Initial attention within the manufacturing or PCB-user facility should be given to reducing the use of PCBs. Manufacturers or users may either use substitute (less contaminating) materials or more efficient methods which produce less waste. However, no matter how many substitutes are developed and no matter how efficient the operation may become, there may still remain some applications for which PCBs are the current optimum material and there still will be waste materials. Spills, damaged goods, and housekeeping materials will require disposal. Recommended options for the disposal of PCB-containing wastes (in priority order) are:

- Reclamation or recycling
- Incineration
- Controlled land disposal

Recycling - Reclamation or recycling of PCBs is usually feasible only with relatively uncontaminated liquids. Monsanto maintains a toll-free telephone number (800/325-3850) for the public for advice on scrap PCBs. If liquids cannot be reused, these liquids needs to be disposed of by high temperature incineration. Several incineration services are available such as Rollins Environmental Services, Inc., Chem-Trol Pollution Services, etc. Addresses are given in Appendix B. Monsanto also has a high temperature incinerator. A technical description of the Monsanto incinerator is provided in Appendix C.

Recycling of transformers is accomplished by General Electric Co. and several independent companies. The tank and inside copper of the transformer is reclaimed; the PCB liquids

if they can't be reused, can be drained and incinerated at facilities such as General Electric's Pittsfield, Massachusetts plant.

It is quite possible to leach out the PCBs from solid wastes with a suitable solvent, e.g., acetone, and then dispose of the decontaminated waste. The solution containing PCBs may be separated by distillation into PCB, which may be reclaimed, and the solvent which may be used again. This technique (of leaching and reclamation) is especially useful after accidental spills of liquid PCBs. The spills should be absorbed on dry sand, ash, sawdust, or commercial absorbents and then processed as above.

Incineration - Present knowledge indicates that the proper incineration of waste PCBs must involve a suitable balance among temperature in the incinerator, dwell time in the firing chamber, plus oxygen availability. Also, a suitable scrubber must be provided on the exhaust stack to remove the hydrochloric acid mist that is formed.

Preferred requirements are: (1) 2-second dwell time at 1100°C(2000°F) and 3% excess oxygen in the stack; or (2) 1 1/2 second dwell time at 1500°C(2700°F) and 2% excess oxygen in the stack gas.* These alternates are recommended. Open hearth incinerators are not considered suitable; the relatively

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* These values are from ANSI C107.1-1974. Guidelines for Handling and Disposal at Capacitor and Transformer-Grade Askarels Containing Polychlorinated Biphenyls, American National Standard Institute.

low operating temperature of this equipment would only volatilize the PCB and pollute the atmosphere.

The above recommendations are suitable for liquids. Incineration of solid wastes containing PCBs has not been demonstrated. However, such destruction does appear feasible. For example, a rotary kiln furnace, with an afterburner and scrubbing system could probably safely incinerate solid wastes containing PCBs. Likewise, other smaller, high temperature incinerators with sufficient residence times may be satisfactory.

Land Disposal - Wastes containing PCBs should not be disposed of with other mixed wastes in a sanitary landfill. Characteristics of transport of PCBs through the soil are not definitively established. The interaction with other decomposing wastes is not well understood. The ubiquity and persistence of PCBs indicate that their disposal should be carefully controlled until additional data are developed. While these data are being gathered, PCBs (when disposed to the land) should only be placed in a secure chemical waste landfill. In general terms, a chemical waste landfill provides complete long-term protection for the quality of surface and subsurface waters from hazardous waste deposited therein, and against hazards to public health and the environment. Such sites should be located or engineered to avoid direct hydraulic continuity with surface and subsurface waters. Generated leachates should be contained, and subsurface flow into the disposal area eliminated. Monitoring wells should be

established and a sampling and analysis program conducted. Additional characteristics of a chemical waste landfill are described in EPA publication, Landfill Disposal of Hazardous Wastes: A Review of Literature and Known Approaches (EPA/530/SW-165)**. Encapsulation of wastes in cement prior to burial in a sanitary landfill has been used for small quantities of solids or sludges contaminated with PCBs. Only those specific sites which have been state-approved for PCB wastes should be used. The EPA publication, Hazardous Waste Management Facilities, (EPA/530/SW-146) provides some information to potential disposers; this data when used in consultation with State solid waste management officials can assist in planning a disposal action.

** Documents referenced here may be obtained from Solid Waste Information, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

Appendix A

Listing of Names Used for PCBs by Manufacturers

Name	Manufacturer
Aroclor	Monsanto
Asbestol	American Corporation
Askarel	*
Chlorextol	Allis Chalmers
Diaclor	Sangamo Electric
Dykanol	Cornell Dubilier
Elemex	McGraw Edison
Hyvol	Aerovox
Inerteen	Westinghouse Electric
No-Flamol	Wagner Electric
Pyronol	General Electric
Saf-T-Kuhl	Kuhlman Electric
Clophen	Bayer (Germany)
Fenclor	Caffaro (Haly)
Kennechlor	Kenneclor (Japan)
Phenoclor	Prodelic (France)
PK	Caffaro (Italy)
Pyrolene	Prodelec (France)
Santotherm	Mitsubishi (Japan)

* generic name used for insulating liquids in capacitors and transfomers; may contain PCBs.

Appendixes

(These Appendixes are not a part of American National Standard Guidelines for Handling and Disposal of Capacitor- and Transformer-Grade Askarels Containing Polychlorinated Biphenyls, C107.1-1974, but are included for information purposes only.)

Appendix B
Disposal Services

In addition to the supervised dry landfill sites that may be used for the disposal of askarel-containing scrap, the following additional known facilities and services have been established, and others may be available.[8]

Chem-Trol Pollution Services, Inc
P.O. Box 200
1550 Balmer Road
Model City, N.Y. 14107
Phone: 716 754-8231

This organization has facilities and services capable of handling:

(1) Liquids. Askarels alone or mixed with solvents or oils. Disposal by high-temperature incineration.

(2) Solids (software). Askarel-soaked compounds, rags cartons, absorbing earths, etc. Disposal by incineration or scientific landfill.

(3) Solids (hardware). Capacitors, transformer tanks, cores, askarel-soaked metals. Disposal by scientific landfill. Has solvent extraction capability.

Monsanto Company
800 North Lindbergh Boulevard
St. Louis, Mo 63166
Phone: 314 694-3352

This organization has facilities and services capable of handling askarel liquids alone or mixed with other oils or solvents by high-temperature incineration. Liquid is pumped through a gun with atomizing steam into incinerator. Temperatures are maintained at 2000°F-2500°F with auxiliary natural gas. Exit gases are quenched to 180°F by contact with water. Gas is then passed through a high-energy venturi scrubber for removal of particulates. Before exhausting to air (110°F), gases are passed through a packed column scrubber to remove HCl.

Nuclear Engineering Company
Eastern Division
P.O. Box 146
Morehead, Ky 40351
Phone: 606 784-6611

Nuclear Engineering Company
Disposal Division
Sheffield, Ill. 61361
Phone: 815 454-2624

This organization provides containerization, transportation, and disposal services of all liquids and solids (including hardware). Disposal is in controlled chemical and scientific landfill area. Licensed by Atomic Energy Commission for radioactive waste disposal. The organization also has two West Coast locations, in the states of California and Washington.

Rollins Environmental Services, Inc
P.O. Box 2349
Wilmington, Del 19899
Phone: 302 658-8451

This organization has facilities and services capable of handling:

(1) Liquids. Askarel alone or mixed with solvents or oils. Disposal is by high-temperature incineration.

(2) Solids (software). Askarel-soaked compounds, rags, cartons, absorbing earths, etc. Disposal is by incineration at combustion temperatures up to 2500°F. Incineration gases are scrubbed, and entrained solids are removed before exhausting to air.

Rollins Environmental Services maintains disposal facilities in the following areas:

Philadelphia/Camden:
Rollins Environmental Services, Inc
Route 322
Logan Township
Bridgeport, N.J. 08014

[8] The listing given herein is representative of some of the sources that provide this service, and is not presumed to be complete. Any other organizations that wish to be listed should notify the Standards Institute so that they may be included in the next edition of this standard.

ACM CCE342

APPENDIX

Baton Rouge:
Rollins Environmental Services, Inc
Scenic Highway & West Chatham Lane
Scotlandville
East Baton Rouge Parish, La 70807

Houston:
Rollins Environmental Services, Inc
Tidal Road & Highway 134
Deer Park, Tex 77536

Appendix C

Description of Monsanto Incineration Facility

Sauget, Illinois

Background

The Krummrich Plant is one of Monsanto's large chemical manufacturing plants. The product line includes sulfuric acid, benzene, chlorine, polychlorinated biphenyls, several rubber compounds, and various chemical intermediates. The plant is located immediately south of East St. Louis, Ill. near the Mississippi River. Since June 1971, Monsanto has operated a liquid injection incinerator to dispose of in-house liquid wastes and contaminated PCBs from customers.

Waste Characteristics

The large majority of the wastes burned are PCB derivatives. The sources of these wastes are process still bottoms, ~~spilled batches~~, and contaminated transformer oils. The heating value of the materials is about 9000 BTU/lb. Other in-house high BTU liquid wastes are also incinerated. Phosphorous compounds cannot be burned due to the formation of particulates (P_2O_5) which foul the injection system. The system is not equipped to handle suspended solids. Four

Air Pollution Control

The fumes exit the oxidizer and enter a water quench column. The main purpose of the quench is to reduce the temperature of the hot fumes. Particulates are removed next in a high energy venturi. Finally, the emissions are cleaned in a packed bed (polypropylene packing) at the base of the stack. The 40 ft. stack is equipped with a demister. Scrubber liquors are drained to the sewer without treatment.

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16. Farb, D. information about hazardous waste management facilities. Environmental Protection Publication SW-145, 1975.

17. Tucker, E., et al. Migration of PCB's in soil induced by percolating water. Monsanto Co. Bulletin of Environmental Contamination and Toxicology, Vol. 13. 1975

18. ASTM. Standard method of test for rapid gas chromatographic estimation of higher boiling homologues of chlorinated biphenyls for capacitor askarels. specification D 1810-63 (1973).

19. HEW. Registry of toxic effects of chemical substances. 1975 Edition NIOSH June 1975.

20. Mitre Corp. Environmental cycling of PCB's. 1975 (unpublished report).

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

October 22, 1975

Mr. D. B. Hosmer
Utilities and Environmental Protection Director
Monsanto Industrial Chemicals Co.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Dear Mr. Hosmer:

It is a great pleasure for me to invite you to attend the "National Conference on Polychlorinated Biphenyls" sponsored by the Environmental Protection Agency in cooperation with the U. S. Department of Agriculture, the Council on Environmental Quality, U. S. Department of Health, Education and Welfare, and the U. S. Department of the Interior. Your attendance and participation will help ensure that the conferees benefit from the presence of recognized authorities in this field.

Please reserve the dates of November 19-21, 1975 for this meeting to be held at The Pick-Congress Hotel, Chicago, Illinois. Enclosed for your convenience is a hotel reservation card. I would suggest that you make reservations as soon as possible.

The program will last for three days. The objectives of the conference are to:

... bring together the latest data and best available expertise to help clarify the problems associated with the manufacture, use and disposal of PCBs.

... help assess the effectiveness of steps taken to reduce the problems associated with PCBs.

... provide a platform for interested parties to present previously neglected data concerning PCBs.

... help clarify the feasibility and complications of steps to reduce the problems associated with PCBs.

PLAINTIFF'S EXHIBIT 910

ADM CC6345

The Administrative Coordinator for the conference is Mr. Franklin A. Ayer, Research Triangle Institute, Post Office Box 12194, Research Triangle Park, North Carolina 27709; telephone (919) 549-8311, extension 640 or 632. You are encouraged to write or telephone him if you have questions concerning this meeting.

In addition to the enclosed hotel reservation card, you will find a conference registration card which you should fill out and return to Mr. Ayer as soon as possible.

I am looking forward to a stimulating conference and hope that you will be able to attend.

Sincerely,

John L. Buckley
General Chairman

Enclosures: Hotel Reservation Card
Conference Registration Card

bmi

PRELIMINARY AGENDA

NATIONAL CONFERENCE ON POLYCHLORINATED BIPHENYLS
PCBs in the Environment - 1975
The Pick-Congress
Chicago, Illinois

November 19-21, 1975

Sponsored by
The Environmental Protection Agency in cooperation with the Department of Agriculture, Council on Environmental Quality, Department of Health, Education and Welfare, and the Department of the Interior.

Program - Outline - General Chairman - John L. Buckley, Ph.D.
Environmental Protection Agency

Wednesday, November 19, 1975

10:00 KEYNOTE ADDRESS - Honorable Russell E. Train, Administrator, United States Environmental Protection Agency

11:00 HEALTH EFFECTS AND HUMAN EXPOSURE - David P. Rall, M.D., Ph.D., Director, National Institute of Environmental Health Sciences and Chairman, Department of Health, Education and Welfare Committee to Coordinate Toxicology
What exposures to PCBs have what effects on man? Review of toxicological, clinical and epidemiological data obtained since 1972.

12:00 Lunch

1:00-3:00 HEALTH EFFECTS AND HUMAN EXPOSURE (CONTINUED)

3:30-5:30 USES, SOURCES, AND IDENTIFICATION - David Garrett, P.E., Chief, Special Projects Branch, Office of Toxic Substances, Environmental Protection Agency
What are PCBs used for now, how much is used, where do they come from, how do they reach the environment? Review of present manufacture, import, use, distribution and disposal, and review of chemical analytical procedures.

Thursday, November 20, 1975

8:30-12:00 ENVIRONMENTAL FATE AND OCCURRENCE - Ian C. T. Nisbet, Ph.D., Research Massachusetts Audubon Society,
How much occurs where, how does it move in the environment, and what happens to it? Report on current levels in various parts of the environment -- water, soil, air, fish, wildlife, human foods and man. Review what is known of transformations and degradation - mechanisms and rates. To the extent possible, synthesize in mass-balance terms, with particular attention to exposure routes and levels for man and other living organisms.

12:00-2:00 LUNCHEON - Speaker (To Be Announced)

2:00-3:30 ECOLOGICAL EFFECTS AND EXPOSURES - Donald I. Mount, Ph.D., Director, National Water Quality Laboratory, Environmental Protection Agency
What is happening in freshwater, marine, estumarine and terrestrial environments because of PCBs? Review of laboratory and field studies completed since 1972.

4:00-5:30 ECONOMICS AND SUBSTITUTES - Warren Muir, Ph.D., Council of Environmental Quality
What are PCBs used for now, what substitutes are available, and what are the economic, health and environmental aspects of proposed substitutes?

5:30 **Dinner**

7:00-9:00 GENERAL SESSION - Christopher M. Timm, Director, Surveillance and Analysis Division, Region V, Environmental Protection Agency
Brief statements by interested groups, or individuals expressing opinions on the PCB situation, and elaboration of discussion points curtailed by lack of time during sessions.

Statements from the floor from persons registering requests prior to the opening of the General Session.

<u>Friday, November 21, 1975</u>

8:30-10:15 APPROACHES TO CONTROL (Chairman to be Announced)

What can be done to reduce amounts of PCBs reaching the environment and to limit human exposure?

Panel discussion by Federal and State Agency spokesmen, and representatives of industry.

10:30-11:45 SUMMARY SESSION - Richard Carpenter, Executive Secretary, Commission on Natural Resources, National Academy of Sciences.

Concise summaries of the information presented and significant points raised during discussions.

11:45-12:30 CONFERENCE HIGHLIGHTS - John L. Buckley, Ph.D.
Integration and synthesis of the most significant findings and recommendations that emerged during the conference. Richard Carpenter.

CONCLUDING REMARKS - Conference Chairman

October 7, 1971

Dr. Ronald G. Webb
Research Chemist
Environmental Protection Agency
Southeast Water Laboratory
Athens, Georgia 30601

Dear Dr. Webb:

Thank you for sending me the chromatograms and isomer samples in which I expressed an interest.

Upon my arrival in St. Louis, I found that the Unilever article which we discussed had been published (J. Chromatography, 60, 15-32, 1971). For this reason, I did not send you a copy of the unedited preprint.

I have, however, enclosed a copy of Dr. Berg's paper which discusses his novel approach to PCB quantitation. We currently do not employ Dr. Berg's procedure in our laboratories, but plan to evaluate the use of the perchlorination technique for quantitation.

I enjoyed listening to your presentation on the "Identities of PCB Isomers" and being able to meet and talk with you afterwards.

Sincerely,

E. S. Tucker
Research Group Leader
Analytical Chemistry Group

db
Encl.
bcc: R. E. Keller
W. B. Papageorge

ADM CC6352

ENVIRONMENTAL PROTECTION AGENCY

SOUTHEAST WATER LABORATORY
Athens, Georgia 30601

September 28, 1971

Dr. E. Scott Tucker
Monsanto Company
1700 South Second St.
St. Louis, Missouri 63177

Dear Dr. Tucker:

As I promised you at the PCB Analysis Meeting in Washington, September 17, I am sending under separate cover samples of 2,5,2',5'-tetrachlorobiphenyl and 2,4,5,2',5'-tetrachlorobiphenyl. I am also including some electron capture gas chromatograms of the compounds.

You mentioned that you have a preprint of Telling, Sissons, and Welti's paper on identification of PCB isomers by MS and NMR. I would like to have a copy of that paper.

Sincerely,

Ronald G. Webb
Research Chemist

ADM 006353

PLAINTIFF'S EXHIBIT 913

OCT 18 1978

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

October 12, 1978

OFFICE OF ENFORCEMENT

Mr. W. B. Papageorge
Monsanto Company
800 North Lindbergh Blvd.
St. Louis, MO 63166

Dear Mr. Papageorge:

This office is in the process of developing a disposal control program for Polychlorinated Biphenyls (PCBs). It would be very helpful to our effort if we were able to discuss past uses of PCBs, and the nature of the former PCB-using community with members of your organization.

Our principal concern is to identify feasible commercial routes for the disposition of PCBs that are available to persons who are disinclined to pay the cost of proper storage and disposal. Your knowledge and experience would be helpful in this analysis.

If you, or other persons in the Monsanto organization could provide some time to discuss PCBs with my staff, I would be grateful. My staff can travel to St. Louis or elsewhere at your convenience.

Thank you for your consideration of this request. I look forward to hearing from you.

Sincerely,

William A. Wallace, Head
Toxics Strategy Unit

ADM CC8354

PLAINTIFF'S EXHIBIT 911

Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

November 29, 1976

Dr. Jerry M. Johnson
Acting Chief, Criteria Documentation, Section 1
NIOSH, DCDSD, CDB, RM 142
4676 Columbia Parkway
Cincinnati, Ohio 45226

Dear Dr. Johnson:

Attached are answers to the questions on the draft criteria document concerning occupational exposure to polychlorinated biphenyls.

We hope our comments are helpful and appreciate the opportunity to participate in the preparation of a responsible criteria document.

Sincerely,

W B Papageorge

W. B. Papageorge
Mgr., Product Acceptability

WBP/ken

attachment

ACM CC8355

POLYCHLORINATED BIPHENYL EXTERNAL REVIEW QUESTIONS

1. The document inadequately documents industrial exposure related effects of PCB. It also inadequately defines clinical tests which could be used to monitor for potential adverse effects of PCB exposure among the industrial population. The document dwells at great length upon the effects observed in a population of Japanese citizens who were accidentally exposed to an acute dose of PCB in a cooking oil. No relation is established between this accidental acute oral exposure to a relatively high concentration of PCB and industrial type exposures. No relationship is established defining relative body burdens resulting from acute oral exposure versus other routes of exposure, dermal absorption and respiratory, that are more likely to occur in an industrial environment. Another study given seemingly unwarranted consideration, involved an unpublished report of an epidemiological study conducted among a group of research workers with some unknown previous exposure to PCB. No sound basis has been established to support the contention that PCBs are human carcinogens. It is suggested that efforts be extended to accurately assess the clinical health of U.S. workers exposed to PCB.

2. In studies with rodents and subhuman primates the most sensitive target organ was usually found to be the liver. In these studies the dietary level which did not produce an effect on the liver was between 1 and 10 ppm. Based upon these studies the most probable toxic effect of excessive PCB exposure would be chronic hepatic injury

3. From the manner in which the document is put together it is impossible to tell if the recommended standard is based upon a logical scientific extrapolation of the information cited. Specifically, no attempt is made to relate the body burdens which would result from an industrial inhalation or dermal exposure to those obtained from animal experimentation or the usual data following oral administration.

   Chapter V consists of a series of data relating the toxic effects observed after many different types or routes of exposure. It then states that on the basis of all this data the environmental limit should be 0.05 mg/M^3 of PCBs in air. There is no logical support for the stated limit as based on the industrial usage this document is intended to relate. There has been no evidence shown to indicate that, as inferred on lines 4071-4072, "teratogenicity, fetotoxicity and carcinogenicity has occurred to man and to laboratory animals when they have been subjected to air-borne PCB levels below the current standard of 1.0 mg/M^3 (42% chlorine)."

4a. To be supportable a standard must be based on the application of a safety factor to experimental animal data and/or upon the utilization of previous work history exposure concentration and clinical worker monitoring data. Which of these was used in establishing this standard is not clear. Specifically, the limit of 0.05 mg/M^3 has not been supported by any data relating industrial worker exposure to clinical effects. In fact, the arrival of 0.05 mg/M^3 as a "safe" level has not been explained at all.

b. The document on line 3929 states that the current PCB standard is based on an 8-hour <u>dermal</u> exposure. This is not entirely correct.

The current standard does include a "skin notation" which refers to the potential contribution to the overall exposure by cutaneous route or particularly by direct skin contact. An environmental limit for air-borne material cannot totally prevent direct skin contact with material and the resulting dermal exposure. This concern has been aptly addressed by the ACGIH TLV committee on line 3925 by their reference to the fact that the current standard may not guarantee protection against dermal effects. The recommended environmental limit cannot guarantee such also since workers can still put unprotected hands in the material if they wish.

c. Inadequate information exists to properly evaluate the need for and type of protection for the pregnant worker.

d. Until better scientific evidence is brought forth supporting a necessary change in the current OSHA standard on PCBs, no justificatic exists for modifying the existing environment limit.

5. We recommend that the current users of PCBs, capacitor and transformer manufacturers, be consulted regarding feasibility of compliance.

6. To exclude biological monitoring in a standard for a material known to accumulate in fatty tissues would not appear advisable.

Biologic testing is an acceptable monitoring device if it is shown that a reasonable correlation exists between body burden, detrimental health effects, and degree of worker exposure. Biological monitoring may well give an indication of dermal exposure and degree of skin absorption that might not be evident through the use of air monitoring

7. We assume that if the composition of PCBs is unknown, the sample chromatogram does not match the chromatogram of any commercial PCB standard mixture. In this case, measurement by electron capture gas chromatography is inadequate for two reasons. First, interferences may be present which may account for the differences in the chromatograms. Secondly, as pointed out in Table I of the draft, electron capture detector response varies by orders of magnitude for different PCB isomers. Hence, the analyst would not know what response factor to apply, even using the weight factor technique of Webb & McCall (see attached comments for line 5354).

Therefore, when the PCB composition is unknown, a more specific and accurate technique must be used. We recommend using GC/MS in the selected ion monitoring mode as the detector device. The parent ion and a characteristic fragment ion are monitored for each PCB homolog. This technique is much less subject to interferences and is more accurate because MS response factors are nearly constant. GC/MS detection can be used with samples collected on Florisil if sensitivit is adequate. If sensitivity is inadequate, samples should be collecte on a porous polymer sorbent such as Tenax GC. Collected components are then thermally desorbed directly into the GC/MS for analysis.

8. In those cases where the sample chromatogram matches a standard PCB chromatogram, the sampling procedure is adequate. However, as mentioned in 7., we recommend sampling with Tenax GC as a more general method. Collected components can be thermally or solvent desorbed from Tenax GC. For further details, see pp 147-160 of the transcript of the Second NIOSH Solid Sorbents Roundtable in December, 1973.

9. No, several deficiencies should be corrected. See attached comments relative to lines 5252, 5253, 5258, 5273, 5291, 5292, 5303, 5310, and 5320 of the draft.

10a. We recommend collection on Tenax GC adsorbent, thermal desorption and measurement by GC/MS. See 7., 8., and attached notes.

b. See attached comments, especially the notes relevant to lines 5354, 5381, 5396, 5410, 5460, 5533, and 5590 of the draft.

11a. Annual comprehensive medical examinations are considered appropriate.

b. The medical requirements listed in the document under Section 2 are patterned after the criteria document on Tetrachloroethylene. It would seem that the medical tests for PCB exposured workers could be more specific for that particular material. Pulmanary function tests should be included as a check on capability of wearing respiratory protective devices.

Contrary to lines 202-203, medical surveillance should be made available to all workers occupationally "exposured" to PCBs who contact the material and yet not be "exposed" on the basis of the NIOSH definition given on lines 176-177.

12. There is no persuasive evidence supporting the "cancer suspect agent" labelling all PCBs, therefore such labelling is inappropriate. Warning signs should be posted in those areas in which workers are exposed above some specified limit or where potential skin contact is possible. To be functional a warning sign must inform the reader of specific effects of a material. PCBs have relatively mild irritant properties and has not been associated with acutely toxic effects. However, tissue accumulation and target organ effects may occur following prolonged exposures above the established permissible limits. A meaningful sign would warn of potential tissue PCB accumulation and indicate avoidance of skin and eye contact.

13. Considering that the concentration limits as listed in Table I-1 represent the protection factors as shown below, the limits are considered to be appropriate and consistent with the respirator decision logic used in the Standards Completion Project.

Along with the protection factor limits are listed various additional respirator types which should provide adequate protection when used in areas of respective air contaminant concentrations.

Concentrations of Polychlorinated Biphenyls	Respirator Type (Modifications to Table)
0.5 mg/M^3 or Less (10x)	3. Chemical cartridge respirator with replaceable cartridges approved for organic vapors and mists and half-mask facepiece.
	4. Gas mask, chin-style or front or back mounted organic vapor and mist cannister.

Concentrations of Polychlorinated Biphenyls cont'd.	Respirator Type (Modifications to Table) cont'd.
2.5 mg/M^3 or Less (50x)	3. A gas mask with a full facepie and front or back mounted vapc cannister with high efficiency filter.
5.0 mg/M^3 or Less (100x)	(No modification)
Greater than 5.0 mg/M^3 (100x)	(No modification)

14. Line 292: Detectable level is mentioned. Since the detectable limit of PCBs has not been addressed, this level is meaningless. It would make more sense to reduce air-borne concentrations of PCBs to below the (TWA) environmental limit or permissible exposure limit.

Lines 379 through 382 should be deleted since it seems unnecessary to have escape type devices available in all areas of "potential" exposure where the exposures might be brief at low or moderate levels. Escape type devices are generally made available in defined high risk areas containing potentially hazardous operations involving extremely toxic substances. The document does not provide data which supports PCBs as being considered extremely toxic.

Earlier comments addressed the modifications in Table I-1 on respirator types vs. concentration limits.

15. Line 405: Do hazards imply only health related hazards or environment hazards also?

In general, Section 5 provides adequate avenues for communicating work hazards to workers.

16. The work practices and control procedures are considered adequate for the protection of workers.

17. The recommended record retention period appears to be appropriate.

18. Additional research is needed in the following areas:

    a. Comparative data on the PCB body burden resulting from oral, dermal and inhalation exposures.

    b. Comparative metabolism studies of an homologous series in humans, non-human primates and rodents. These studies should include both a characterization of the metabolites formed and kinetic studies to determine the rates of mobilization and excretion.

    c. Clinical evaluation including liver function tests on industrial populations with previously documented PCB exposure.

    d. Epidemiological studies on major populations of PCB-exposed worker

19. Attached is a report compiled by Monsanto and distributed in November, 1975 to representatives of concerned governmental agencies, (NIOSH, OSHA, EPA, FDA, NCI, NIH) relating to histopathological evaluation of livers from rats treated with PCBs.

COMMENTS ON SAMPLING AND ANALYTICAL METHODS

Minor comments are on the original NIOSH draft.

General comments: In using trade names, the document should be consistent. Any shorthand such as dropping registration notation should be documented at the earliest opportunity and then a standard format adopted thereafter e.g. Aroclor ®
Florisil ®

Environmental Sampling and Analytical Methods

3714 ....evaluated under laboratory conditions using aerosol generation techniques. Field studies were also performed in a PCB environment containing aerosol and vapor components.

The statement as it stands leaves open the question of aerosol or vapor studies. The document should be completed by inclusion of this information in a manner similar to the above amended statement, and expressing the true nature of the exercise. Both aerosol and vapor concentrations must be included.

3724 -3726 Earlier in the text, 2 solvents are mentioned along with the use of single and multiple impingers.

Which solvent was used should be clarified (toluene or ethylene glycol) and the number of impingers.

The conclusions reached imply a study using an aerosol of PCBs or an equilibrated vapor environment. Is this true?

3737 to use when personal sampling for PCBs.

This circumvents other techniques such as area monitoring for calculating effective exposures.

3738 NIOSH has not tested all available solid sorbents (e.g. porous polymers). Hence, this line should be reworded to reflect only those methods tested.

3752 Electron capture gas chromatography is the most widely used method, but not necessarily the "preferred" method. For example, the wide variance in response factors referred to in Table I is a distinct disadvantage.

3801 -3803 In this day, it is not possible to eliminate a method based on the lack or expense of a computer. In many small companies, the OSHA requirements will rapidly force the purchase of such a unit for many applications.

3809 -3810 One might prefer NBS as a repository for "standard" samples.

3824 Perchlorination should definitely not be used to quantitate PCBs. We have confirmed that not only biphenyl, but also substituted biphenyls, cause large positive errors. At least one of the replacement fluids for PCBs in capacitors is a substituted biphenyl (Chemical and Engineering News, p. 25, Nov. 15, 1976). Hence this interference is already present in the manufacturing facility and precludes use of perchlorination. See attached copy of letter from J. Coleman Weber to Dr. I. E. Wallen.

ADM CC6360

3834 -3835 See comments on alternate standardization procedure, line 5354.

3843 -3845 See above comments on perchlorination.

APPENDIX I

5248 Samples collected must be representative of the personal exposure of individual workers.

5252 -5253 Records should include: Pump model & Serial no.
Sampling Tube type and no.
i.e. sampling equipment details

5258 -5260 Calibration data should also be recorded.

5266 -5268 The aim of sampling is to permit determination of the personal exposure level primarily. This leads to a decision on compliance/non-compliance situations. It cannot lead to the "lowest feasible level" without other major input beyond the scope of sampling and analysis.

5273 Airflow through the pump shall be controllable within ±5% of the desired rate during the entire sample period.

5291 A more frequent requirement for pump calibration is required. At least monthly and preferably in the method for a daily setup calibration.

5292 -5293 Spot-checked is an open statement and means nothing.
For digital readout pumps specify parity check between expected stroke count versus actual.
For pump with rotameters specify before and after readings. We would prefer a calibration after flow stabilization and again before pump is turned off, for each sample.

5303 The sorbent tube should not be vertical.
Pointing down - loses glass wool and Florisil
Pointing up - dust from overhead, hard hat, etc. enters.
Suggest a close to horizontal location, attached to the collar of the worker.

5304 Air being sampled should pass directly into the open inlet of the sorbent tube
This precludes filters.

5308 The recommended sample volume for this method is 50 liters (U.S. spelling)

5310 The sorbent tubes should be labelled. At this point it should reiterate checking label and I.D. Number.

5320 A bulk air sample is of no value unless the restraints required to obtain a good and recoverable sample are fully documented.

5324 Throughout Appendix II nomenclature for PCB and PCBs is confused. In general, PCBs should be used as a noun describing a PCB mixture, while PCB is an adjective.

5346 This reads more smoothly if written, "This would correspond to a detection limit of 40 ng ~~of~~ in 5 ml of desorbent".

5354 This alternate standardization procedure is of highly questionable utility. As pointed out in line 5358, it has not been evaluated in NIOSH laboratories. As correctly stated in the draft, the reason an alternate procedure is needed are two-fold. First, most of the GC peaks in a chromatogram of a PCB product contain more than one component. Secondly, electron capture detector response differs significantly for different PCB isomers (See Table I of the draft). These two factors indicate that the absolute quantity of PCB represented by a given peak containing unresolved components varies depending on the relative amounts of the components.

The relative composition of a given peak can vary for the following reasons:

1. PCBs with a given degree of chlorination (i.e. 42%) from different manufacturers contain different isomer ratios.

2. Component ratios vary for products with different degrees of chlorination. For example, from Table XII - 6, the ratio of dichloro- to trichlorobiphenyls for the peak with RRT 28 in Aroclor 1221 is 85:15. From Table XII - 8, the same peak in Aroclor 1242 has a ratio of 25:75. Similarly, for peak RRT 70 in Aroclor 1242 and 1254, the tetrachloro-to pentachlorobiphenyl ratios are 90:10 and 25:75.

3. Vapor pressure differences alter the composition of vaporized PCBs relative to the liquid. (See attached figure showing chromatograms of liquid and vapors from Aroclor 1016).

4. Interfering components may be present which distort the sample chromatogram. This is likely to be a major problem in capacitor and transformer manufacturing facilities because several of the PCB replacement products (i.e. phthalate esters and chlorobutyl-diphenyl ether) have similar GC retention times to PCBs and give an electron capture response.

   The weight factor technique of Webb and McCall does not adequately account for these difficulties.

   For those situations where the sample chromatogram closely matches the chromatogram of a reference PCB mixture, the Standard Analysis described in 5554 ff should be followed. However, if the chromatograms do not match, we believe the only satisfactory analytical method which will yield accurate results is gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring (SIM). The detection limit of this technique for Aroclor 1016 is about one nanogram of PCB injected into the instrument. Considering the environmental limit of 0.05 mg/m^3 recommended in this document, it might be possible to reach this lower detection limit for the total procedure by sampling as outlined in the draft, evaporating the hexane desorbent and analyzing the concentrate by GC/MS.

Alternatively, thermal desorption from a suitable solid sorbent directly into the GC/MS can be used. This well documented technique analyses the entire collected sample at once, rather than only an aliquot at a time. Response factors vary only slightly for different PCB isomers and most interferences are eliminated.

5381 The bulk sample must not be shipped in the same container as the sample tubes.

5396 The volume of air sampled can be measured to within at least ±5%. Delete next sentence.

5410 Delete 100% and conclude sentence with ".... recovered with a relative standard deviation of 4.4% for 27 spiked samples". Delete next sentence.

5460 Type of electron capture detector is not important.

5515 rinsing with pesticide grade acetone and hexane should follow the water rinses.

5533 Argon/methane is also a suitable GC carrier gas. The flow rate for either carrier gas should be only about 30 ml/min for a 2 mm id column.

5590 Actual retention times should be used in calculations if available. If not available, then the measurements described here can be used.

6118 The vapor pressures in Table XIII - 5 appear to be too high. What is the source of these data, and has their accuracy been verified?

March 15, 1976

Dr. I. E. Wallen
Environmental Protection Agency
Office of Toxic Substances
401 M Street S.W.
Washington, DC 20460

Dear Dr. Wallen:

Monsanto has a concern over the validity of the perchlorination technique used by EPA and others to measure and/or confirm polychlorinated biphenyls in environmental materials.

In our investigation of the perchlorination method, we have found that such chemicals as biphenyl, alkylated biphenyl, and many other substituted biphenyls, interfere with the perchlorination technique. It also appears that various petroleum components may interfere. If these chemicals were present in environmental materials that were being tested for PCB's using the perchlorination method, erroneously high PCB concentrations would be reported.

A recent article in the Journal of the AOAC (Vol.58, No.3, 1975) points out two other limitations of the perchlorination procedure:

1. High and variable reagent blanks, which cause erroneously high findings.

2. Formation of bromononachlorobiphenyl, which causes low recoveries.

A copy of the article is attached.

ADM CCE364

Since these limitations can lead to significant errors in determining trace levels of PCB's in environmental samples, we suggest that EPA carefully review the validity of the perchlorination technique. Results that have been obtained using this technique may not be valid.

If any other information is needed, please let us know.

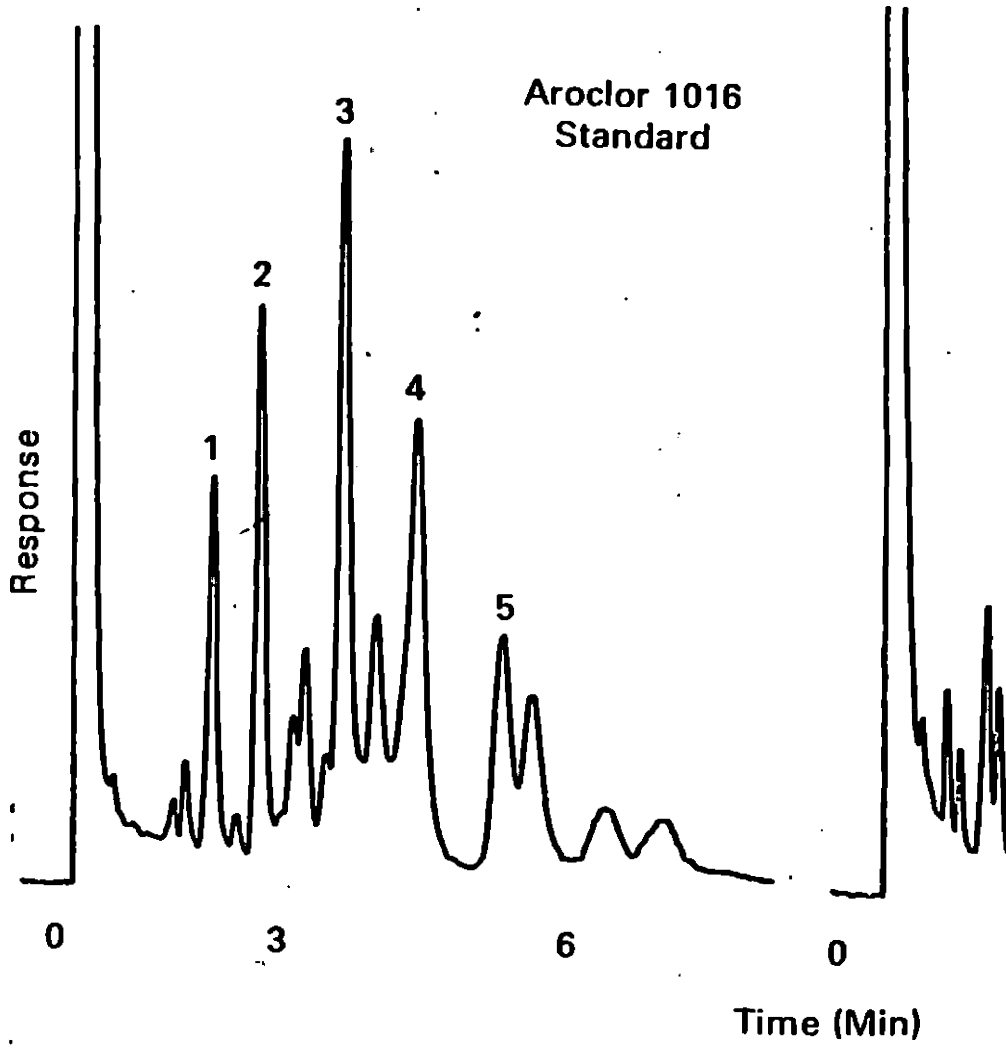
Sincerely,

J. Coleman Weber
Manager, Product Acceptability

mah

cc: Dr. A. C. Trakowski
Environmental Protection Agency

bcc: W. C. Hammann - T3A
R. E. Keller - T1B
J. P. Micure - T2F
D. Wood - B2SC
K. W. Easley - Washington 1920
R. G. Kaley - T2F



ACM CC6366

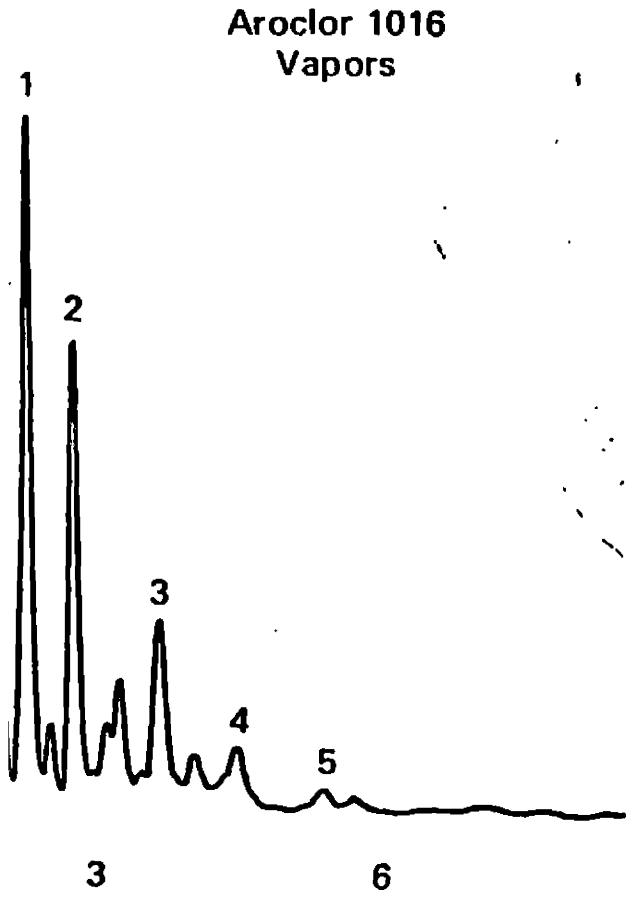


Figure 7

Monsanto

File-EPA DEC 7 1976

SPECIALTY CHEMICALS DIVISION

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

December 6, 1976

Mr. Thomas Kopp
Environmental Protection Agency
Office of Toxic Substances
401 M Street, S.W.
Washington, D.C. 20460

Dear Mr. Kopp:

Enclosed are the first thru third quarter production and sales figures for Monsanto's Aroclor products which you requested.

Sincerely,

J. Coleman Weber
Manager
Product Acceptability

mg

Enclosure

bcc: K. W. Easley
C. Paton
R. A. Stohr
D. Wood

ACM 008367

PLAINTIFF'S EXHIBIT 915

MONSANTO INDUSTRIAL CHEMICALS COMPANY
PCB MANUFACTURE AND SALES
(THOUSANDS OF POUNDS)

	1Q	2Q	YTD	3Q	YTD	4Q	YTD
US PRODUCTION	10645	6261	16906	5691	22597		
SALES[1]							
DOMESTIC	6955	5991	12946	5202	18148		
EXPORT	1383	960	2343	1062	3405		
TOTAL	8338	6951	15289	6264	21553		
DOMESTIC SALES BY PCB GRADE							
Aroclor 1221	4	15	19	--	19		
Aroclor 1242	1376	732	2108	862	2970		
Aroclor 1254	476	396	872	377	1249		
Aroclor 1016	5099	4848	9947	3963	13910		
Total	6955	5991	12946	5202	18148		

ADM CCE366

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OCT 17 1975

OFFICE OF ENFORCEMENT

Monsanto Industrial Chemicals Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

OCT 22 1975

Gentlemen:

Recent governmental sampling data indicate the presence of Polychlorinated Biphenyls (PCBs) and comparable chemical substances in the air, in water bodies, and in fish in several areas of the country. In order to determine the nature and extent of the possible adverse effects resulting from the presence of PCB compounds in the environment, the Environmental Protection Agency (EPA), in cooperation with other federal and State agencies, is attempting to determine the sources and amounts of PCBs entering the environment. It is important that this effort be carried out without delay.

It is our understanding that your company handles PCB compounds or mixtures or comparable chemical substances in its operations. I am therefore requesting, pursuant to the authority provided by Section 308 of the Federal Water Pollution Control Act, as amended, 33 U.S.C. 1318, and Section 114 of the Clean Air Act, as amended, 42 U.S.C. 1857c-9, that your company furnish EPA with information pertaining to your use and handling of PCBs and comparable chemical substances. In addition to a general description, which should include information as to sources, quantities, uses, and ultimate disposition, you should respond in detail to the enclosed questions. If any question is not applicable to your company or operations, please so indicate by responding "not applicable."

The information requested herein must be provided notwithstanding its possible characterization as confidential information or trade secrets. Should you so request, however, any information (other than effluent or emission data) which the Administrator of this Agency determines to constitute methods or processes entitled to protection as trade secrets will be maintained as confidential, pursuant to procedures specified in 40 CFR Part 2.

ACM CC63C9

PLAINTIFF'S EXHIBIT 916

Within 14 days of receipt of this letter, your company must provide all information concerning your current status and activities and covering the twelve month period immediately preceding receipt of this letter.

Within 30 days following receipt of this letter, your company must provide all information for all of the prior years indicated.

The information required herein should be sent directly to the address indicated below. If you have any questions you may call the person indicated below or Mr. Blake A. Biles of our office at (202) 755-0731.

We appreciate your prompt cooperation in this matter.

Sincerely yours,

Stanley W. Legro
Assistant Administrator
for Enforcement

Enclosure

Regional Contact:
Mr. Earl J. Stepuemoh
Director, Enforcement Division
Environmental Protection Agency
1735 Baltimore
Kansas City, Missouri 64108
Telephone: (816) 374-2576

POLYCHLORINATED BIPHENYL (PCB) COMPOUNDS OR MIXTURES

Within 14 days of receipt of this letter, your company must provide all information concerning your current status and activities and covering the twelve month period immediately preceding receipt of this letter.

Within 30 days following receipt of this letter, your company must provide all information for all of the prior years indicated.

FOR PURPOSES OF THIS LETTER, THE PHRASE "PCB COMPOUND OR MIXTURE" INCLUDES ALL CHEMICAL SUBSTANCES KNOWN OR BELIEVED BY YOU TO BE PCB COMPOUNDS OR MIXTURES OR OF A SIMILAR CHEMICAL NATURE, IRRESPECTIVE OF TRADE NAME, AND SPECIFICALLY INCLUDING CHLORINATED TERPHENYLS.

1. For each PCB compound or mixture produced or imported by your company, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. The total amount of each PCB compound or mixture produced or imported.

   b. The name and address of each of your company's facilities which handle PCB compounds or mixtures (including production facilities and wholesale and retail outlets), and the amount of each PCB compound or mixture distributed through each facility.

   c. The name and address of each customer of each PCB compound or mixture, the amount of each PCB compound or mixture obtained by each customer from each facility, and each customer's delivery point(s) for the receipt of each PCB compound or mixture.

2. For each PCB compound or mixture incorporated by your company into its products, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. A description of each product.

   b. For each product the total amount incorporated of each PCB compound or mixture.

2. (continued)

   c. For each product the name and address of each source from which your company obtained each PCB compound or mixture, and the amount of each PCB compound or mixture obtained from each source.

   d. The name and address of each of your company's facilities which handle such products (including production facilities and wholesale and retail outlets), and the amount of each product distributed through each facility.

   e. The name and address of each customer of each product, and the amount of each product obtained by each customer from each facility. For consumer products list only the total production of each product at each facility and the total number of customers. Do not provide the name and address of each customer of consumer products.

3. For each PCB compound or mixture used by your company in its operations other than for incorporation into its products, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. A description of each use.

   b. For each use the total amount of each PCB compound or mixture.

   c. For each use the name and address of each source from which your company obtained each PCB compound or mixture, and the amount of each PCB compound or mixture obtained from each source.

4. For each PCB compound or mixture reclaimed by your company, for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

   a. A description of each method of reclamation.

   b. For each method of reclamation, the total amount of each PCB compound or mixture reclaimed.

   c. The total amount of each PCB compound or mixture reclaimed.

d. The name and address of each source from which your company obtained PCB compounds or mixtures, and the amount of each PCB compound or mixture obtained from each source.

e. For each method of reclamation, the location of every reclamation site, the name and address of each party involved in the reclamation of each PCB compound or mixture, and the amount of each PCB compound or mixture reclaimed by each party.

5. For each PCB compound or mixture disposed of by your company (with or without the involvement of other parties), for each company facility, during each year of 1971, 1972, 1973, 1974, and the first two quarters of 1975:

Keurig Records

a. A description of each method of disposal.

b. For each method of disposal the total amount of each PCB compound or mixture disposed.

c. The total amount of each PCB compound or mixture disposed.

d. The name and address of each source from which your company obtained PCB compounds or mixtures, and the amount of each PCB compound or mixture obtained from each source.

Difficult x

e. For each method of disposal, the location of every disposal site, the name and address of each party involved in the disposal of each PCB compound or mixture, and the amount of each PCB compound or mixture disposed of by each party.

6. The composition by chemical name and percent by weight of each PCB compound or mixture produced, imported, sold, reclaimed, used, and/or disposed of by your company since January 1, 1971.

7. The results of any and all sampling and analysis performed by your company, its agents or contractors since January 1, 1971, concerning the following:

a. Concentrations of PCB compounds or mixtures in the effluent of any discharges by the company (into waters of the United States or Publicly Owned Treatment Works) or in the emissions of the company into the air.

b. The flow and/or composition of any discharges or emissions by the company (into waters of the United States or Publicly Owned Treatment Works, or into the air) which contain PCB compounds or mixtures.

c. Concentrations of PCB compounds or mixtures in receiving waters (both upstream and downstream) of any discharges by the company which contain PCB compounds or mixtures and concentrations of PCB compounds or mixtures in the air in the area of the company.

8. The methods by which PCB compounds or mixtures are transported to, by, and/or from your company, including:

a. A description of each method of transportation, and the form in which PCB compounds or mixtures are transported by each method. Where different methods of transportation are used at different facilities specify which transportation method is used at each facility.

b. The names and addresses of all known transportors of PCB compounds or mixtures.

9. All occasions (including spills) of which you are aware on which PCB compounds or mixtures have or may have been introduced into the environment. In particular, describe such occasions insofar as they involved PCB compounds or mixtures in their liquid state, as incorporated into closed systems, or as incorporated into open systems. For each occasion, indicate name and address of party involved; dates, time, and location of the discharge or spill; and the amounts involved.

10. A description of any adverse health or environmental effects which you know or believe to have resulted from the introduction of PCB compounds or mixtures into the environment. Indicate any specific occasions including dates, times, locations, amounts, and parties involved for which such effects are known.

11. Any and all other information which you possess concerning:

a. The production, importation, reclamation, use, distribution, and disposal of PCB compounds or mixtures.

b. The discharge of PCB compounds or mixtures into the environment.

In addition to the above, EPA would appreciate receiving any other information which you possess concerning the distribution and discharge of PCB compounds or mixtures by sources other than your company, including your company's customers and sources.

Copy to Mr. Bissell, 8-11-75
Per Request

bcc: Mr. H. H. Bible AUG 11 '75

8 August 1975

Mr. Stanley W. Legro
Assistant Administrator
for Enforcement
Environmental Protection Agency
Room 1111 - West Tower
EG-329
4th and M Streets, N.W.
Washington, D. C. 20460

Dear Mr. Legro:

In accordance with your request of yesterday and in the national interest, I violate our and industry's usual practice by handing you herewith a copy of Monsanto's present customer list with respect to its sale of PCBs.

As I indicated in our two telephone conversations, Monsanto, about three years ago, voluntarily cut back its production of PCBs and terminated its sales of such products to all except those who 1) could satisfy us that they are using PCBs in closed systems and 2) either executed indemnification agreements in favor of Monsanto or obtained liability insurance satisfactory to Monsanto. The last page of the list, which sets forth four company names, has to do with those customers whose insurance has expired and, therefore, are not now able to buy PCBs from Monsanto, but who presumably will be able to satisfy Monsanto's insurance requirements and resume purchases sometime in the future.

Because we do not believe it appropriate to reveal details concerning customers of products which we make and sell, we are particularly sensitive to the transmission of this customer list. We, therefore, request that it be handled with care and not used with the media or in any other fashion that might identify it with Monsanto or cause the company any type of embarrassment.

Sincerely,

Edwin J. Putzell, Jr.

ALM CC837c

bcc: H. S. Bergen - B2SL
C. P. Cunningham - B2SA
W. B. Papageorge - B2NF

March 3, 1972

Mr. Paul DeFalco, Jr.
Regional Administrator
U.S. Environmental Protection Agency
Region IX
100 California Street
San Francisco, California 94111

Dear Mr. DeFalco:

I have been asked to respond to your letter addressed to Mr. E. J. Bock, asking for certain information regarding sales of polychlorinated biphenyls by Monsanto and Central Solvents and Chemicals in the Los Angeles County area. I know that you have discussed this by telephone with Mr. W. B. Papageorge and I have reviewed the situation with him.

It has always been Monsanto's policy not to divulge the names of our customers for the products we make, nor the quantities of products these customers purchase. We consider this to be proprietary information and therefore hold it confidential. Consequently we do not feel free to comply with your request for data on customer names and quantities purchased.

On the other hand, last November we did release to governmental agencies, including the EPA, Monsanto's total production and sales figures on PCB's for the years 1960 through 1971. These statistics have been released publicly and earlier this year we discussed them in detail with members of the scientific

ACM CC8377

PLAINTIFF'S EXHIBIT 918

community and with representatives of the Washington multi-agency PCB task force of which EPA is a member. For your ready reference I am enclosing a copy of this information.

We certainly share your concern and desire to control the discharge of PCB's into the environment. It is because of this concern that we implemented a program of self-imposed curtailment of sales of these products so that now we are only offering continuing supplies for closed system dielectric applications where the potential danger of environmental contamination is carefully controlled.

Furthermore, as another step in safeguarding the environment we have informed all customers of PCB materials of the potential dangers should these materials escape and have strongly urged them to take every precaution to prevent losses through spills, usage, leakage, disposal, vaporization or otherwise.

I regret we cannot comply with your request for customer information but if we can be of assistance to you in other ways we will be glad to visit you or your designees to discuss the PCB situation further.

Sincerely,

W. R. Corey, Director
Functional Product Groups

/jf

Enclosure

cc: Mr. Charles H. Sommer/Monsanto

NEWS

Monsanto

FOR RELEASE
IMMEDIATELY 1971

MONSANTO INDUSTRIAL CHEMICALS COMPANY

E. V. John
PUBLIC RELATIONS DEPARTMENT
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
(314) 694-2891
(314) 567-3628 (Home)

MONSANTO RELEASES PCB PRODUCTION FIGURES TO DEPARTMENT OF COMMERCE

WASHINGTON, D.C., Nov. 30 -- Monsanto Company announced today it has released figures to the United States Department of Commerce showing the company's U.S. production and sales of polychlorinated biphenyl (PCB) from 1960 through estimated 1971.

Closed-system electrical uses ranged from 11,000 tons per year to 20,000 tons per year during the period.

The report also shows Monsanto voluntarily reduced its nonelectrical sales of PCB from the high of 16,000 tons in 1970 to 4,400 tons in 1971. Substantial further reduction will be accomplished in 1972, the company said.

C. P. Cunningham, managing director of Monsanto Industrial Chemicals Co., an operating unit of Monsanto, said, "As part of our control program, the data were originally prepared for the Federal PCB Joint Task Force and other concerned scientists for use on a confidential basis so scientists can properly evaluate the figures and relate them as to impact on the environment."

-more-

Monsanto has now chosen to release the figures publicly "because scientists have continued to express a need for the data to make a proper estimate of how much PCB might be in the environment. We also believe the figures will inform the public about Monsanto's positive actions to limit the sale of PCB to confined applications," the company executive said.

"Now that the figures are public information," Cunningham added, "we are confident both the scientific community and the public press will interpret the data properly. These are production and sales figures only. It should be clearly understood that all this material is not in the environment.

"For example," Cunningham said, "over 60 per cent of all sales in the past 12 years have been for closed-system electrical uses. It would be a completely false and irresponsible conclusion to say all PCB produced is in the environment. Much of the material is still contained in sealed electrical equipment where it acts as a fire-resistant safety fluid, protecting human lives and property from the danger of fire and explosion."

-more-

- Cunningham concluded, "Monsanto continues its program to control the uses and prevent the release of PCB into the environment. To-date, we have cut off all sales to paints, plasticizers, sealants, adhesives and all other open-system uses. We are receiving used PCB from customers for regeneration or safe disposal. And we are engaged in an all-out research effort to develop less persistent forms of PCB or suitable products which retain the fire safety features of PCB. We call on other producers, worldwide, to join in this effort."

-oOo-

NOTE TO EDITORS: PCB production and sales figures attached.

PRODUCTION AND SALES
POLYCHLORINATED BIPHENYLS (PCB)
MONSANTO INDUSTRIAL CHEMICALS COMPANY
(SHORT TONS)

YEAR	U.S. PRODUCTION	DOMESTIC SALES		U.S. EXPORT SALES
		Electrical* Insulating Liquids Uses	All** Other Uses	All Uses
1971 (Est)	20236	14417	4401	4938
1970	42527	20268	16263	6826
1969	38194	18564	15034	5312
1968	41427	20568	11990	5616
1967	37655	20387	10846	4062
1966	32925	18897	10642	3426
1965	30240	16203	9695	2117
1964	25417	13769	8666	2048
1963	22367	11448	7618	1824
1962	20986	11683	7339	1809
1961	20333	11108	7661	2076
1960	20786	12444	5163	1827

* Closed Systems - Transformers and Capacitors

** Including Heat-transfer Systems, Hydraulics/Lubricants, Plasticizers

ACM CC8382

PCB MANUFACTURE AND SALES
MONSANTO INDUSTRIAL CHEMICALS COMPANY
1957 Thru 1964
(Thousands of Pounds)

	1957	1958	1959	1960	1961	1962	1963	1964
U.S.PRODUCTION	(1)	(1)	(1)	37919	36515	38353	44734	50833
DOMESTIC SALES (LBS.)	32299	26061	31310	35214	37538	38043	38132	44869
U.S. EXPORT SALES	(2)	(2)	(2)	(2)	(2)	(2)	3647	4096
DOMESTIC SALES BY CATEGORY								
Heat Transfer	-	-	-	-	-	157	582	929
Hydraulics/Lubricants	1612	1549	2685	2523	4110	3915	3945	4374
Misc. Industrial	704	755	1569	1559	2114	1681	1528	1692
Transformer	12955	5719	5984	7921	6281	7984	7290	7997
Capacitor	17028	14099	16499	16967	15935	15382	15606	19540
Plasticizer Applications	(1)	3939	4573	6244	9098	8924	9181	10337
Petroleum Additives	-	-	-	-	-	-	-	-
DOMESTIC SALES BY PCB GRADE								
Aroclor 1221	23	16	254	103	94	140	361	596
Aroclor 1232	196	113	240	155	241	224	13	13
Aroclor 1242	18222	10444	13598	18196	19827	20654	18510	23571
Aroclor 1248	1779	2559	3384	2827	4023	3463	5013	5238
Aroclor 1254	4461	6691	6754	6088	6294	6325	5911	6280
Aroclor 1260	7587	5982	6619	7330	6540	6595	7626	8535
Aroclor 1262	31	184	359	326	361	432	414	446
Aroclor 1268	-	72	102	189	158	210	284	190
Aroclor 1016	-	-	-	-	-	-	-	-

(1) Production figures and Plasticizer Applications figures unavailable during year indicated.
(2) U.S. Export Sales figures unavailable during year indicated.

ACW CC83E3

PCB MANUFACTURE AND SALES
MONSANTO INDUSTRIAL CHEMICALS COMPANY
1965 Thru 1971 + 1972 Estimate
(Thousands of Pounds)

	1965	1966	1967	1968	1969	1970	1971	Est. 1972
U.S.PRODUCTION	60480	65849	75309	82854	76387	85054	34994	
DOMESTIC SALES (LBS.)	51796	59078	62466	65116	67194	73061	34301	
U.S. EXPORT SALES	4234	6852	8124	11231	10624	13651		
DOMESTIC SALES BY CATEGORY								
Heat Transfer	1237	1766	2262	2529	3050	3958	3060	0
Hydraulics/Lubricants	4616	4258	4643	5765	8039	7403	1552	0
Misc. Industrial	1841	1779	1426	1283	1079	1627	1155	0
Transformer	8657	8910	11071	11585	12105	13828	11134	(25000 to 30000
Capacitor	23749	28884	29703	29550	25022	26708	14141	(total dielectri
Plasticizer Applications	11696	13481	13361	14404	16460	19537	3259	0
Petroleum Additives	-	-	-	-	1439	-	-	0
DOMESTIC SALES BY PCB GRADE								
Aroclor 1221	369	528	442	136	507	1476	2215	300
Aroclor 1232	7	16	25	90	273	260	171	300
Aroclor 1242	31533	39557	43055	44853	45491	48588	21981	4000
Aroclor 1248	5565	5015	4704	4894	5650	4073	213	0
Aroclor 1254	7737	7035	6696	8891	9822	12421	4661	6000
Aroclor 1260	5831	5875	6417	5252	4439	4890	1725	600
Aroclor 1262	558	768	840	720	712	1023	1	0
Aroclor 1268	196	284	287	280	300	330	-	0
Aroclor 1016	-	-	-	-	-	-	3334	17000

AUM CCE384

AROCLOR APPLICATIONS

CURRENT USES

Electrical Capacitors: Aroclor 1016*, the major product used; Aroclor 1221; Aroclor 1254; very limited usage.

Electrical Transformers: Aroclor 1242; Aroclor 1254; Aroclor 1260.

* Similar to Aroclor 1242 with 5 chlorine and higher isomers removed.

FORMER USES

Electrical Capacitors: Aroclor 1242; Aroclor 1254.

Electrical Transformers: Aroclor 1242; Aroclor 1254; Aroclor 1260.

Heat Transfer Systems: Aroclor 1242; Aroclor 1248; Aroclor 1254.

Vacuum Pumps: Aroclor 1248; Aroclor 1254.

Gas Transmission Turbines: Aroclor 1232; Aroclor 1242.

Hydraulic Fluids: Aroclor 1232; Aroclor 1242; Aroclor 1248; Aroclor 1254; Aroclor 1260.

Plasticizers in Synthetic Resins: Aroclor 1248; Aroclor 1254; Aroclor 1260; Aroclor 1262; Aroclor 1268.

In Adhesives: Aroclor 1221; Aroclor 1232; Aroclor 1242; Aroclor 1248; Aroclor 1254.

In Surface Coatings: Aroclor 1221; Aroclor 1248; Aroclor 1254; Aroclor 1260; Aroclor 1262.

AROCLOR APPLICATIONS

FORMER USES Continued

Plasticizer in Rubbers: Aroclor 1221; Aroclor 1232; Aroclor 1242; Aroclor 1248; Aroclor 1254; Aroclor 1260.

Wax Extenders: Aroclor 1242; Aroclor 1254; Aroclor 1268.

Dedusting Agents: Aroclor 1254; Aroclor 1260.

Pesticide Extenders: Aroclor 1254.

Lubricants, Cutting Oils: Aroclor 1254.

Carbonless Reproducing Paper: Aroclor 1242.

Inks: Aroclor 1254.

ACM CC8386

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
REGION IX
100 CALIFORNIA STREET
SAN FRANCISCO, CALIFORNIA 94111

Mr. E.J. Bock
President and Chief Executive Officer
Monsanto Company
800 N. Lindbergh
St. Louis, Missouri 63166

Dear Mr. Bock:

Information available to this office indicates that quantities of polychlorinated biphenyls are being discharged to the Pacific Ocean via the Los Angeles County Sanitation District's sewerage system. In order to take steps to bring about a reduction in this discharge, it is necessary that the points of entry of this material into the sewerage system be determined.

To assist us in making that determination, it is requested that you provide us with the following information:

1. A list of all shipments of polychlorinated biphenyls by Monsanto to Los Angeles County, California within the past eighteen (18) months with the name and address of each addressee as well as the quantity delivered.

2. A similar listing of all sales of polychlorinated biphenyls made by the Central Solvents and Chemicals Company, Los Angeles, California.

We would hope to hear from you in this regard within the next two weeks. Your cooperation in responding to this request will be appreciated.

Sincerely,

Paul De Falco, Jr.
Regional Administrator

PLAINTIFF'S EXHIBIT 919

Copy for Bob Gale

July 1, 1977

Ms. Kaye Jacobs
Attorney
United States Environmental
Protection Agency
Region V
230 S. Dearborn Street
Fourteenth Floor
Chicago, Illinois 60604

Re: Letter Request for Information, Dale S. Bryson to John R. Eck, June 6, 1977

Dear Ms. Jacobs:

In the above referenced letter the U. S. EPA asked for certain information concerning operations at Monsanto's William G. Krummrich Plant, located at Sauget, Illinois. This letter was subsequently discussed and clarified during our telephone conversation June 21, 1977. The information contained herein is provided to you in response to said letter and discussion.

Beginning July 1, 1977 for a period of six months we will monitor the incinerator discharge and the combined discharge, taking a 24-hour vertically integrated composite sample once a week at each location.

A substantial rehabilitation project is underway concerning the plant's sewer system. A description of this project is as follows.

> The main operation area of the plant occupies an area of approximately 100 acres. All effluent discharges from the plant operating departments and facilities are discharged into a complex network of sewer systems. This sewer system drains approximately 140 acres. A map of the plant premises and sewer system is attached.

The plant sewer effluents are collected into small service sewers, transferred to larger laterals, and then finally discharged into three large trunk lines which are part of the Village of Sauget sewer system. Wastes from the entire Village of Sauget flow to the Village of Sauget Treatment Plant, and after treatment are discharged to the Mississippi River. Both domestic and industrial sewage are handled by this system.

The attached map divides the plant into five main areas of drainage. Areas 3 and 4 are the main operating areas of the plant. An examination of the sewer system indicated that the sewers servicing area 3 were deteriorated and in need of replacement or repair. Accordingly a major project was initiated to perform the necessary repairs or replacement of this system. No major leaks, failures or deterioration were discovered in the sewers servicing areas 1, 2, 4 and 5.

The rehabilitation project replaces the existing trunk sewer for section 3 by extending two existing sewers northward along "G" and "E" streets plus the installation of a new sewer along "D" street. The existing usable sewer lines will be tied into the new system. Sewer lines being replaced will either be excavated and removed, or filled with grout and abandoned in place.

The old sewers which are being replaced are shown in light blue on the attached drawing, with the new sewers shown in red.

New sewer piping will be one of these three types:

a. Ductile iron soil pipe, schedule 40

b. Reinforced concrete culvert

c. Vitrified clay pipe with a reinforced concrete encasement. All joints will be sealed with furan resin and poured sulfur.

New manholes will be acid proof brick lined, with an average box depth of 11 feet below grade.

The project will include installation of approximately 2,475 feet of vitrified clay pipe, sizes 6" diameter through 36" diameter; 230 feet of ductile iron sewer

pipe, 4" through 12" diameter; and 600 feet of reinforced concrete culvert. Additionally, repairs will be made to other existing sewer lines as necessary to upgrade the entire system to "like new" condition. Nineteen new manholes will be constructed, and several existing manholes will be repaired. Total cost of the project is estimated to be $2,450,000. Work commenced in January, 1977, and is expected to be completed by December, 1977.

This project does not directly affect the sewer system servicing the Monsanto PCB production facility, located in Area 4 on the attached map. Effluent from this facility flows south on the map across Area 4, and then west in a 24" trunk line leaving the plant and flowing into the Village of Sauget sewer system. As far as we are aware, these sewers have no major leaks or failure points and are adequate for present and future use. The sewers within the PCB manufacturing area will be disconnected and sealed off as part of the PCB shutdown program.

The above referenced letter requested information concerning the total amount of PCBs currently being stored on site, plans for distribution of any PCBs not distributed by October 31, 1977, and disposition of PCB contaminated equipment. As I pointed out to you during our discussion, the EPA Office of Toxic Substances will be promulgating regulations in the near future on the handling and disposal of PCBs. We will, of course, comply with those regulations.

At this time the amount of waste PCB awaiting incineration at the plant varies from around 1,000,000 to 1,500,000 pounds. It is contained in storage tanks at the incineration location. The amount of PCB product inventory on hand averages around 1,500,000 pounds. It is contained in storage tanks in the production department and in tank cars. Some drum inventory of product is maintained in protected indoor warehouses. We plan to incinerate any PCBs which have not been distributed on or before October 31, 1977.

As mentioned during our discussion, we plan to deal in an orderly manner with equipment which has been used in the production and handling of PCB. Such equipment which can be adequately cleaned will be reused internally for industrial type chemicals. Nonreusable equipment, including all remaining

processing equipment and piping, will be drained thoroughly to remove PCBs. Liquids will be incinerated. All equipment will be sealed and buried in an approved landfill.

After all equipment has been removed, the production site will be cleared to approximately one foot below grade level. Sewers will be disconnected and sealed off. All contaminated rubble will be removed to an approved landfill for proper disposal.

All washings used in the decontamination will be treated to remove PCB and/or will be incinerated.

In summary, we plan to proceed in an orderly and environmentally sound manner in closing down our PCB operations. We hope that the information provided above satisfactorily responds to your questions. Please direct any further inquiries on this subject to me at the above address.

Yours very truly,

Phocion S. Park
Environmental Counsel

jf

Enclosure

bcc: R. E. Bilger
J. R. Eck
R. W. Flint
R. L. Harness
A. E. Leisy
J. W. Molloy
M. A. Pierle

ALM CCt44C

bcc: [redacted]
W. B. Papageorge
W. R. Richard
R. H. Munch
D. Wood
H. S. Bergen

May 12, 1975

Dr. Leonard J. Guarria
USEPA
Waterside Mall, East Tower
401 M Street, S.W.
Washington, D.C. 20460

Dear Dr. Guarria:

We want to thank you for allowing Mr. Papageorge and I to present our comments on the March 13 version of the PCB criteria document for the Toxic Pollutant Effluent Standards. We enjoyed our discussions with you and Mr. Lewis and look forward to a continuing exchange of pertinent information.

On my return to St. Louis I learned that two of our papers on biodegradation of polychlorinated biphenyls have recently been accepted for publication. For your information the titles of these articles and journals in which they will appear are as follows:

1. "Degradation of Polychlorinated Biphenyls by Micro-Organisms" by Baxter, et al, Science of the Total Environment.

2. "Activated Sludge Biodegradation of Polychlorinated Biphenyls", by Tucker, et al, Bulletin of Environmental Contamination and Toxicology, Volume 14, Issue #6.

The first reference is the same as the draft we left with you during our visit. The second is a compilation of data previously supplied to Mr. Lewis describing our semi-continuous activated sludge studies.

We will continue to keep you informed of any new developments from our laboratories regarding the environmental significance of PCBs.

Sincerely yours,

James P. Mieure

Dr. James P. Mieure
Research Group Leader

db

PLAINTIFF'S EXHIBIT 921

ACM 008441

bcc M. A. Pierle
P. S. Park
A. E. Leisy - 1740
C. F. Buckley - 1740

June 14, 1976

Mr. Blake Biles
Enforcement Division (EN-342)
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Dear Mr. Biles:

This is in response to Mr. Stanley Legro's letter of May 29, 1976 concerning the EPA inspection report of our W. G. Krummrich plant.

We have examined the data enclosed with Mr. Legro's letter and find an error in the calculations used to determine the air losses from storage tank emissions. The vapor pressure of Aroclor 1242 is 0.35mm at 100°C, not 3mm at 100°C as used in the report. This means that the correct storage tank emissions should be 70.6 Kg/year, not 597.4 Kg/year. These corrections apply to pages number 509 and 548.

The other information present appears to be correct.

Sincerely,

J. Coleman Weber
Manager
Product Acceptability

cs

cc S. W. Legro

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

29 MAY 1978

OFFICE OF ENFORCEMENT

JUN 4 1978

Mr. W. B. Papageorge
Manager, Product Acceptability
Process Chemicals Division
Monsanto Industrial Chemical Co.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Dear Mr. Papageorge:

An Environmental Protection Agency (EPA) inspection team recently visited a facility operated by your company to obtain information concerning the handling of PCB materials. The inspection was conducted under authority of section 308 of the Federal Water Pollution Control Act (FWPCA), as amended, 33 U.S.C. 1318, and section 114 of the Clear Air Act, as amended, 42 U.S.C. 1857C-9. Enclosed is a copy of the plant visit report prepared by the inspection team which records its findings with regard to the handling of PCB materials at your facility.

It is possible that EPA will receive public requests for release of the information contained in the enclosed report. Such requests will be handled by EPA in accordance with provisions of the Freedom of Information Act (FOIA), 5 U.S.C. 552, and EPA regulations issued thereunder, 40 CFR Part 2. EPA is required to make this inspection report available in response to FOIA requests unless the Administrator of this Agency determines that the report contains information characterized as confidential commercial information or methods and processes entitled to protection as trade secrets. Pursuant to the FWPCA and the Clean Air Act, effluent and emission data may not be considered confidential information or trade secrets subject to exemption from mandatory disclosure requirements of the FOIA.

ACM CC8365

PLAINTIFF'S EXHIBIT 923

In order to facilitate the Agency's timely response to any public inquiries, while giving due consideration to your company's right to request confidentiality, please provide the following information:

1. Notice of any factual inaccuracies that you find in the report which you believe should be corrected. Although the report itself cannot be altered or modified in responding to FOIA requests, we would appreciate your comments concerning any facts which you believe to have been recorded inaccurately.

2. Any information, except effluent and emission data, contained in the report which you believe to be commercial confidential information or trade secrets entitled to exemption from the mandatory disclosure requirements of the FOIA.

Your comments should be addressed to Mr. Blake Biles, Enforcement Division (EN-342), Environmental Protection Agency, 401 M Street, S. W., Washington, D. C. 20460, and should reach this address not later than 14 days after your receipt of this letter. Failure by your firm to submit within that period of time a written request that information be characterized as confidential or privileged will be treated by EPA as a waiver by your company of any claims for confidentiality regarding information contained in the PCB investigation report.

Thank you for your cooperation in responding to our inquiries concerning PCBs.

Sincerely yours,

Stanley W. Legro
Assistant Administrator
for Enforcement

Enclosures

ACM CC8390

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

5

SUBJECT: PCB Inspection, Monsanto Krummrich Plant, Sauget, Illinois. DATE: March 9, 1

FROM: Chief, Air Surveillance Branch, Surveillance and Analysis Division

TO: Karl Bremer, Member, Lake Michigan Toxic Substances Committee

A preliminary survey was made of the above installation to identify and sample point sources of potential PCB emissions to the atmosphere. The sampling and analysis were carried out at this source to furnish information to arrive at a further decision that may require an intensiv testing program to quantify the PCB emissions. The sample analysis revealed the following:

SAMPLING LOCATION	NO. OF SAMPLES	PCB CONCENTRATION ug
Steam Ejector - Ground Level, Site #1	2	* 3A - 27.5 3B - 33.9
Steam Ejector - Top Level, Site #2	2	3A - N.A. 3B - N.A.
Calculated Storage Tank Emissions		
Virgin Product		597.4 Kg/year
Product Loading and Waste Storage		0.02 Kg/year

Monsanto has performed a stack test at the Sauget location quantify the PCB emissions to the atmosphere. Stack-sampling and other reports describing process and sampling methodology used at this site are attache

* 3A - Right Side of sampling train - 3B - Left Side

EPA Form 1320-6 (Rev. 6-72)

PLAINTIFF'S EXHIBIT 924

ADM CC8391

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SUBJECT: Emissions of PCB from the Incinerator at Monsanto - Sauget, Illinois. DATE: February 11, 1976

FROM: R. Edwin Zylstra, Technical Advisor, Special Projects Section

TO: Chief, Air Surveillance Branch

On January 27-28, 1976 sampling was conducted at the Krummrich Plant of Monsanto in Sauget, Illinois to determine emissions to the air. The samples were taken near the exits of the steam jet ejectors of the non-fractionating distillation process. The exits of the fractionating distillation steam ejector were not sampled because of inaccessibility. The incinerator used to destroy waste PCB's was not sampled because Monsanto had tested the stack and the results were made available to us.

I have reviewed the test procedures and the data from three stack tests and I feel that the test results accurately indicate the quantity of PCB being emitted into the atmosphere from the incinerator. The Monsanto procedure for stack testing the incinerator for PCB and particulate is shown in Appendix A. The method is a modified EPA Method 5. The front half is identical to Method 5 and consists of a sample nozzle, a heated probe, and a heated glass fiber filter. The back half is as follows: 1. First impinger empty; 2. Second impinger with 150 ml. of N, N-dimethyl formamide; 3. Third impinger with 75 ml. NaOH solution and 75 ml. Na_2CO_3 solution; 4. Fourth impinger with 200 g silica gel. Sampling is performed the same as Method 5. To determine the PCB emissions the sample is handled as follow:

1. Probe, nozzle and filter are rinsed with hexane. The rinse is mixed with any condensate from the first impinger and then analyzed for PCB by means of electron capture gas chromotograph.

2. The NN dimethy formamide in the second impinger is analyzed for PCB by means of electron capture gas chromotograph.

The table shows the results of stack tests for PCB on the incinerator performed by Monsanto. Emission ranged from .00001 to .000248 lbs/hr. Computer printouts of data collected and the results of the last three tests performed were supplied to us for evaluation. The calculations were checked and no errors were found. Monsanto's and our computer printouts are in Appendix B.

PLAINTIFF'S EXHIBIT 925

EPA Form 1320-6 (Rev. 6-72)

ADM 00e392

STACK TESTS ON MONSANTO PCB INCINERATOR

The following tests were made using a modification of Illinois EPA Method 5 and both flow and concentrations were determined.

Date	PCB conc^{n} in mg/m^3	Flow m^3/min.	Lbs/
7/25/73	0.0063	63.5	.53
8/7/73	0.0157	94.8	2.09
8/16/73	0.0176	106.5	2.45
8/24/73	0.0166	106.8	2.34
10/26/73	0.0077	48.3	.49
11/7/73	0.0056	58.1	.4
11/20/73	0.0119	63.8	.91
11/22/73	0.0013	66.7	.11
8/23/74	0.0149	71.1	1.49
9/12/74	0.0289	51.1	1.93
5/23/75	0.0300	44.5	1.7
10/1/75	0.0182	92.2	2.2

APPENDIX A

MONSANTO PROCEDURE FOR STACK TESTING FOR PCBs

INCINERATOR STACK TEST FOR PCB'S AND PARTICULATES

SCOPE: This procedure determines the amount of PCB's and particulates present in the incinerator stack gas.

EQUIPMENT:

1. R.A.C. portable stack gas sampler
   a. sample box
   b. unbilical cord 25 feet (2 each)
   c. nozzles 0.250 or 0.375
   d. clamps (10 each) 28/15 Fisher 5-885F
   e. 3' combination probe and pitot tube (glass)
   f. glass connectors (4 each)
   g. 500 ml Greenburg-Smith impinger (4 each) Fisher Scientific Company, St. Louis, MO cat. no. 9-257, or equivalent. The fourth impinger is modified by replacing the standard tip with a 1/2 inch ID glass tube extending to one-half inch from bottom of impinger flask.
2. Glass orifice to regulate air flow through pitot tube. (2each) Can be made from broken thermometer
3. Thermometer 0-220°F
4. Thermocouple and potentiometer
5. Nomograph
6. Clip board
7. Air Pump (Dyna pump)
8. Stopwatch (2 each)
9. Tape ruler
10. 3 way plug
11. Stopcock grease
12. 50 ft. of 5/8" rope
13. Adjustable wrenches (2 each)

FOR PARTICULATE TEST ADD:

1. Cyclone and Erlenmeyer flask
2. Clamps 2 each 28/15

3. Glass fiber filter holder

4. Glass fiber size 7.0 CM (Fisher cat. no. 9-8[illegible]
Dry in oven and leave in desiciator.

REAGENTS:

a. Sodium Sulfite, Fisher Scientific Company, St. Louis, Missouri Cat. No. S-430 in unstandardized solution. Weight 63 grams; dissolve in water and make up to 1 liter.

b. N,N-Dimethyl Formamide, Fisher Scientific CO., St. Louis, Missouri, Cat. No. D-119.

c. Sodium Hydroxide 50% solution, Fisher Scientific Company, St. Louis, Missouri, Cat. No. SO-S-254, in unstandardized solution. Add 52.4 ml to 500 ml distilled water and make up to a liter.

d. Hexane; nonograde (Mallinckrodt Chemical Works, St. Louis, Missouri, Cat. No. 4159)

e. Silica Gel Grade 938 Darison Code 938-08-08-226 Davison Chemical; Baltimore, Maryland, 21203.

f. Crushed ice.

SAMPLING PROCEDURE:

1. Measure stack diameter and determine minimum number of sampling points needed.
2. Measure stack temperature
3. Determine percent moisture. This may be found from previous tests.
4. Place sample box on duorail and assemble impingers. Leaving the first impinger empty. Fill the second impinger with 150 ml of DMF solution. Add 75 ml in NaOH plus 75 ml in Na_2SO_3 in the third impinger. The last impinger will contain 200 g silica gel in a modified impinger. (Weigh silica gel for mate determination later).
5. Place the cyclone and glass fiber filter in the heat chamber and connect to impingers.
6. Connect vacuum line of umbilical cord to inlet of meter box and outlet of last impinger. Plug up the inlet to the filter holder and pull 15 in. Hg vacuum to check for leaks. Leakage rate should not exceed 0.02 C.F.M.
7. Connect glass probe to cyclone.
8. Complete all connections on umbilical cord.
9. Purge air through pitot tube using tubing which is attached to umbilical cord and connect to air pump.
10. Pack ice around impinger and add water.
11. Make a traverse of stack on one side to determine velocity and stack pressure. Be sure you have balanced draft gage before you take your readings.
12. Heat probe and chamber in box to a temperature of 10° higher than the stack temperature.
13. Record temperature at gas meter. (inlet and outlet.)
14. Use Nomograph to determine nozzle size and isokinetic sampling rate.
15. Record gas meter readings.
16. As soon as heat chamber in sampling box is up to temperature start your test.

SAMPLE TRAIN OPERATION

1. For each run, record the data required on the example sheet shown in Figure 1-2.

2. Determine the time required at each sampling point. A minimum time of one hour is required for this test.

3. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point.

4. Record temperature at gas meter inlet and outlet, about one minute before it is time to change traverse points. Also be sure to read temperature of last impinger.

5. Add more ice during test to keep the temperature of gases leaving the last impinger as low as possible and preferably at 70° F or less.

6. Turn off pumps at the conclusion of sample run and record final reading.

7. Remove probe from stack and disconnect from impingers. Take probe and impingers and prepare them for lab analysis.

8. Measure the increase in volume of each impinger plus the increase in weight of the silica gel to determine percent water.

9. Rinse probe and cyclone with hexane and pass rinsing through glass fiber filter. Mix this extract with the water (condensate) from the first impinger.

10. Carefully remove the filter pad plus rubber washer and dry in oven then place in desicator before weighing for particulates.

11. Collect all washings and give to lab for analysis.

12. Upon receipt of analysis from lab, record results in grams on sheet shown in Figure 1-1 and complete for computer run.

DISCUSSION:

ACM 006399

The collection system in this test may also be used to determine other components of the stack gas. The ones of most interest would be HCl, H_3PO_4, and Cl_2. To do this have the lab save all aqueous layers from washing used in preparing the solutions for PCB analysis. Take the aqueous layer from the first impinger (water condensate) and run for HCl and H_3PO_4 analysis. Analyze the dimethyl formamide from the second impinger for Cl_2 and H_3PO_4 and the Na_2SO_3 impinger for Cl_2.

1 [1] Number of sets of data
(1-2)

2 [2] Number Components to be analyzed
(1-2)

3 [06/12/1973] [1:50 PM] [DICKERMAN STACK]
(1-12) Date (13-20) Time (21-44) Stack Sampled

[3311] [8] Zones [19.01] in [27.82] in Hg [0.375] in. [ ]
(45-48) Source OpNo. (49-50) (51-56) StackDiam. (57-61) Bar. (62-66) Nozzle (67-72) Stack Wall

4 [6134.0] [POUNDS PER HOUR]
(1-5) Process Wt. (6-40) Units of production per hour

5 [DELTA ENVIRONMENTAL AND DALE RICHELL]
(1-50) Sampling done by:

6 [EPA METHOD #5 BY DeFORD AND NELSON IMPINGERS]
(1-48) Sampling Method - indicate modifications.

K [.1505] FS [0.993] Correction Factors Degree: [FA] CEntigrade or FAhrenheit N [1.02]
(51-54) Orifice (55-58) Pitot (59-60) (61-64) Meter

Gas Analysis in MoleFractions (Identify Component Z if present by M.W. and name or formula)

7 [21.0] [78.4] [0.1] [0.0] [ ] [0.0] [0.0] [NONE]
(1-5) O_2 (6-10) N_2 (11-15) CO_2 (16-20) CO (21-25) H_2O (26-30) Z (31-34) MWZ (35-43) name of Z

Moisture determination by absorption on Drierite and weighing Leak test on Sampler

8 [216.1] C.F. [81.6] [0.0] "Hg [737.195] [927.941] [0.002] [15.0] "
(1-6) SampleVol. (7-11) Temp. (12-15) Press (16-23) Tare wt. (24-31) Gross wt. (32-36) C.F. at (37-41) Pres.

Analysis for Components

PARTICULATE	37.0	7.5030	2.5230	BY
[illegible]	35.0	0.0	2.0020185	
[illegible]	98.0	0.0	0.0001	
[illegible]	21.0	0.0	0.0053	

(1-11) Name of Comp. (12-15) M.W. (16-25) Tare W (26-35) Gross Wt.(g) (36-47) How determined

M.W. Fr. HCl = 36.5

ACF CCe4CC

ZONE	Pitot Velocity Head. HP (3-7)	Stack Temp. Deg. TS (8-13)	Stack Press inches H_2O PS (14-18)	Time at end of ZONE Min T (19-23)	Meter Volume at end ZONE Cu.ft. VM (24-29)	Temp. W=Wet D=Dry Deg. TC (30-34)	Inlet at end ZONE THI (35-39)	Outlet at end ZONE THO (40-44)	At start of ZONE In Hg PMI (45-49)	At end of ZONE In Hg PM2 (50-54)	Pressure across Orifice HO (55-59)
1		1401.00	01.700	0.0	218.10	D	61.0	60.0			
11	01.130	1401.00	01.700	7.0	223.58	42.0	75.0	61.0			2.100
12	0.110	1401.00	01.700	14.0	229.01	46.0	87.0	64.0			2.500
13	0.110	1401.00	01.700	21.0	234.71	50.0	96.0	68.0			2.750
14	01.160	1401.00	01.700	28.0	240.19	52.0	100.0	72.0			2.500
15	0.110	1401.00	01.700	35.0	244.69	46.0	93.0	77.0			1.600
16	0.130	1401.00	01.700	42.0	249.72	50.0	101.0	79.0			2.100
17	01.110	1401.00	01.700	49.0	255.50	56.0	106.0	81.0			2.500
18	0.110	1401.00	01.700	56.0	260.72	60.0	102.5	82.0			2.350

ACM CC64C1

APPENDIX B

STACK TEST COMPUTER PRINTOUTS

MONSANTO INDUSTRIAL CHEMICALS CO.

E.S. KUMMRICH PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE SEPT 12 1974 START TIME 1:00 PM
STACK SAMPLED- INCINERATOR SOURCE OPERATION NO. 001
SAMPLING DONE BY NEIL SULLIVAN AND ED HEUMANN

SAMPLING METHOD-EPA METHOD #5 + DMF AND NA2SO3 IMPINGERS

DETERMINATION OF EMISSION RATE OF

A:PARTICULATE
B:P.C.B.
C:HCL
D:H3PO4

PROCESS WEIGHT RATE= 772.00 POUNDS PER HOUR

TEST RESULT:

	/ACTUAL CFM AT / STACK CONDITIONS/	/STD CFM AT 70 DEG.F	DRY STD CFM / AND 29.92 IN. HG/
STACK VOLUME	1903.1	1803.8	1711.6

DUST,MIST,OR GAS CONCENTRATION IN WET & DRY STACK GAS AT STD CONDITI

COMPONENT	GRAINS PER CUBIC FT	LBS. PER MILLION CUBIC FT	LBS. PER 1000 LBS. GAS	MGS. PER CUBIC METER	PARTS PER MILLION	
A:	0.0708	10.1163	0.1331	162.0496	134.9245	IN WET G
A:	0.0746	10.6611	0.1374	170.7756	142.1910	IN DRY G
B:	0.0000	0.0018	0.0000	0.0289	0.0028	IN WET G
B:	0.0000	0.0019	0.0000	0.0304	0.0029	IN DRY G
C:	0.0307	4.3816	0.0576	70.1866	46.4308	IN WET G
C:	0.0323	4.6176	0.0595	73.9665	48.9313	IN DRY G
D:	0.0827	11.8131	0.1554	189.2287	46.6235	IN WET G
D:	0.0871	12.4493	0.1604	199.4194	49.1344	IN DRY G

EMISSION RATE:

COMPONENT	LBS. PER HOUR	GRAMS PER SEC.	LBS. PER UNIT OF PRODUCTION
A:	1.0948	0.1379	0.0014
B:	0.0002	0.0000	0.0000
C:	0.4742	0.0597	0.0006
D:	1.2785	0.1611	0.0017

ACM CC84C3

MONSANTO INDUSTRIAL CHEMICALS CO.

W.G. KRUMMRICH PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE SEPT 12 1974 START TIME 1:00 PM
STACK SAMPLED- INCINERATOR SOURCE OPERATION NO. 03

FIELD DATA:

ORIFICE CONSTANT K=0.506 PITOT TUBE FACTOR FS= 0.83
TEMPS. RECORDED IN FA DEGREES
METER CORRECTION FACTOR= 1.02

GAS ANALYSIS: Z=NONE MOLECULAR WT OF Z= 0.0
MOLECULAR WT. OF STACK GAS = 29.40
DRY MOLECULAR WT. OF GAS = 30.02

O2	N2	CO2	CO	H2O	Z	VOL	TM	PM	
0.106	0.802	0.092	0.0	0.051	0.0	40.630	100.20	29.64	4

PARTICULATE	DETERMINED BY	BY WEIGHT	=	0.1884 GRAMS
P.C.B.	DETERMINED BY	BY WEIGHT	=	0.0000 GRAMS
HCL	DETERMINED BY	BY WEIGHT	=	0.0816 GRAMS
H3PO4	DETERMINED BY	BY WEIGHT	=	0.2200 GRAMS

LEAK TEST ON ENUIPMENT=0.001 CFM AT 15.00 IN.HG
BAROMETER= 29.64 IN.HG; STACK DIAM= 19.000 INCH NOZZLE DIAM = 0.3

ZONE	VEL HEAD HP	STACK TEMP TS	STACK PRESS H2O	TIME AT END ZONE	VOLAT END ZONE	COND TEMP	METER TEMP IN	METER TEMP OUT	METER PRESS START HG	METER PRESS FIN HG	FLO ORI H2
0	0.0	95.0	0.8	0.0	935.30	0	90.0	90.0	0.0	0.0	0.1
1	0.060	95.0	0.8	8.0	939.71	64.0	98.0	90.0	0.0	0.0	1.1
2	0.080	95.0	0.8	16.0	944.74	64.0	106.0	91.0	0.0	0.0	1.3
3	0.095	95.0	0.8	24.0	950.22	65.0	111.0	92.0	0.0	0.0	1.4
4	0.095	95.0	0.8	32.0	955.71	65.0	111.0	94.0	0.0	0.0	1.4
5	0.065	95.0	0.8	40.0	960.50	63.0	106.0	95.0	0.0	0.0	1.2
6	0.080	95.0	0.8	48.0	965.28	64.0	110.0	98.0	0.0	0.0	1.5
7	0.090	95.0	0.8	56.0	970.65	65.0	113.0	97.0	0.0	0.0	1.7
8	0.090	95.0	0.8	62.0	975.93	68.0	114.0	97.0	0.0	0.0	1.7

ADM CCE4C4

MONSANTO INDUSTRIAL CHEMICALS CO.

W.G. KRUMMRICH PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE SEPT 12 1974 START TIME 1:00 PM
STACK SAMPLED- INCINERATOR SOURCE OPERATION NO. 831
CALCULATION AND EVALUATION:
THE ISOKINETIC CONSTANT HO/HP FOR THIS EQUIPMENT IS 23.6264
THE TABLE BELOW SHOWS FOR EACH ZONE THE METER VOL. AND THE AVG. METER AND PRESS. IN ABSOLUTE UNITS. FROM THIS IS CALCULATED THE EQUIVALENT STACK CONDITIONS AND DIVIDED BY TIME TO GIVE THE FLOW IN THE NOZZLE. COMPARED WITH THE ISOKINETIC FLOW RATE CALCULATED FROM THE STACK VELOC PERCENTAGE DEVIATION IS RECORDED.

	SAMPLE/STACK/AVG.		PRESS/ AVG.		TEMP/SAMPLE VOL./SAMPLE			RATE	/P.C.	
ZONE	TIME	VEL.	METER	STACK	METER	STACK	METER	STACK	ACTUAL	ISOKIN	DEV
1	8.0	13.8	29.7	29.7	552.0	555.0	4.4	4.8	0.60	0.64	-6.34
2	8.0	16.0	29.8	29.7	556.3	555.0	5.0	5.4	0.68	0.74	-8.09
3	8.0	17.4	29.8	29.7	560.0	555.0	5.5	5.9	0.73	0.80	-8.67
4	8.0	17.4	29.8	29.7	562.0	555.0	5.5	5.8	0.73	0.80	-8.83
5	8.0	14.4	29.7	29.7	561.5	555.0	4.8	5.1	0.64	0.66	-3.88
6	8.0	16.0	29.8	29.7	562.3	555.0	4.8	5.1	0.64	0.74	-13.60
7	8.0	16.9	29.8	29.7	564.5	555.0	5.4	5.7	0.71	0.78	-6.51
8	6.0	16.9	29.8	29.7	565.3	555.0	5.3	5.6	0.93	0.78	19.39
TOTAL											
	62.0	16.1	29.8	29.7	560.5	555.0	40.6	43.3	0.70	0.74	-5.75
	T	AV	AV	AV	AV	AV	T	T	AV	AV	AV

TOTAL SAMPLE VOL. CORRECTED FROM STACK CONDITIONS TO STD CONDITIONS=
41.06 CUBIC FT. OF WET GAS
TOTAL SAMPLE VOL. CORRECTED TO DRY STD CONDITIONS = 38.96 CUBIC FT.

ACM 0084C5

MONSANTO INDUSTRIAL CHEMICALS CO.

W.G. KRUMMRICH PLANT SAUGET, IL 62201. ID NO. 63 121 AAC
DATE OCT 1 1975 START TIME 1:30 PM
STACK SAMPLED- INCINERATOR SOURCE OPERATION NO. 831
SAMPLING DONE BY NEIL SULLIVAN AND ED HEUMANN

SAMPLING METHOD-EPA METHOD #5 + DMF AND NA2SO3 IMPINGERS

DETERMINATION OF EMISSION RATE OF
A:PARTICULATE
B:P.C.B.
C:CL2

PROCESS WEIGHT RATE= 0.90 THOUSAND POUNDS PER HOUR
TEST RESULT:

	/ACTUAL CFM AT /STACK CONDITIONS/	/STD CFM AT 70 DEG.F	DRY STD CFM / AND 29.92 IN. HG/
STACK VOLUME	3749.6	3257.1	2353.4

DUST, MIST, OR GAS CONCENTRATION IN WET & DRY STACK GAS AT STD. CONDITIONS

COMPONENT	GRAINS PER CUBIC FT	LBS. PER MILLION CUBIC FT	LBS. PER 1000 LBS. GAS	MGS. PER CUBIC METER	PARTS PER MILLION	
	0.0725	10.3620	0.1494	165.9835	138.2010	IN WET GAS
	0.1004	14.3408	0.1836	224.7183	191.2679	IN DRY GAS
B:	0.0000	0.0011	0.0000	0.0182	0.0018	IN WET GAS
B:	0.0000	0.0016	0.0000	0.0252	0.0024	IN DRY GAS
C:	0.0079	1.1335	0.0163	18.1570	6.1749	IN WET GAS
C:	0.0110	1.5687	0.0201	25.1290	8.5460	IN DRY GAS

EMISSION RATE:

COMPONENT	LBS. PER HOUR	GRAMS PER SEC.	LBS. PER UNIT OF PRODUCTION
A:	2.0250	0.2551	2.2450
B:	0.0002	0.0000	0.0002
C:	0.2215	0.0279	0.2456

ACM CC64C6

W.G. KRUMMRICH PLANT SAUGET, IL 62201. ID NO. 63 121 AAC

DATE OCT 1 1975 START TIME 1:30 PM

STACK SAMPLED= INCINERATOR SOURCE OPERATION NO. 331

FIELD DATA:

ORIFICE CONSTANT K=0.506 PITOT TUBE FACTOR FS= 0.83

TEMPS. RECORDED IN FA DEGREES

METER CORRECTION FACTOR= 1.02

GAS ANALYSIS: Z=NONE MOLECULAR WT OF Z= 0.0

MOLECULAR WT. OF STACK GAS = 26.83

DRY MOLECULAR WT. OF GAS = 30.22

	O2	N2	CO2	CO	H2O	Z	VOL	TW	PW	
	0.068	0.818	0.114	0.0	0.277	0.0	30.200	70.89	29.90	244.

PARTICULATE	DETERMINED BY	BY WEIGHT GC	=	0.2002 GRAMS
P.C.B.	DETERMINED BY	BY ~~TITRATION~~	=	0.0000 GRAMS
CL2	DETERMINED BY	BY TITRATION	=	0.0219 GRAMS

LEAK TEST ON EQUIPMENT=0.005 CFM AT 15.00 IN.HG

BAROMETER= 29.90 IN.HG; STACK DIAM= 19.000 IN.; NOZZLE DIAM = 0.3[illegible]

ZONE	VEL HEAD HP	STACK TEMP TS	STACK PRESS H2O	TIME ATEND ZONE	VOLAT END ZONE	COND TEMP	METER TEMP IN	METER TEMP OUT	METER PRESS START HG	METER PRESS FIN HG	ORIF H2O
0	0.0	149.0	-0.4	0.0	428.50	D	64.0	64.0	0.0	0.0	0.0
1	0.200	149.0	-0.4	8.0	431.84	51.0	68.0	64.0	0.0	0.0	0.6[illegible]
2	0.300	149.0	-0.4	16.0	435.82	51.0	74.0	64.0	0.0	0.0	0.9[illegible]
3	0.340	149.0	-0.4	24.0	439.97	53.0	80.0	65.0	0.0	0.0	1.1[illegible]
4	0.330	149.0	-0.4	32.0	444.11	55.0	80.0	66.0	0.0	0.0	1.0[illegible]
5	0.170	149.0	-0.4	40.0	447.29	53.0	74.0	66.0	0.0	0.0	0.5[illegible]
6	0.230	149.0	-0.4	48.0	450.84	54.0	80.0	66.0	0.0	0.0	0.7[illegible]
7	0.300	149.0	-0.4	56.0	454.84	56.0	83.0	68.0	0.0	0.0	0.9[illegible]
8	0.270	149.0	-0.4	64.0	458.70	58.0	82.0	68.0	0.0	0.0	0.8[illegible]

ACM CC64C7

W.G. KRUMMRICH PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE OCT 1 1975 START TIME 1:30 PM
STACK SAMPLED- INCINERATOR SOURCE OPERATION NO. 031
CALCULATION AND EVALUATION:
THE ISOKINETIC CONSTANT HO/HP FOR THIS EQUIPMENT IS 13.0114
THE TABLE BELOW SHOWS,FOR EACH ZONE,THE METER VOL. AND THE AVG. METER AND PRESS. IN ABSOLUTE UNITS. FROM THIS IS CALCULATED THE EQUIVALENT STACK CONDITIONS AND DIVIDED BY TIME TO GIVE THE FLOW IN THE NOZZLE. COMPARED WITH THE ISOKINETIC FLOW RATE CALCULATED FROM THE STACK VEL PERCENTAGE DEVIATION IS RECORDED.

	SAMPLE/	STACK/	AVG. PRESS/		AVG. TEMP/		SAMPLE VOL./		SAMPLE RATE	/P.
ZONE	TIME	VEL.	METER	STACK	METER	STACK	METER	STACK	ACTUAL	ISOKIN CE
1	8.0	27.6	29.9	29.9	525.0	609.0	3.3	5.5	0.69	1.27-46.
2	8.0	33.8	30.0	29.9	527.5	609.0	4.0	6.5	0.81	1.56-47.
3	8.0	36.0	30.0	29.9	530.8	609.0	4.2	6.7	0.84	1.66-49.
4	8.0	35.5	30.0	29.9	532.8	609.0	4.1	6.7	0.84	1.63-48.
5	8.0	25.5	29.9	29.9	531.5	609.0	3.2	5.2	0.64	1.17-45.
6	8.0	29.6	30.0	29.9	531.5	609.0	3.6	5.8	0.72	1.36-47.
7	8.0	33.8	30.0	29.9	534.3	609.0	4.0	6.5	0.81	1.56-48.
8	8.0	32.1	30.0	29.9	535.3	609.0	3.9	6.2	0.78	1.48-47.
TOTAL	64.0	31.7	30.0	29.9	531.1	609.0	30.2	49.0	0.77	1.46-47.

T	AV	AV	AV	AV	AV	T	T	AV	AV	A

TOTAL SAMPLE VOL. CORRECTED FROM STACK CONDITIONS TO STD CONDITIONS=
42.59 CUBIC FT. OF WET GAS
TOTAL SAMPLE VOL. CORRECTED TO DRY STD CONDITIONS = 30.78 CUBIC

ADM CCE4C8

MONSANTO INDUSTRIAL CHEMICALS CO.

E.G. [illegible] PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE MAY 23 1975. START TIME 10:30 AM
STACK SAMPLED INCINERATOR STACK SOURCE OPERATION NO. 001
SAMPLING DONE BY NEIL SULLIVAN AND ED H

SAMPLING METHOD-EPH METHOD #5 & DMF AND NA2SO3 IMPINGERS

DETERMINATION OF EMISSION RATE OF

A:PARTICULATE
B:P.C.B.
C:HCL
D:CL2

PROCESS WEIGHT RATE= 1.00 THOUSAND POUNDS PER HOUR
TEST RESULT:

	/ACTUAL CFM AT / STACK CONDITIONS/	/STD CFM AT 70 DEG.F	DRY STD CFM / AND 29.92 IN. HG/
STACK VOLUME	1711.6	1649.0	1569.5

DUST,MIST,OR GAS CONCENTRATION IN WET & DRY STACK GAS AT STD CONDITIONS

COMPONENT	GRAINS PER CUBIC FT	LBS. PER MILLION CUBIC FT	LBS. PER 1000 LBS. GAS	MGS. PER CUBIC METER	PARTS PER MILLION	
A:	0.0522	7.4692	0.0962	119.5068	99.4946	IN WET GAS
A:	0.0549	7.8343	0.0991	125.5580	104.5420	IN DRY GAS
B:	0.0000	0.0016	0.0000	0.0247	0.0025	IN WET GAS
B:	0.0000	0.0017	0.0000	0.0270	0.0026	IN DRY GAS
C:	0.0027	0.3787	0.0049	6.0656	4.0126	IN WET GAS
C:	0.0028	0.3979	0.0050	6.3731	4.2160	IN DRY GAS
D:	0.0021	0.2970	0.0038	4.7580	1.6181	IN WET GAS
D:	0.0022	0.3121	0.0039	4.9991	1.7001	IN DRY GAS

EMISSION RATE:

COMPONENT	LBS. PER HOUR	GRAMS PER SEC.	LBS. PER UNIT OF PRODUCTION
A:	0.7381	0.0930	0.7381
B:	0.0002	0.0000	0.0002
C:	0.0375	0.0047	0.0375
D:	0.0294	0.0037	0.0294

ADM CC64C9

MONSANTO INDUSTRIAL CHEMICALS CO.

W.G. KRUMMRICH PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE MAY 23 1975 START TIME 10:30 AM
STACK SAMPLED- INCINERATOR STACK SOURCE OPERATION NO. 831

FIELD DATA:

ORIFICE CONSTANT K=0.504 PITOT TUBE FACTOR FS= 0.83
TEMPS. RECORDED IN FA DEGREES
METER CORRECTION FACTOR= 1.02

GAS ANALYSIS: Z=NONE MOLECULAR WT OF Z= 0.0
MOLECULAR WT. OF STACK GAS = 30.00
DRY MOLECULAR WT. OF GAS = 30.60

O2	N2	CO2	CO	H2O	Z	VOL	TM	PM
0.028	0.824	0.148	0.0	0.048	0.0	45.630	114.40	29.64

PARTICULATE	DETERMINED BY	KY WEIGHT	=	0.151?	GRAMS
P.C.B.	DETERMINED BY	KY WEIGHT	=	0.0001	GRAMS
HCL	DETERMINED BY	KY WEIGHT	=	0.0177	GRAMS
CL2	DETERMINED BY	KY WEIGHT	=	0.0060	GRAMS

LEAK TEST ON EQUIPMENT=0.004 CFM AT 15.00 IN.HG
BAROMETER= 29.64 IN.HG STACK DIAM= 19.000 IN.; NOZZLE DIAM = 0.375

ZONE	VEL HEAD DP	STACK TEMP TS	STACK PRESS H2O	TIME ATEND ZONE	VOLAT END ZONE	COND TEMP	METER TEMP IN	METER TEMP OUT	METER PRESS START HG	METER PRESS FIN HG	FLOW ORIFICE H2O
0	0.0	86.0	0.8	0.0	926.60	D	86.0	86.0	0.0	0.0	0.0
1	0.090	86.0	0.8	8.0	932.60	0.0	106.0	94.0	0.0	0.0	1.92
2	0.090	86.0	0.8	16.0	938.71	0.0	122.0	104.0	0.0	0.0	2.10
3	0.060	86.0	0.8	24.0	944.48	0.0	132.0	104.0	0.0	0.0	1.--
4	0.060	86.0	0.8	32.0	950.04	0.0	134.0	108.0	0.0	0.0	1.--
5	0.050	86.0	0.8	40.0	955.74	0.0	128.0	110.0	0.0	0.0	1.2
6	0.070	86.0	0.8	48.0	960.50	0.0	134.0	112.0	0.0	0.0	1.70
7	0.070	86.0	0.8	56.0	967.85	0.0	134.0	114.0	0.0	0.0	1.70
8	0.070	86.0	0.8	64.0	972.23	0.0	134.0	118.0	0.0	0.0	1.70

ACM CC6410

MONSANTO INDUSTRIAL CHEMICALS CO.

W.G. KRUMMRICH PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE MAY 23 1975 START TIME 10:30 AM
STACK SAMPLED- INCINERATOR STACK SOURCE OPERATION NO. 831
CALCULATION AND EVALUATION:
THE ISOKINETIC CONSTANT HO/HP FOR THIS EQUIPMENT IS 24.7938
THE TABLE BELOW SHOWS,FOR EACH ZONE,THE METER VOL. AND THE AVG. METER AND PRESS. IN ABSOLUTE UNITS. FROM THIS IS CALCULATED THE EQUIVALENT STACK CONDITIONS AND DIVIDED BY TIME TO GIVE THE FLOW IN THE NOZZLE. THIS COMPARED WITH THE ISOKINETIC FLOW RATE CALCULATED FROM THE STACK VELOCITY PERCENTAGE DEVIATION IS RECORDED.

	SAMPLE/STACK/AVG.		PRESS/ AVG.		TEMP/SAMPLE VOL./			SAMPLE RATE		/-%
ZONE	TIME	VEL.	METER	STACK	METER	STACK	METER	STACK	ACTUAL	ISOKIN	DEV.
1	8.0	15.7	29.8	29.7	553.0	546.0	6.0	6.4	0.80	0.72	10.33
2	8.0	16.6	29.8	29.7	566.5	546.0	6.1	6.3	0.79	0.77	3.33
3	8.0	13.6	29.7	29.7	575.5	546.0	5.8	5.9	0.73	0.63	17.--
4	8.0	13.6	29.7	29.7	579.5	546.0	5.6	5.6	0.70	0.62	12.--
5	8.0	12.4	29.7	29.7	580.0	546.0	5.7	5.8	0.72	0.57	25. -
6	8.0	14.7	29.8	29.7	581.0	546.0	4.8	4.8	0.60	0.66	-1.. -
7	8.0	14.7	29.8	29.7	583.5	546.0	7.3	7.4	0.92	0.66	39.--
8	8.0	14.7	29.8	29.7	585.0	546.0	4.4	4.4	0.55	0.66	-16. -
TOTAL											
	64.0	14.5	29.8	29.7	575.5	546.0	45.6	46.5	0.73	0.67	9.--
	T	AV	AV	AV	AV	AV	T	T	AV	AV	AV

TOTAL SAMPLE VOL. CORRECTED FROM STACK CONDITIONS TO STD CONDITIONS= 44.83 CUBIC FT. OF WET GAS
TOTAL SAMPLE VOL. CORRECTED TO DRY STD CONDITIONS = 42.67 CUBIC FT.

ADM CC6411

U.S. ENVIRONMENTAL PROTECTION AGENCY REGION V
AIR SURVEILLANCE BRANCH FIELD SURVEYS SECTION
STACK TEST REVIEW

COMPANY [illegible]

STACK IDENTIFICATION [illegible]

RUN NUMBER _____ DATE OF RUN Sept. 2, 1975

1. Amount of water collected (milliliters) = 40.0
   Volume of water vapor collected (SCF) = 2.[illegible]

2. Dry gas meter volume at meter conditions (cubic feet) = 40.[illegible]
   Barometric pressure (inches of mercury) = 23.[illegible]
   Average orifice pressure drop (inches of water) = 1.[illegible]
   Average meter temperature = 100 °F

3. Gas meter volume at STP (dry cubic feet) = 38.32

4. Percentage of moisture in gas stream = 5.1[illegible] %

5. Percent composition of gas stream:

   Oxygen..... 19.6%
   Nitrogen..... 80.[illegible]%
   Carbon Dioxide... 0.[illegible]%
   Carbon Monoxide.. .[illegible]%

6. Percentage of excess air = 100.3%

7. Dry molecular weight of gas stream (lb./lb-mole) = 28.[illegible]
   Wet molecular weight of gas stream (lb./lb-mole) = 28.[illegible]

8. Pitot tube coefficient (dimensionless) = .83
   Number of pitot tube readings = 8
   Average of square roots of velocity pressures = .[illegible]
   Average gas stream temperature (°F) = 93°F
   Gas stream velocity (ft/sec) = 16.165
   Pitot tube readings:

   .96 .98 .99 .99 .9[illegible] .9[illegible] .9[illegible]
   .99

9. Stack dimensions, circular with diameter (feet) = 1.55
   Stack area (square feet) = 1.96
   Volumetric flow at STP (cubic feet/min) = 1710

10. Nozzle diameter used for sampling (inches) = .375
    Sampling time (minutes) = 42.[illegible]
    Weight of particulate matter collected (milligrams) = .[illegible]

11. Particulate concentration (lb./SCF) = .[illegible]
    Particulate concentration (grain/SCF) = .[illegible]
    Particulate concentration corrected to 50 % excess air (lb./SCF) = .[illegible]
    Particulate concentration corrected to 50 % excess air (grain/SCF) = .[illegible]

12. Isokinetic rate (%) = 92.15

13. Mass emission rate (lb./hr) = .[illegible]

Date Feb. 10 1976

Signature R. Edwin Bolte

ADM CC6414

U.S. ENVIRONMENTAL PROTECTION AGENCY REGION V
AIR SURVEILLANCE BRANCH — FIELD OPERATIONS SECTION
STACK TEST DIVISION

COMPANY [illegible]

STACK IDENTIFICATION [illegible]

RUN NUMBER _____ DATE OF TEST [illegible]

1. Amount of water collected (milliliters) = 44.70
   Volume of water vapor collected (SCF) = 2.1077

2. Dry gas meter volume at meter conditions (cubic feet) = 47.53
   Barometric pressure (inches of mercury) = 29.74
   Average orifice pressure drop (inches of water) = 1.660
   Average meter temperature = 114 °F

3. Gas meter volume at STP (dry cubic feet) = 41.67

4. Percentage of moisture in gas stream = 4.81 %

5. Percent composition of gas stream:

   Oxygen..... 2.3%
   Nitrogen..... 82.6%
   Carbon Dioxide... 14.7%
   Carbon Monoxide.. .0%

6. Percentage of excess air = 14.77%

7. Dry molecular weight of gas stream (lb./lb-mole) = 30.48
   Wet molecular weight of gas stream (lb./lb-mole) = 29.07

8. Pitot tube coefficient (dimensionless) = .83
   Number of pitot tube readings = 8
   Average of square roots of velocity pressures = .2513
   Average gas stream temperature (°F) = 91°F
   Gas stream velocity (ft/sec) = 14.537
   Pitot tube readings:

   .05 .09 .06 .06 .05 .07 .07 .07

9. Stack dimensions, circular with diameter (feet) = 1.38
   Stack area (square feet) = 1.86
   Volumetric flow at STP (cubic feet/min) = 1563

10. Nozzle diameter used for sampling (inches) = .375
    Sampling time (minutes) = 64.00
    Weight of particulate matter collected (milligram) = .03

11. Particulate concentration (lb./SCF) = .0000009
    Particulate concentration (grain/SCF) = .000012
    Particulate concentration corrected to 50 % excess air (lb./SCF) = [illegible]
    Particulate concentration corrected to 50 % excess air (grain/SCF) = [illegible]

12. Isokinetic rate (%) = 106.64

13. Mass emission rate (lb./hr) = .09

Date Feb. 10, 1976

Signature R. Edwin Hyde

ACM 008413

COMPANY Monsanto

STACK IDENTIFICATION PCB Incinerator

RUN NUMBER _____ DATE OF RUN Oct. 1,1975

1. Amount of water collected (milliliters) = 244.61
   Volume of water vapor collected (STP) = 11.50451

2. Dry gas meter volume at meter conditions (cubic feet) = 39.20
   Barometric pressure (inches of mercury) = 29.90
   Average orifice pressure drop (inches of water) = .860
   Average meter temperature = 71 °F

3. Gas meter volume at STP (dry cubic feet) = 30.18

4. Percentage of moisture in gas stream = 27.75 %

5. Percent composition of gas stream:

   Oxygen..... 6.80%
   Nitrogen..... 81.80%
   Carbon Dioxide... 11.40%
   Carbon Monoxide.. .00%

6. Percentage of excess air = 45.96%

7. Dry molecular weight of gas stream (lb./lb-mole) = 30.00
   Wet molecular weight of gas stream (lb./lb-mole) = 26.73

8. Pitot tube coefficient (dimensionless) = .83
   Number of pitot tube readings = 8
   Average of square roots of velocity pressures = .5139
   Average gas stream temperature (°F) = 140°F
   Gas stream velocity (ft/sec) = 31.823
   Pitot tube readings:

   .20 .30 .34 .33 .17 .23 .30
   .27

9. Stack dimensions, circular with diameter (feet) = 1.50
   Stack area (square feet) = 1.96
   Volumetric flow at STP (cubic feet/min) = 2352

10. Nozzle diameter used for sampling (inches) = .375
    Sampling time (minutes) = 64.00
    Weight of particulate matter collected (milligram) = .02

11. Particulate concentration (lb./SCF) = .0000000
    Particulate concentration (grain/SCF) = .000011
    Particulate concentration corrected to 50 % excess air (lb./SCF) = .000010
    Particulate concentration corrected to 50 % excess air (grain/SCF) = .000

12. Isokinetic rate (%) = 51.23

13. Mass emission rate (lb./hr) = .00

ADM CC6414

Date E.I. 10/15/75

MONSANTO INDUSTRIAL CHEMICALS CO.

W.G. KRUMMRICH PLANT SAUGET, IL 62201. ID NO. 63 121 AAC
DATE MAY 23 1975 START TIME 10:30 AM
STACK SAMPLED- INCINERATOR STACK SOURCE OPERATION NO. 831
CALCULATION AND EVALUATION:
THE ISOKINETIC CONSTANT HO/HP FOR THIS EQUIPMENT IS 24.7938
THE TABLE BELOW SHOWS, FOR EACH ZONE, THE METER VOL. AND THE AVG. METER TEMP AND PRESS. IN ABSOLUTE UNITS. FROM THIS IS CALCULATED THE EQUIVALENT VOL. STACK CONDITIONS AND DIVIDED BY TIME TO GIVE THE FLOW IN THE NOZZLE. THIS COMPARED WITH THE ISOKINETIC FLOW RATE CALCULATED FROM THE STACK VELOCITY. PERCENTAGE DEVIATION IS RECORDED.

	SAMPLE/	STACK/	AVG. PRESS/		AVG. TEMP/		SAMPLE VOL./		SAMPLE RATE	/P.C.
ZONE	TIME	VEL.	METER	STACK	METER	STACK	METER	STACK	ACTUAL ISOKIN	DEV
1	8.0	15.7	29.8	29.7	553.0	546.0	6.0	6.4	0.80 0.72	10.23
2	8.0	16.6	29.8	29.7	566.5	546.0	6.1	6.3	0.79 0.77	3.38
3	8.0	13.6	29.7	29.7	575.5	546.0	5.8	5.9	0.73 0.63	17.49
4	8.0	13.6	29.7	29.7	579.5	546.0	5.6	5.6	0.70 0.63	12.42
5	8.0	12.4	29.7	29.7	580.0	546.0	5.7	5.8	0.72 0.57	26.08
6	8.0	14.7	29.8	29.7	581.0	546.0	4.8	4.8	0.60 0.68	-11.06
7	8.0	14.7	29.8	29.7	583.5	546.0	7.3	7.4	0.92 0.68	36.74
8	8.0	14.7	29.8	29.7	585.0	546.0	4.4	4.4	0.55 0.68	-18.72
TOTAL										
	64.0	14.5	29.8	29.7	575.5	546.0	45.6	46.5	0.73 0.67	9.04
	T	AV	AV	AV	AV	AV	T	T	AV AV	AV

TOTAL SAMPLE VOL. CORRECTED FROM STACK CONDITIONS TO STD CONDITIONS=
44.83 CUBIC FT. OF WET GAS
TOTAL SAMPLE VOL. CORRECTED TO DRY STD CONDITIONS = 42.67 CUBIC FT.

MONSANTO INDUSTRIAL CHEMICALS CO.

W.G. KRUMMRICH PLANT- SAUGET, IL 62201. ID NO. 63 121 AAC
DATE OCT 1 1975 START TIME 1:30 PM
STACK SAMPLED- INCINERATOR SOURCE OPERATION NO. 831
SAMPLING DONE BY NEIL SULLIVAN AND ED HEUMANN

SAMPLING METHOD-EPA METHOD #5 + DMF AND NA2SO3 IMPINGERS

DETERMINATION OF EMISSION RATE OF
A:PARTICULATE
B:P.C.B.
C:CL2

PROCESS WEIGHT RATE= 0.90 THOUSAND POUNDS PER HOUR
TEST RESULT:

	/ACTUAL CFM AT / STACK CONDITIONS/	/STD CFM AT 70 DEG.F	DRY STD CFM / AND 29.92 IN. HG/
STACK VOLUME	3749.6	3257.1	2353.4

DUST, MIST, OR GAS CONCENTRATION IN WET & DRY STACK GAS AT STD CONDITIONS

COMPONENT	GRAINS PER CUBIC FT	LBS. PER MILLION CUBIC FT	LBS. PER 1000 LBS. GAS	MGS. PER CUBIC METER	PARTS PER MILLION	
A:	0.0725	10.3620	0.1494	165.9835	138.2010	IN WET GAS
A:	0.1004	14.3408	0.1836	229.7183	191.2679	IN DRY GAS
B:	0.0000	0.0011	0.0000	0.0182	0.0018	IN WET GAS
B:	0.0000	0.0016	0.0000	0.0252	0.0024	IN DRY GAS
C:	0.0079	1.1335	0.0163	18.1570	6.1749	IN WET GAS
C:	0.0110	1.5687	0.0201	25.1290	8.5460	IN DRY GAS

EMISSION RATE:

COMPONENT	LBS. PER HOUR	GRAMS PER SEC.	LBS. PER UNIT OF PRODUCTION
A:	2.0250	0.2551	2.2450
B:	0.0002	0.0000	0.0002
C:	0.2215	0.0279	0.2456

ADM CC6416

W.G. KRUMMRICH PLANT SAUGET,IL 62201. ID NO. 63 121 AAC
DATE OCT 1 1975 START TIME 1:30 PM
STACK SAMPLED- INCINERATOR SOURCE OPERATION NO. 831

FIELD DATA:

ORIFICE CONSTANT K=0.506 PITOT TUBE FACTOR FS= 0.83
TEMPS. RECORDED IN FA DEGREES
METER CORRECTION FACTOR= 1.02

GAS ANALYSIS: Z=NONE MOLECULAR WT OF Z= 0.0
MOLECULAR WT. OF STACK GAS = 26.83
DRY MOLECULAR WT. OF GAS = 30.22

	O2	N2	CO2	CO	H2O	Z	VOL	TW	PW	WG
	0.068	0.818	0.114	0.0	0.277	0.0	30.200	70.89	29.90	244.6

PARTICULATE	DETERMINED BY	BY WEIGHT GC	=	0.2002 GRAMS
P.C.B.	DETERMINED BY	BY ~~TITRATION~~	=	0.0000 GRAMS
CL2	DETERMINED BY	BY TITRATION	=	0.0219 GRAMS

LEAK TEST ON EQUIPMENT=0.005 CFM AT 15.00 IN.HG
BAROMETER= 29.90 IN.HG; STACK DIAM= 19.000 IN.; NOZZLE DIAM = 0.375

ONE	VEL HEAD HP	STACK TEMP TS	STACK PRESS H2O	TIME ATEND ZONE	VOLAT END ZONE	COND TEMP	METER TEMP IN	METER TEMP OUT	METER PRESS START HG	METER PRESS FIN HG	ORIFICE H2O
0	0.0	149.0	-0.4	0.0	428.50	D	64.0	64.0	0.0	0.0	0.0
1	0.200	149.0	-0.4	8.0	431.84	51.0	68.0	64.0	0.0	0.0	0.650
2	0.300	149.0	-0.4	16.0	435.82	51.0	74.0	64.0	0.0	0.0	0.960
3	0.340	149.0	-0.4	24.0	439.97	53.0	80.0	65.0	0.0	0.0	1.100
4	0.330	149.0	-0.4	32.0	444.11	55.0	80.0	66.0	0.0	0.0	1.070
5	0.170	149.0	-0.4	40.0	447.29	53.0	74.0	66.0	0.0	0.0	0.560
6	0.230	149.0	-0.4	48.0	450.84	54.0	80.0	66.0	0.0	0.0	0.740
7	0.300	149.0	-0.4	56.0	454.84	56.0	83.0	68.0	0.0	0.0	0.960
8	0.270	149.0	-0.4	64.0	458.70	58.0	82.0	68.0	0.0	0.0	0.870

ACM 008417

[illegible] INDUSTRIAL CHEMICALS CO.

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W.G. KRUMMRICH PLANT SAUGET, IL 62201. ID NO. 63 121 AAC
DATE OCT 1 1975 - - START TIME 1:30 PM
STACK SAMPLED- INCINERATOR ..... SOURCE OPERATION NO.. 831
CALCULATION AND EVALUATION:
THE ISOKINETIC CONSTANT HO/HP FOR THIS EQUIPMENT IS 13.0114
THE TABLE BELOW SHOWS, FOR EACH ZONE, THE METER VOL. AND THE AVG. METER T
AND PRESS. IN ABSOLUTE UNITS. FROM THIS IS CALCULATED THE EQUIVALENT VO
STACK CONDITIONS AND DIVIDED BY TIME TO GIVE THE FLOW IN THE NOZZLE. T
COMPARED WITH THE ISOKINETIC FLOW RATE CALCULATED FROM THE STACK VELOCI
PERCENTAGE DEVIATION IS RECORDED.

ZONE	SAMPLE/STACK/AVG. PRESS/ AVG. TEMP/SAMPLE. VOL./SAMPLE RATE /P.C. TIME	VEL.	METER	STACK	METER	STACK	METER	STACK	ACTUAL	ISOKIN DEV
1	8.0	27.6	29.9	29.9	525.0	609.0	3.3	5.5	0.69	1.27-46.07
2	8.0	33.8	30.0	29.9	527.5	609.0	4.0	6.5	0.81	1.56-47.74
3	8.0	36.0	30.0	29.9	530.8	609.0	4.2	6.7	0.84	1.66-49.10
4	8.0	35.5	30.0	29.9	532.8	609.0	4.1	6.7	0.84	1.63-48.66
5	8.0	25.5	29.9	29.9	531.5	609.0	3.2	5.2	0.64	1.17-45.03
6	8.0	29.6	30.0	29.9	531.5	609.0	3.6	5.8	0.72	1.36-47.19
7	8.0	33.8	30.0	29.9	534.3	609.0	4.0	6.5	0.81	1.56-48.14
8	8.0	32.1	30.0	29.9	535.3	609.0	3.9	6.2	0.78	1.48-47.35
TOTAL										
	64.0	31.7	30.0	29.9	531.1	609.0	30.8	49.0	0.77	1.46-47.55
	T	AV	AV	AV	AV	AV	T	T	AV	AV AV

TOTAL SAMPLE VOL. CORRECTED FROM STACK CONDITIONS TO STD CONDITIONS=
42.59 CUBIC FT. OF WET GAS
TOTAL SAMPLE VOL. CORRECTED TO DRY STD CONDITIONS = 30.78 CUBIC FT.

ADM CC6418

Facility: Monsanto Company
W.G. Krummrich Plant
Route 3
Sauget, IL 62201

Date of Inspection: January 27, 1976

Participants: Monsanto
Paul Heisler
Clarence Buckley

U.S. Environmental Protection Agency
Edwin Zylstra
John Connell
Charles Miller

Background:

Monsanto is the sole manufacturer of PCB in the United States. Production figures for the first nine months of 1975 are listed below:

Aroclor	Thousands of Pounds
1016	10350
1242	5120
1254	6980

Starting during the latter part of 1972, the only use for PCB compounds is in the manufacture of transformers and capacitors.

Process:

The chlorinator is charged with biphenyl and ferric chloride (catalyst) and then heated. Vaporized chlorine is fed into the chlorinator. The contact time varies from 12 to 36 hours, depending on the type of Aroclor to be produced, which determines the degree of chlorination. The vapor from the chlorinator (HCl containing PCB) goes to the scrubber where it is washed with liquid Aroclor. The gaseous HCl is sent to the purification section of the plant. The crude Aroclor goes to the Blower tank where it is blown with dry air for several hours. The air is scrubbed with water and vented to the atmosphere through a demister, the crude product is sent to a storage tank where a few tenths of 1% of alkali is added to react with any remaining hydrogen chloride or ferric chloride.

The method of distillation of the raw Aroclor varies depending upon the product to be produced. For types 1254, 1242, and 1221, the process is the same. Each is distilled in a vacuum still, the condensate being the finished product and the bottoms being the Montars which are sent to incineration. For Aroclor 1016, the crude aroclor is distilled in a vacuum distillation tower. The steam from the steam jet ejectors is partially condensed; the condensate being discharged into the plant discharge sump and the vapor exhausted to atmosphere. The overhead from the distillation tower is the product 1016 and is sent to storage. The bottoms are sent through another chlorination and distillation cycle. The overhead from this still is the finished product and the bottoms are the Montars which are sent to incineration. The three possible places where PCB can escape into the atmosphere are: vapor from jet ejectors, exhaust from the scrubber; and surface area evaporation (in general).

All aroclors are stored at 150°F with a layer of nitrogen on top of the liquid.

Incineration:

There are three points in the process that go to the incinerator: Montars, bottoms from separator sump, collection from all drip pans. In addition waste material from the users of PCB is sent to Monsanto to be destroyed. The type and concentration of these waste are unknown but it is estimated that they contain about 90% PCB. The amount of contaminated waste disposed of for the first nine months of 1975 is listed below:

	Thousands of Pounds
Customer returns, records exists	1109
Monsanto, records exists	322
Total receipts	1431
Destroyed by incineration	2808

The liquid waste stream is steam atomized and fed into the fire box. The feed is incinerated at a temperature above2200°F with natural gas used for combustion with 5% excess oxygen and a retention time of 2-3 seconds. The gases go through a quench pot, the exhaust of which passes through a venturi scrubber and then through a packed tower which is irrigated by the weak muriatic acid originating from the quench pot. The exhausts are vented to atmosphere through a demister and are monitored.

Loading and Unloading:

The majority of the PCB components and the products made using PCB are liquid and are transported in bulk or in steel drums. Bulk shipments are made in railroad tank car and tank trucks. Waste material shipped in from other locations in 55 gallon drums or tank trucks are unloaded into a concrete pit; the material in this pit is periodically pumped to one of four 20,000 gallon incinerator waste feed tanks. The waste material that is shipped in by rail truck is unloaded into a 500,000 gallon storage tank and is pumped into the feed tanks when required. In the truck or railcar loading area, drainage is directed into a small concrete pit which is periodically pumped into the basins located in the manufacturing area. Relief valve lines and atmosphere vents are routed through catch tanks or are redirected to underground settling basins.

UNITED STATES GOVERNMENT

Memorandum

TO : Gerald F. Regan, Chief, Air Surveillance Branch

DATE: March 5, 1976

FROM : Technical Advisor, Special Projects Section
Air Surveillance Branch

SUBJECT: Calculation of PCB Air Emissions from Storage and Dispensing Operations at the Krummrich Plant of Monsanto

Potential air emissions from the storage and dispensing of PCB were calculated based on information supplied by Monsanto. The results of these calculations are:

Storage tanks for virgin product	- 597.4 kg/year
Product loading	- 0.0184 kg/year
Storage and handling waste aroclors	- 0.00066 kg/year

R. Edwin Zylstra

Attachment (Calculations)

ADM C08422

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Clarence Buckley of Monsanto estimated that storage and loading operations at the plant would displace the following volume of headspace gases:

1. Storage tanks 635,000 ft^3
2. Loading 460,000 ft^3

Calculation of emissions:

From Fig. 2.2 from the Draft Mitre report the vapor pressure of Aroclor 1242 is 3 mm Hg at 100°C and 10^{-4} at 21°C. The aroclors are stored at 100°C. It may be assumed that the temp. in the tanks being loaded would be approximately 70°F (21°C).

From Dolton's law of partial pressure:

$Bx = \frac{Px}{P\ mix.}$ where Bx = proportion by volume of a gas component

Px = partial pressure of gas component and
P mix. = absolute pressure of gas mixture.

$Bx = \frac{3}{760} = \frac{0.0039}{1}$ or 3900 ppm at 100°C

To change ppm to mg/M^3 use the following formula:

$$mg/M^3 = ppm \times \frac{mol.\ wt.}{molecular\ volume}$$

mol. wt. = 261

molecular volume = 30.62 liters/mol. at 100°C

$mg/M^3 = 3900 \times \frac{261}{30.62} = 33242$

Emissions from storage tanks:
Emissions kg/year = Vol. of gas displaced/year x concentration of PCB

$Kg/yr = 635000\ ft^3 \times .0283 \frac{M^3}{ft^3} \times 33242 \times \frac{1\ kg}{10^6\ mg}$

kg/year = 597.4

Emissions from loading operations:

$Bx = \frac{Px}{P\ mix.} = \frac{10^{-4}}{760} = 1.3 \times 10^{-7}$ or .13 ppm

$mg/M^3 = .13 \times \frac{261}{24.04} = 1.41\ mg/M^3$

Emissions:

$$\text{Kg/yr.} = 460{,}000 \times .0283 \times 1.41 \times \frac{1\ \text{kg}}{10^6\ \text{mg}}$$

$$\text{Kg/yr.} = 0.0184$$

Emissions from handling of waste aroclors:

Total waste material received into plant as reported by Monsanto for 9 mos. of 1975 - 1,431,000 lbs. Assume that all this material is received and stored at 70°F and that it displaced an equal volume of tank headspace gas at 70°F.

$$\text{Volume of produce} = 1{,}431{,}000\ \text{lbs.} \times \frac{1\ \text{gal.}}{11.5\ \text{lbs.}} \times 3.785\ \frac{\text{liter}}{\text{gal.}}$$

$$\frac{1}{X10^3\ \frac{\text{liters}}{M^3}} = 471\ M^3$$

The concentration would be the same as in the loading operation that is 1.41 mg/M^3.

Emissions:

$$\text{Kg/yr.} = 471\ M^3 \times 1.4\ \text{mg}/M^3 \times \frac{1\ \text{kg}}{10^6\ \text{mg}}$$

$$\text{Kg/yr.} = .00066$$

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

5

SUBJECT: PCB Monitoring - Monsanto, Krummrich Plant, Sauget, Illinois. DATE: FEB 13 1976

FROM: Charles Miller/Ed Zylstra/John Connell, Technical Advisors, SPS

TO: Gerald F. Regan, Chief, Air Surveillance Branch

On January 27, 1976, the SPS field team (Miller, Zylstra, Connell) performed ambient air monitoring for PCB's at the Monsanto Krummrich Plant, Sauget, Illinois. Although Monsanto presently manufactures PCB's at this facility, production of PCB's is to be gradually phased-out.

After a brief discussion and orientation period with Monsanto officials, ASB and ILDO personnel toured the PCB manufacturing area including the incinerator facility. The "plant" area where PCB's are manufactured is not an enclosed structure per se. It is an open structure constructed of steel grating (floors, stairs), safety railings, a maze of piping, collection and reaction vessels, valves, etc. all of which are completely exposed to the elements. Mr. Claire Buckley of Monsanto was assigned as escort for ASB personnel.

Only two locations were deemed appropriate as sampling sites for PCB's. Other possible sites were inaccessible or had recently been tested by Monsanto - ie. - the recent incinerator test results were furnished by Monsanto. These two sampling locations, the cleaning of glassware, equipment used, sampling procedure, samples obtained, etc. is described below:

Site Location #1 (SEG) - Steam Ejector - Ground Level.

This steam ejector pipe terminated just above a grate which covered a recessed concrete trough in the floor at ground level. For collection of the samples, the SPS field team used the glass bubblers, Y-connector with reducer coupling, U-tube, cold trap and vacuum pump. The H-frame base, and 2x4 manifold support and glass manifold were not used. Sampling was performed for a one-hour period, 1046 - 1146 hours.

Site Location #2 (SET) - Steam Ejector - Top Level or 2nd Level Above Ground.

These twin steam ejector pipes (somewhat of a candy-cane configuration) terminated out beyond the 2nd level safety railing. Sample collection was performed using the same equipment as at Site Location #1 and included the H-frame base, one section of 2x4 manifold support, and one section of glass manifold. Sampling was performed for a one-hour period, 1205 - 1305 hours.

The following narrative defines the process for cleaning of the sampling glassware, the actual preparation for sampling, and handling of the samples collected in the bubbler train.

The ASB, SPS field team cleaned all PCB monitoring glassware via the following procedure:

1. Thoroughly wash all glassware with a solution of PCB free detergent. The concentration of the detergent is determined by the manufacturer's instructions.
2. Rinse thoroughly with tap water.
3. Rinse thoroughly with distilled water.
4. Rinse thoroughly with acetone (reagent grade or better).
5. Rinse with hexane, rinse each bubbler three times with 50 ml. of hexane for each rinse and discard.
6. Wrap all small glass parts in aluminum foil and ensure proper sealing, crimping of the foil. Seal all ball joints of the bubblers with aluminum foil (alternately, appropriate ball joint fittings - sealed on one end and thoroughly cleaned - may be clamped in place instead of using aluminum foil; the purpose of the above is to prevent contamination of the now PCB free glassware).

Upon determination of a sampling site location, the sampling equipment supportive framework is set-up and all glassware bubbler box, pump, etc. are positioned. The sampling procedure is as follows:

1. Remove seals (foil or ground joints and clamps) from the bubblers.
2. Place 300 ml. hexane into bubbler #1, shake, pour into bubbler #2, shake, pour into bubbler #3, shake, pour into a sample bottle appropriately designated as a reagent blank. This procedure is performed for both sides (A and B) of the sampling train.

3. Pour hexane, 400 ml., 200 ml., and 300 ml. into bubblers #1, #2, and #3, respectively.

4. Connect the entire sampling system - U-tube, manifold, reducer coupling, Y-tube, U-tubes between each bubbler and the copper tee (containing hypodermic needles - one for each side), the quick - disconnects between the tee and the cold trap and between the cold trap and the vacuum pump. Ensure that all ball joints are tightly clamped. Do not use any lubricant/sealing compound on the ground glass ball joints.

5. Fill the plywood box (containing 4 of the six bubblers) and the cold trap with crushed dry ice.

6. Start the vacuum pump; note the time and vacuum gage reading; sample for one-hour.

7. At the conclusion of the one-hour sampling period, note vacuum gage reading, tightly double the rubber hose between the copper tee and the quick-disconnect thus stopping air flow, pull both disconnects apart, and release the previously clamped or kinked rubber hose; shut off the vacuum pump.

8. Disconnect the Y-tube from the train.

9. Disconnect the bubbler U-tubes and the rubber hose - glass connection from last bubbler to the copper tee on one side of the train.

10. Pour the absorbing solutions from one side of the train (3-bubblers) into one sample bottle appropriately identified. All sample bottle screw caps must have Teflon liners. Absorbing solutions and rinses from each side of the train must be in separate sample bottles - 1 bottle per side of train.

11. Introduce approximately 50 ml. of hexane into bubbler #1, shake, pour into bubbler #2, shake, pour into bubbler #3, shake, and pour into the appropriate sample bottle from Step 10 above. Repeat this with another 50 ml. portion of hexane. Repeat for the second or other side of the sampling train.

12. Introduce 300 ml hexane into bubbler #1, shake, pour into bubbler #2, shake, pour into bubbler #3, shake, and pour into another appropriately identified sample bottle. This is also a reagent blank. Repeat for the other side of the train.

13. The bubblers can now be properly filled with the designated amounts of hexane (400 ml., 200 ml., 300 ml.) for the next sampling period. If additional sampling is not required, the equipment (glassware) must be wrapped/sealed as defined in Step #6 of the cleaning procedure.

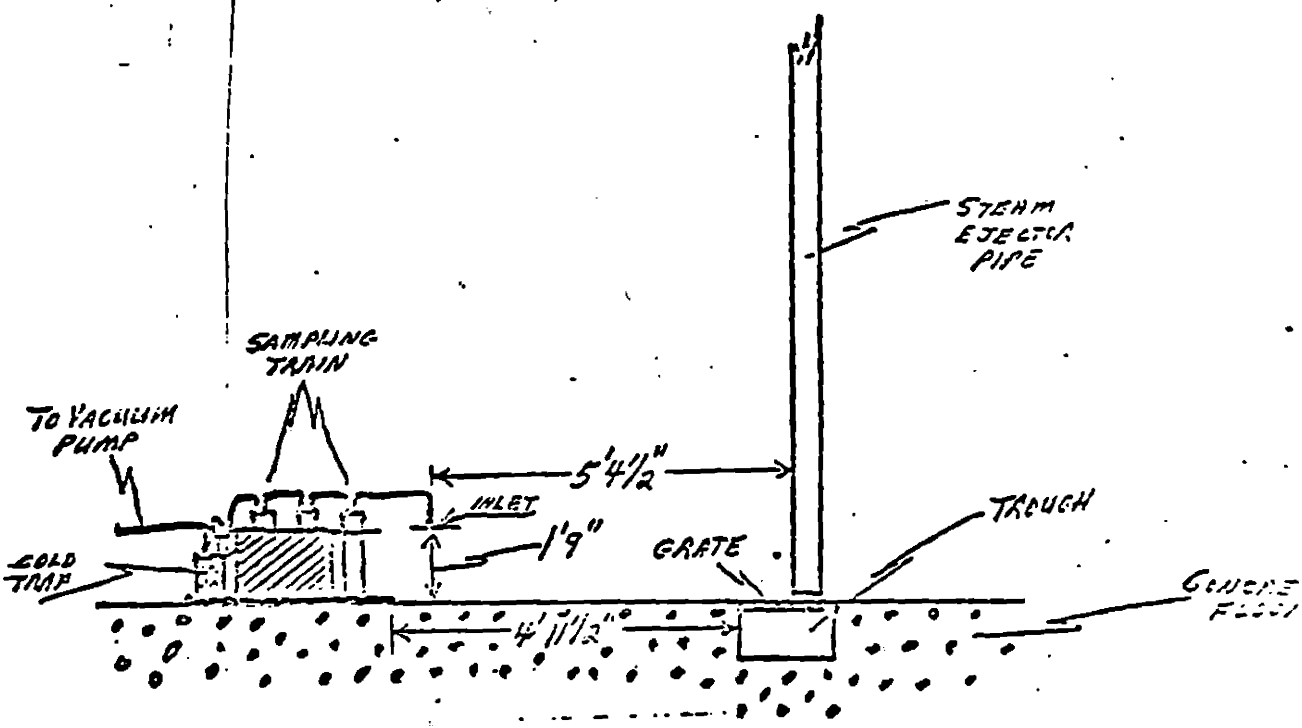
cc: Timm
Hallgren
Torrez
Zylstra
Connell

ACM CC8428

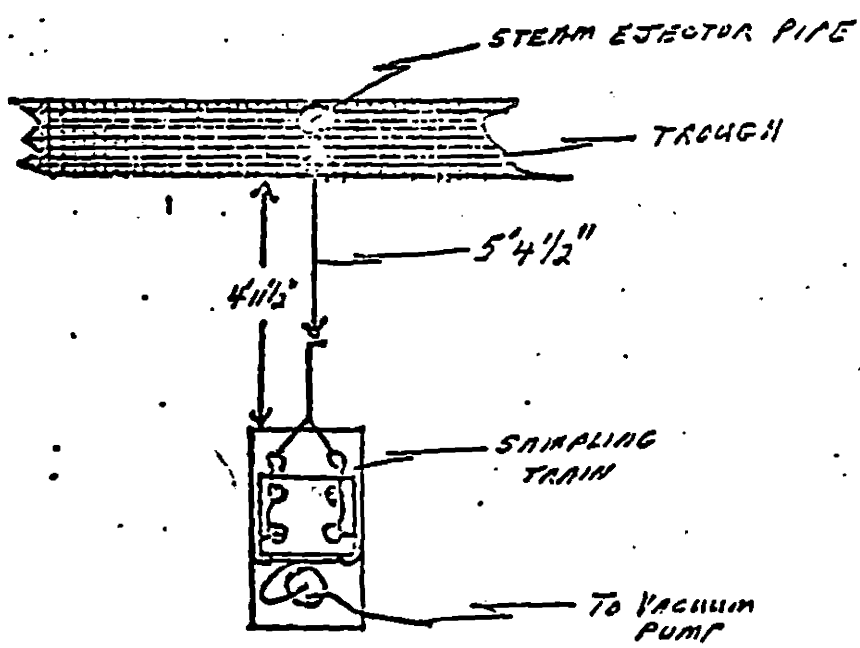
The table below defines the various samples collected at the Monsanto PCB manufacturing facility:

DATE	LOCATION	ASB DESIGNATION	LAB. NO.
1/27/76	Reagent Blank, Pre (SEG)	3A-T27-1	76-13656
1/27/76	Reagent Blank, Pre (SEG)	3B-T27-2	76-13657
1/27/76	Sample (SEG)	3A-T27-3	76-13658
1/27/76	Sample (SEG)	3B-T27-4	76-13659
1/27/76	Reagent Blank, Pre (SET)	3A-T27-5	76-13660
1/27/76	Reagent Blank, Pre (SET)	3B-T27-6	76-13661
1/27/76	Sample (SET)	3A-T27-7	76-13662
1/27/76	Sample (SET)	3B-T27-8	76-13663
1/27/76	Reagent Blank, After (SEG) Sample	3A-T27-9	76-13664
1/27/76	Reagent Blank, After (SEG) Sample	3B-T27-10	76-13665
1/27/76	Reagent Blank, After (SET) Sample	3A-T27-11	76-13666
1/27/76	Reagent Blank, After (SET) Sample	3B-T27-12	76-13667

SITE LOCATION #1 (SEG)



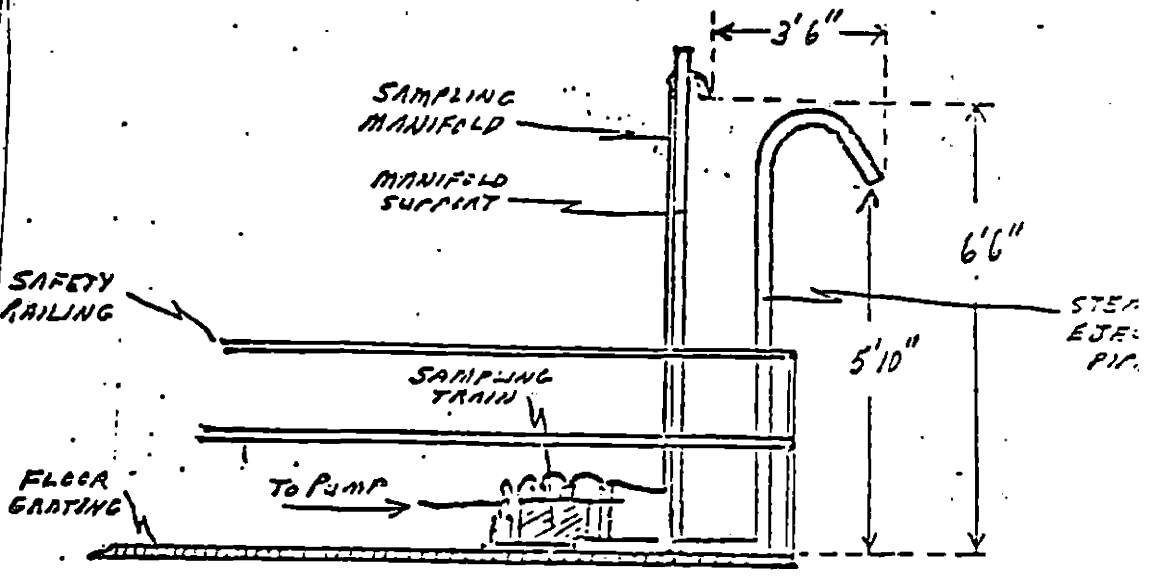
SIDE VIEW



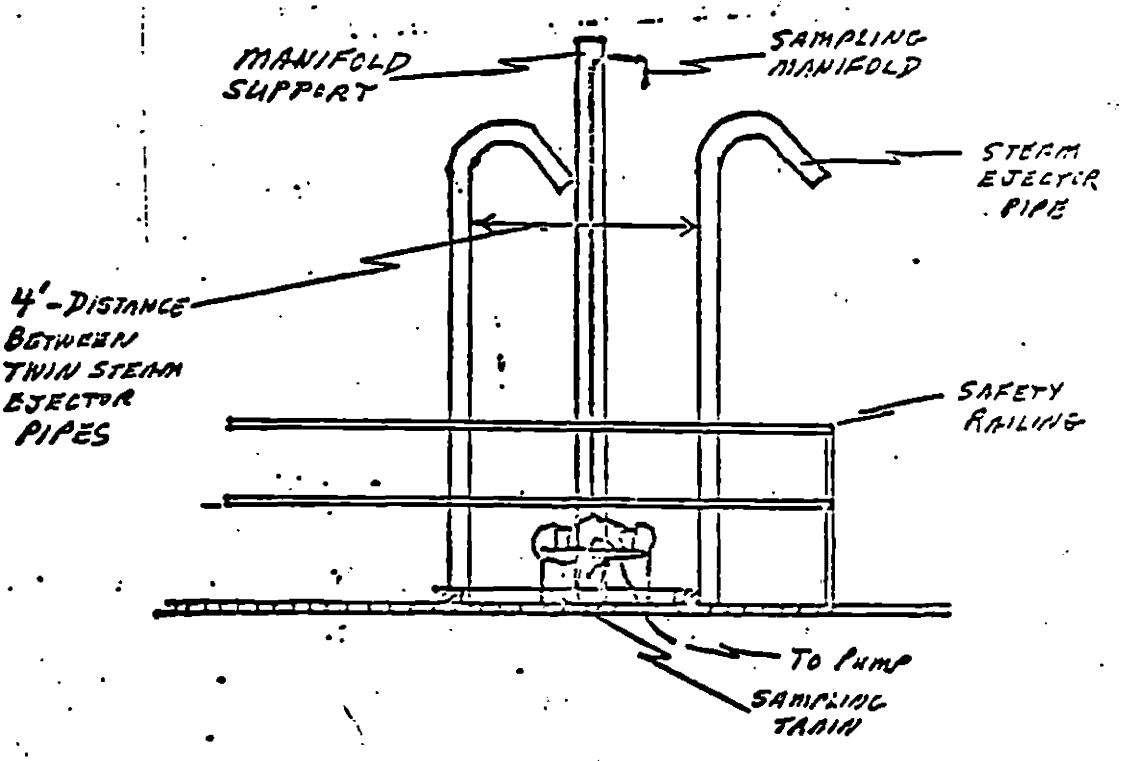
TOP VIEW

ACM CC843C

SITE LOCATION #2 (SET)



SIDE VIEW



FRONT VIEW

ACM CC6431

U. S. ENVIRONMENTAL PROTECTION AGENCY
REGION V, CENTRAL REGIONAL LABORATORY
1819 W. PERSHING ROAD, CHICAGO, ILLINOIS 60609

DATA TRANSMITTAL SLIP

Date: Feb. 26, 1976

TO:

Chief, Air Surveillance Branch
Surv. & Anal. Division

DATA IDENTIFICATION

Data - Sample Numbers 13652--13667

RECEIVED
FEB 27 1976
AIR SURVEILLANCE BRANCH
EPA, REGION V

REMARKS

FROM

DATA COORDINATOR, CENTRAL REGIONAL LABORATORY

ADP CCE432

CRL-SAN [illegible]

ENVIRONMENTAL PROTECTION AGENCY, REGION V BASIC DATA FORM

AIR SURVEILLANCE BRANCH

Sampling Date 1-27-76 (Day Month Year) Lab Arrival Date 1-28-76 (Day Month Year) Analysis Due Date [illegible] Data

AIR SAMPLES (SAMPLE)

Account No. _____ Study PCB

All units are micrograms per liter or milligrams-per-kilogram

Water				39500	39504	39508						
CRL Sample Log Number			[illegible]	Aroclor 1248	Aroclor 1254	Aroclor 1260						
Sediment	HYCO NUCLEPORE		[illegible]	39503	MICROGRAMS/M³	39511	MONSANTO - SAUGET, ILL. 1015					
1 5 6 5 4	3A		7.0		9.80		REAGENT BLANK BAE-S	BLANK AIR EJ	CR-GROUND	LEVEL		
5 5 7	3B		4.7		2.39		"	"	"	"		
5 5 3	3A		31.5		44.12		SAMPLE STEAM	EJECTOR	-GROUND	LEVEL		
5 5 2	3B		25.0		39.31		"	"	"	"		
5 6 9	3A	[illegible]	[illegible]				REAGENT BLANK AIR ST	BLANK IN EJECTOR	-TOP	LEVEL		
5 6 1	3B		12.1		19.03		"	"	"	"		
5 6 2	3A	3 65	72.5		101.54		SAMPLE STEAM	EJECTOR	-TOP	LEVEL		
[illegible]	3B		[illegible]				"	"	"	"	[illegible]	[illegible]
5 5 4	3A		16.8		23.53		REAGENT BLANK AFTER	STEAM	EJECTOR	GROUND	LEVEL	
5 5 5	3B		3.3		5.19		"	"	"	"	"	
5 6 8	3A	[illegible]	[illegible]				REAGENT BLANK AFTER	STEAM	EJECTOR	-	LEVEL	
5 6 7	3B		8.4		13.21		"	"	"	"		
			3A - FLOWRATE		.91402	m³/Sec						
			" "	"	[illegible]	m³/Sec						

ACM C06433

1.06

ACM CC6434

Monsanto-Sauget, Illinois

Sampling Location	Sample No.	Critical Orifice Flowrate m^3/hour	Reagent Blank Values Before & After Each Sample ug/sample	Average Reagent Blank Values ug/sample	Sample Values ug/sample	Difference-Sample Minus Ave. Blank Value	Final Value ug/m^3
Site #1							
Steam Ejector-Ground Level (SEG)	76-13658	3A-0.71402	7.0 / 16.8	11.9	31.5	19.6	27.5
	76-13659	3B-0.63602	4.7 / 3.3	4.0	25.0	21.6	33.9
Site #2							
Steam Ejector-Top Level-(SET)	76-13662	3A-0.71402	N.A. / N.A.		72.5		
	76-13663	3B-0.63602	12.1 / 8.4	10.3	N.A.		

Monsanto

Interpretation of the data chart:-

Column 1- Sampling Location - corresponds to the preceding narrative defining sampling sites.

Column 2- Sample Numbers - assigned by ASB and for use by the analytical laboratory.

Column 3- Critical Orifice Flowrate (m3/hour) - calibrated flowrate of the critical orifice utilized on each side of the sampling train.

Column 4- Reagent Blank Values - Before and After Each Sample (ug/sample_ - defines the analytical results determined for each reagent blank.

Column 5- Average Reagent Blank Values - simply the average of the two values in the preceding column.

Column 6- Sample Values (ug/sample) - analytical results of the samples submitted.

Column 7- Difference - Sample Value Minus Average Blank Value - defines a value representing only the sample.

Column 8- Final Value (ug/m3) - defines the final or actual value of PCB's obtained at the particular sampling location; determined by dividing the true sampling air flowrate into the corrected value (Column 7).

Environmental Polychlorinated Biphenyl Contamination near Sites of Manufacture and Use

prepared by

Environmental Science and Engineering, Inc.
P.O. Box 1354, Gainesville, Florida 32604

for

OFFICE OF TOXIC SUBSTANCES
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Contract 68-01-2978

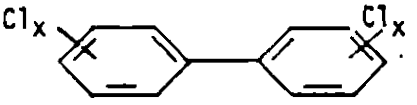
July 1975

ACM CC8443

PLAINTIFF'S EXHIBIT 926

INTRODUCTION

Polychlorinated biphenyls (PCBs) have a basic chemical structure as follows:



From one to ten chlorine atoms may be attached to the structure resulting in 210 possible isomers. PCB's have certain physical properties; including high heat capacity, chemical stability, and excellent dialectric properties which make them highly desirable for a number of industrial uses. Concern has been expressed in recent years over the widespread dispersion of PCB's in the environment. These compounds are suspected to have significant adverse effects on organisms at the top of the food web, including man. Biomagnification of this contaminant in natural predator-prey food chains has been documented by numerous studies. To complicate the problem, the rate of degradation of PCB's in the environment, particularly the higher substituted isomers, is postulated to be extremely slow. This situation allows for the possibly significant accumulation of these persistent chlorinated organic compounds in the environment. A thorough discussion of the problem and of the environmental data that are available has been presented by Selikoff (1972) and the U.S. Government Interdepartmental Tasks Force (1972).

In response to the rising concern over PCB's in the environment, the single domestic manufacturer of these materials (Monsanto Co.) has voluntarily taken two actions to reduce the environmental hazard. The trade name for these domestically-manufactured compounds is Aroclor. Beginning in 1970, the production of Aroclor was voluntarily reduced by the manufacturer and supply was discontinued to those users who could not control release to the environment. Production of the more highly chlorine substituted Aroclor mixtures has since been curtailed or discontinued and a lower-substituted, refined mixture (Aroclor 1016) has been introduced. Some researchers have concluded that the lower substituted PCB isomers do not persist as long in the environment as the higher substituted isomers, and that they may be amenable to biological degradation. Aroclors are still employed in electrical capacitors, transformers, vacuum pumps and gas-transmission turbines (Hutzinger, Safe and Zitko, 1974).

There are a number of foreign producers of PCB. The major foreign products are listed in Table 1. Some domestic industries, whose supply of Aroclor has been curtailed by the producer, have turned to foreign supplied PCB's. The extent of the use of these foreign products in the U.S. is not know at the present time.

The Environmental Protection Agency, Office of Toxic Substances has undertaken an environmental monitoring program to assess the magnitude and potential hazard of PCB contamination of the environment and to assess the effectiveness of voluntary controls on use of these compounds. The first phase of this monitoring program has been completed. The initial effort was directed toward the evaluation of PCB contamination

Table 1. THE WORLD'S MAJOR PRODUCERS OF PCB*

Producer	Country	Tradename of PCB
Monsanto	U.S.A. and Great Britain	Aroclor
Bayer	Germany	Clophen
Prodelec	France	Phenoclor and Pyralene
Kanegafuchi	Japan	Kanechlor
Mitsubishi-Monsanto	Japan	Santotherm
Caffaro	Italy	Fenclor
Sovol	U.S.S.R.	
Chemko	Czechoslovakia	

*after Hutzinger, Safe and Zitko (1974).

of soils in the vicinity of potential industrial sources and of waste-waters from these sources.

Soil samples have been taken in the vicinity of Yates Manufacturing Co. in urban Chicago, Illinois; Valcast, Inc. in Troy, Michigan, a suburb of Detroit; and the Monsanto Co., Krummrich Plant in Sauget, Illinois, near East St. Louis. Prior to 1972, the Yates Manufacturing Co. used Aroclors 5460, 6090 and 5442 in the production of wax mold material for the investment casting (lost wax) process. These mixtures contain both PCB and polychlorinated terphenyl (PCT). Subsequent to 1972, this company has been purchasing a PCB of foreign origin. Fenclor DK, a product of Caffero Corporation in Milan, Italy, has been substituted for the unavailable Aroclors. Valcast, Inc. is an investment casting facility. It has been reported that Valcast purchases the necessary wax compounding materials from Yates Manufacturing Co. The Krummrich Plant of Monsanto Co. is the only PCB production facility in the U.S. All domestic Aroclors are produced at this location.

EXPERIMENTAL

Sampling Methods

Surface soil samples were collected at each site from the plant boundary to a distance of approximately one mile at ¼ mile intervals in each direction subject to the physical constraints encountered. At each sample point, five sub-samples were collected within a radius of 10 m to a depth of 2.5 cm over a 100 cm^2 area. This mode of sampling, which was designed to collect a homogeneous surface soil sample representative of the chosen sample point, is illustrated in Figure 1. Vegetative matter was removed with forceps and the five sub-samples were composited and thoroughly mixed. Every attempt was made to select sample points where surface vegetation was sparse and where it appeared unlikely wind scour would be a major soil transport factor. Samples were placed in pre-cleaned, wide-mouth glass jars with aluminum foil-lined closures.

Water samples were collected from a drainage ditch adjacent to the Valcast plant, of Valcast effluent cooling water and from the sanitary sewer system downstream of Valcast. Wastewater samples were taken from the influent and effluent of the Sauget, Illinois sewage treatment plant. The Monsanto facility uses this treatment plant for wastewater treatment. These latter water samples were 24-hour composites of the treatment plant influent and effluent; the former were grab samples. All samples were taken in 1 l. glass containers, composited and stored in 4 l. pre-cleaned glass-stoppered reagent bottles.

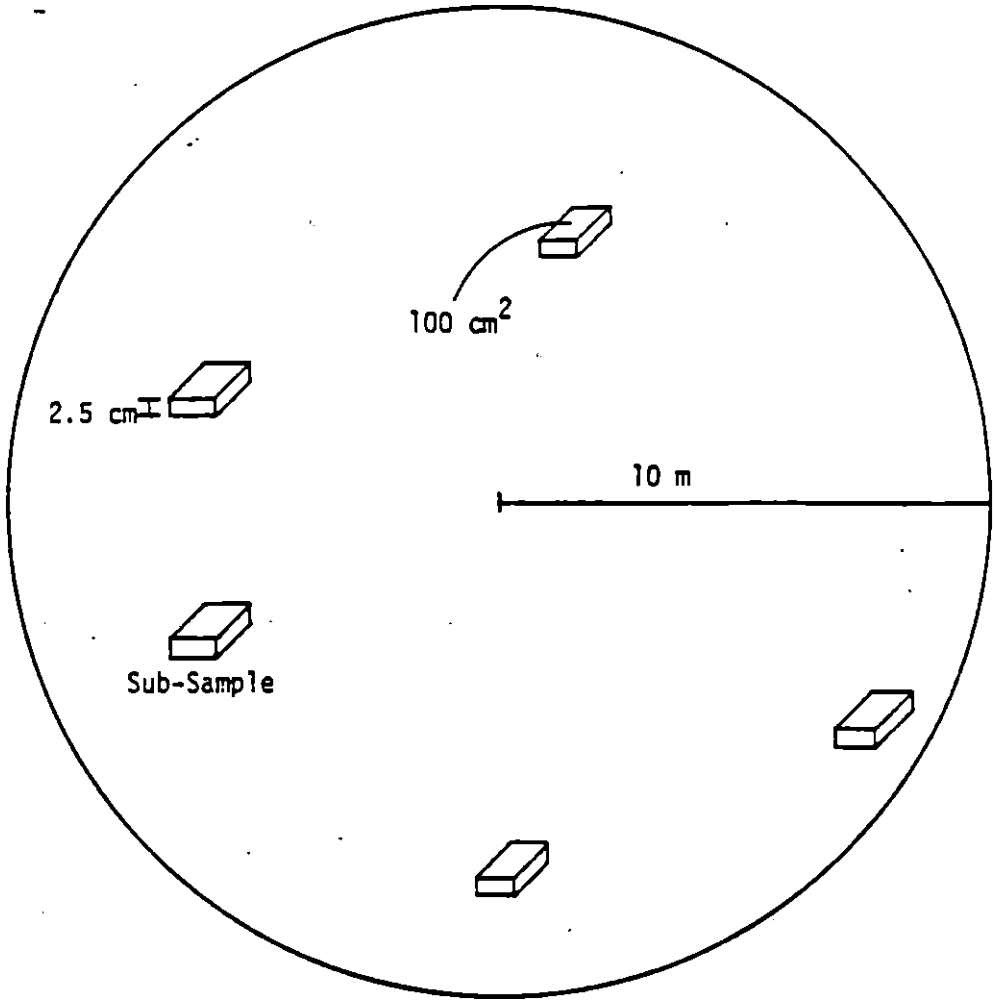


Figure 1. Diagram showing surface soil sampling method. Not to scale. Five sub-samples are composited to yield a single sample.

Extraction and Concentration

The soil sample is thoroughly mixed and sectioned into quarters. Two of the quarters are rejected and the remaining quarters are again mixed and quartered. This is continued until a representative sample size of about 50 g is obtained. This sample fraction is allowed to air dry at room temperature. PCBs are extracted from the soil using a soxhlet apparatus and 75 ml of 1:1 nanograde hexane/acetone for a 10 g soil sample. The extract is concentrated to 5 ml on a Kuderna-Danish apparatus and dried with sodium sulfate. This concentrate is evaporated to dryness under dry N_2 at room temperature then redissolved in 1 ml of nanograde hexane. This procedure basically follows that described by the EPA (1974).

Water samples are triple extracted with 15 percent nanograde ehtyl ether in hexane, dried with sodium sulfate, concentrated on a Kuderna-Danish apparatus, evaporated to dryness under N_2 and redissolved in 1 ml nanograde hexane. This method is similar to that recommended by the EPA (1973).

Sample Cleanup

Both the soil and water extracts are cleaned-up by the use of a silica-gel column. The column is eluted with nanograde pentane followed by nanograde benzene. The PCBs present in the extract appear in the pentane fraction; pesticides appear in the benzene fraction. The pentane fraction is further treated with concentrated H_2SO_4 to eliminate unstable organic compounds. The silica gel separation procedure is described by Snyder and Reinert (1971). The sulfuric acid cleanup was adapted from Murphy (1972).

Analytical Methods

All analyses are by gas chromatography. A dual-column Varian 2760 instrument is employed with the following conditions:

a) detection and quantifications

glass column, 6' length, 1/8 ID
1.5%/1.95% OV-17/QF-1 liquid base
Chrom W-HP, 80/100 mesh support
N_2 38 psig inlet pressure, 68 ml/min
detector temperature 225° C
column temperature 200° C
injector temperature 215° C

b) confirmation

stainless steel column, 5' length, 1/8 ID
1.5% OV-101 liquid phase
Chrom G-HP, 100/120 mesh support
N_2 30 psig inlet pressure, 43 ml/min
detector temperature 225°C
column temperature 205° C
injector temperature 210° C

Detection is by electron capture using a tritium detector. Mass spectrographic confirmation has also been obtained on selected samples.

The PCBs are quantified in a two-step process. First, the elution pattern is compared to those of standard mixtures and the closest pattern match is considered to be the PCB present. The relative peak heights in a mixture are a good indication of a match with a standard, as is the presence or absence of later eluting peaks. Good matches with standard Aroclor mixtures have been obtained. The presence of decachlorobiphenyl is easy to ascertain since it is a single peak. Once the elution pattern is subjectively matched to a standard PCB pattern, quantification is conducted by electronic integration of peak areas using a Hewlett-Packard Integrator Model 3380A. The total area of all accepted matching peaks in the elution pattern of the sample is compared

with the total area of the same peaks in the standard mixture and a sample concentration is calculated.

The Aroclors used for preparation of standards were obtained from the Monsanto Company and the EPA Southeast Environmental Research Laboratory. Fenclor DK was provided by EPA Region V personnel.

Sample Replication and Recovery Studies

A number of replicate analyses were conducted to determine the reproducibility of both the analytical method and the sampling method. The results of these replications are tabulated in Tables 2 and 3. All replications conducted to date are of soil samples. Table 2 lists the results of the analysis of two fractions of a single soil sample. Table 3 lists the results of the analysis of replicate samples and, hence, represents both sampling and analytical variability.

The results of several PCB recovery studies are tabulated in Table 4.

Table 2. ANALYTICAL REPLICATES OF SOIL SAMPLES

Replicate	Aroclor 1260 (ppm)	Decachlorobiphenyl (ppm)
Y-1	0.86	0.65
	0.51	0.50
	mean 0.69	mean 0.58
V-1	<0.01	
	0.11	
	mean 0.06	
V-2	0.07	
	<0.01	
	0.01	
	mean 0.04	
V-3	0.13	
	0.11	
	mean 0.12	
V-4	0.13	
	0.15	
	mean 0.14	
V-5	<0.01	
	<0.01	
	<0.01	
V-6	<0.01	
	0.03	
	0.04	
	mean 0.02	
M-1	0.06	0.084
	0.13	0.16
	mean 0.10	mean 0.12
M-2	0.21	0.066
	0.30	0.096
	mean 0.26	mean 0.081
M-3	1.8	0.95
	0.95	0.84
	mean 1.4	mean 0.90
M-4		0.49
		0.67
		mean 0.58

Table 3. SAMPLE REPLICATES OF SOIL SAMPLES

Replicate	Aroclor 1260 (ppm)	Decachlorobiphenyl (ppm)
Y-1	0.53	1.0
	0.40	1.4
	mean 0.47	mean 1.2
M-1	9.8	1.3
	9.3	1.0
	mean 9.6	mean 1.2
M-2	0.12	0.015
	0.46	0.069
	mean 0.29	mean 0.042
M-3	0.23	0.64
	<0.01	0.58
	0.12	mean 0.61

Table 4. RESULTS OF RECOVERY STUDIES FOR PCBs

PCB Type	Percent Recovery
Aroclor 1242	105
Aroclor 1260	85
Aroclor 1260	122

RESULTS AND DISCUSSION

PCBs were detected in soils at all three sampling locations. The elution patterns obtained most closely matched Aroclor 1242, Aroclor 1260 and decachlorobiphenyl. Soil concentrations ranged from the detection limit of 0.001 ppm to over 20 ppm.

Data from Vicinity of Yates Manufacturing Co., Chicago, IL.

Figure 2 illustrates: a) a chromatogram of Fenclor DK, the foreign supplied PCB presently used by Yates Mfg. Co. in the production of investment casting wax compounds; b) a chromatogram of a standard Aroclor 1260 and; c) a typical chromatogram of a soil extract taken in the vicinity of the site.

Figure 2a demonstrates that Fenclor DK is nearly pure decachlorobiphenyl. This compound is unusually pure for a technical grade material. One minor peak elutes just before the predominate decachlorobiphenyl peak. The retention time of the minor contaminant peak is such that it may be expected to be an octachlorobiphenyl since it exhibits the same retention time as the latest eluting peak in a standard Aroclor 1260 mixture. It is apparent by comparison of peak retention times with the sample chromatogram, Figure 2c, that decachlorobiphenyl is present in the soil sampled. The measured concentration of decachlorobiphenyl in this particular sample was 1.0 ppm. The presence of decachlorobiphenyl in this sample has been confirmed by mass spectrometry. Figure 3 illustrates a portion of the mass spectrum of the sample and a standard decachlorobiphenyl obtained from a different source.

The sample elution pattern also indicates the presence of Aroclor 1260 as can be seen by comparison with the Aroclor 1260 elution pattern.

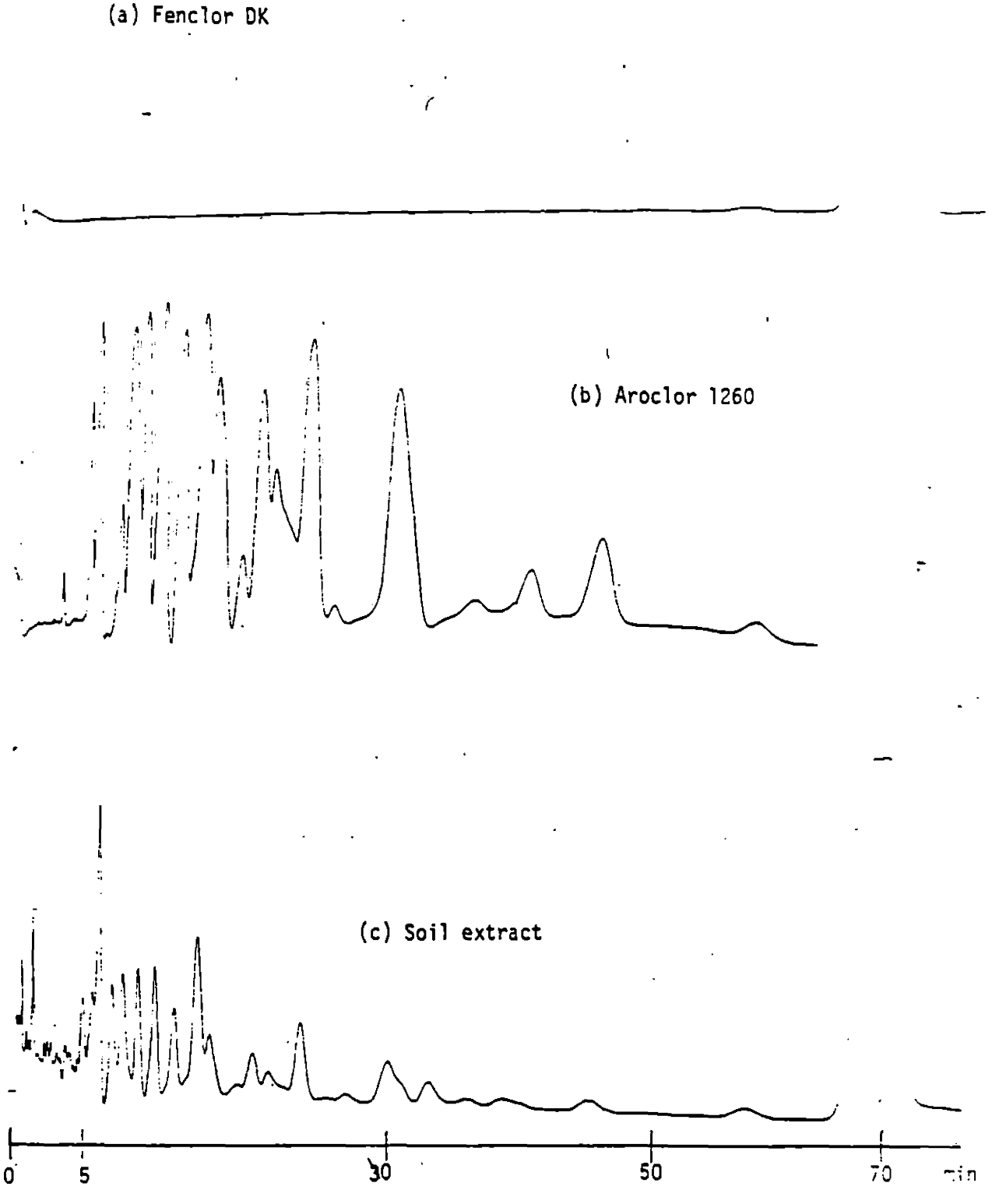


Figure 2. Typical chromatograms of standard PCBs and of a soil sample taken in the vicinity of Yates Mfg. Co., Chicago, Illinois.

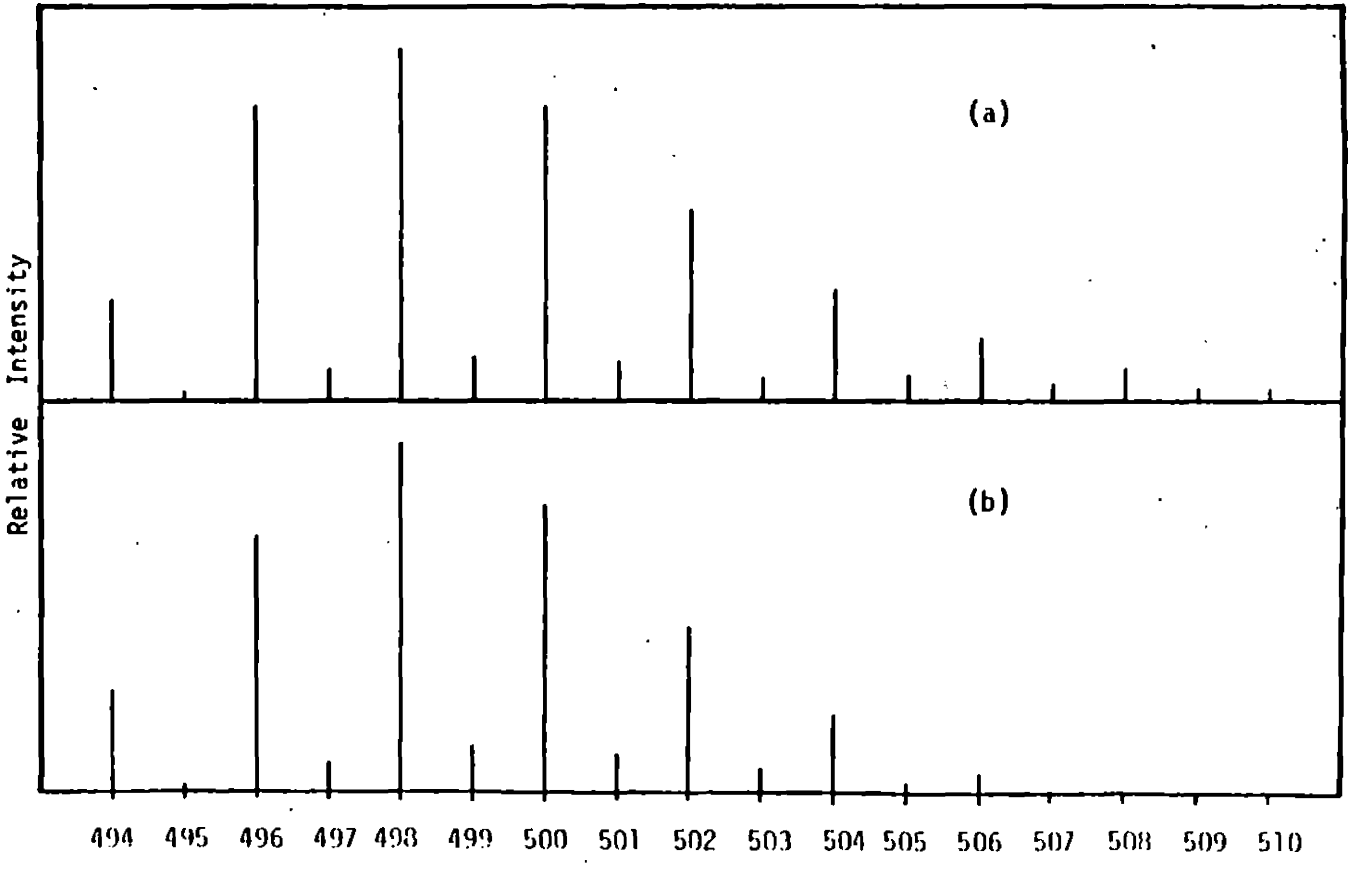


Figure 3. (a) Portion of mass spectrum of sample taken in vicinity of Yates Mfg. Co.
(b) Parent molecule mass cluster of decachlorobiphenyl.

ACM CC8458

The concentration of Aroclor 1260 in this sample is 0.53 ppm. There is no indication of degradation of the Aroclor 1260 since virtually all peaks in the sample chromatogram are present in the same relative proportion as in the standard. There are no significant, undefined peaks in the chromatogram following the acid cleanup procedure. Certain of the sample chromatograms indicate the presence of lower weight PCBs, however the quantities present tend to be far less than either Aroclor 1260 or decachlorobiphenyl at this site.

Figure 4 depicts the quantity of Aroclor 1260 measured in samples taken in the vicinity of Yates Mfg. Co. There exists no apparent spatial pattern of Aroclor 1260 distribution over the study site. There is little to indicate the source of the Aroclor 1260 contamination is Yates Mfg.Co. Aroclor 1260 has not, in fact, been used by Yates. Prior to 1972 Aroclors 5442, 5460, and 6090 were purchased by this company. Subsequent to 1972, Fenclor DK and Aroclor 5460 have been in use. Aroclors 5442 and 5460 are terphenyl mixtures with 42 percent and 60 percent chlorine by weight, respectively. Aroclor 6090 is 90 percent terphenyl and 10 percent Aroclor 1221. Aroclor 1221 does not appear in the soils at this site.

Figure 5 illustrates the distribution of decachlorobiphenyl in soils near the Yates facility. The distribution has some elements of a pattern of higher levels closer to the Yates facility with decreasing concentration with distance. Such a pattern may be expected if Yates were the source of the decachlorobiphenyl (or Fenclor DK) contamination.

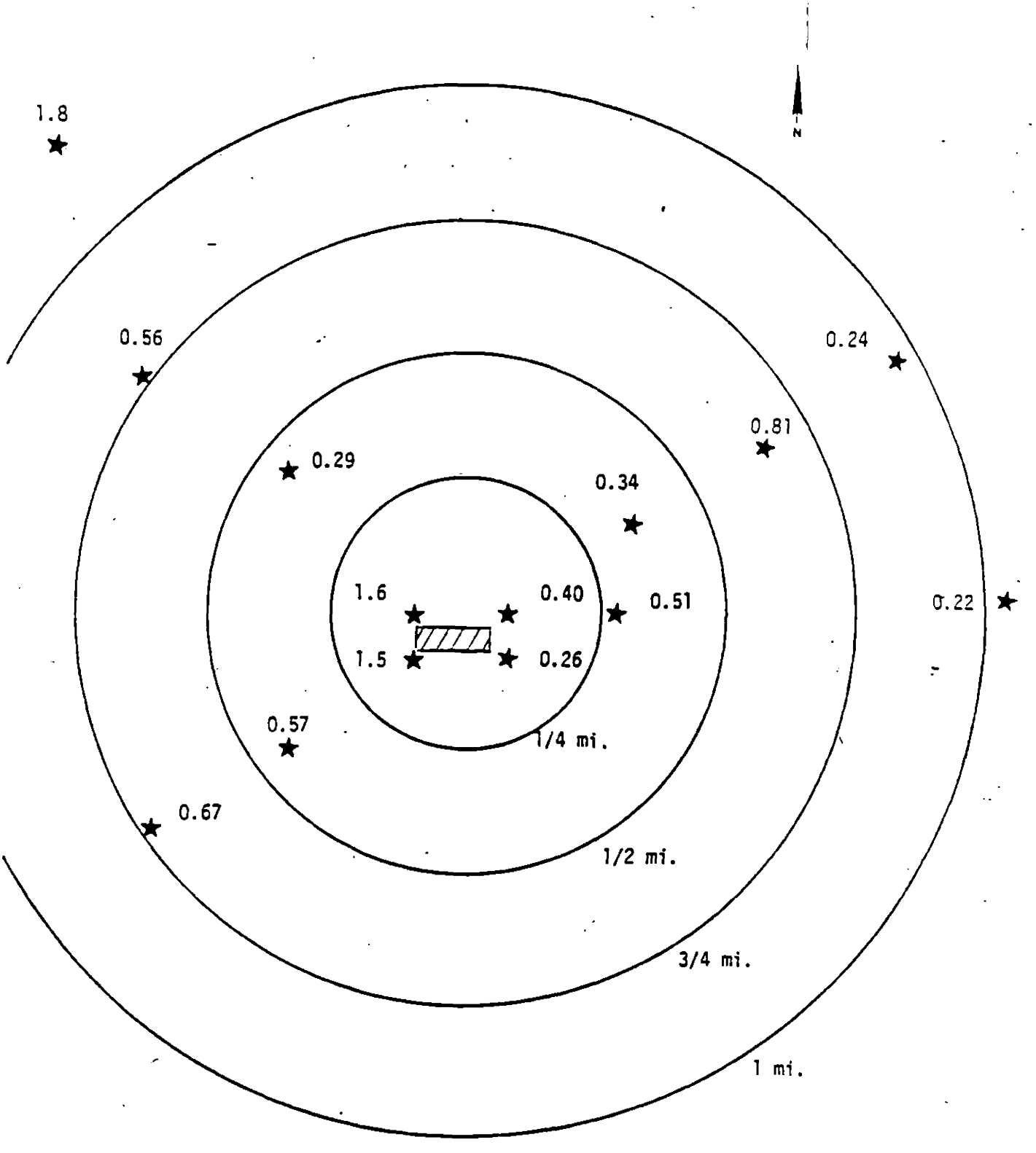


Figure 4. Concentration of Aroclor 1260 in soil as a function of distance from Yates Mfg. Co. Concentrations are expressed in ppm.

ADM CC646C

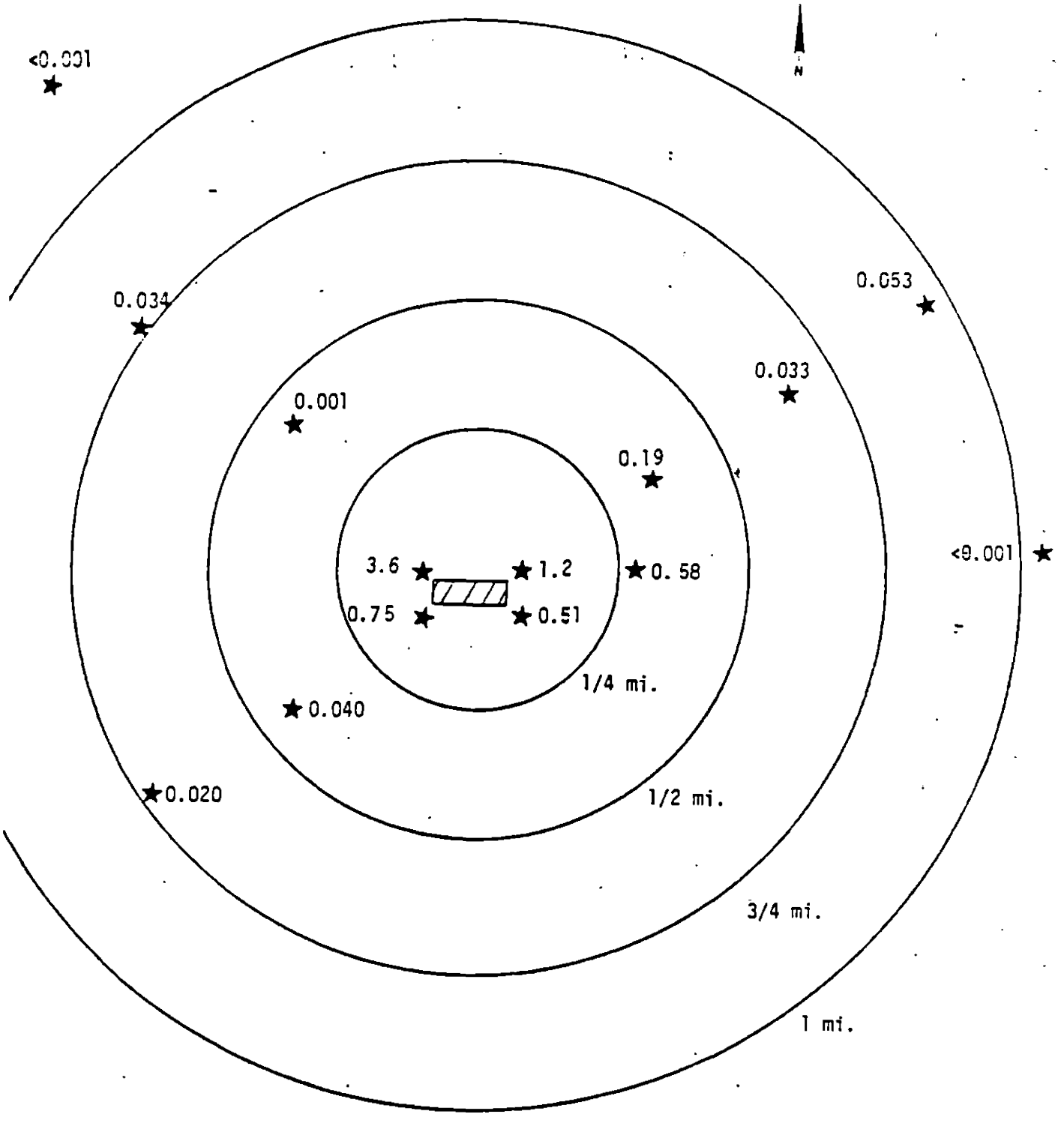


Figure 5. Concentration of decachlorobiphenyl in soil as a function of distance from Yates Mfg. Co. Concentrations are expressed in ppm.

ADM CC6461

Data from Vicinity of Valcast Corp., Troy, MI.

Valcast Corp. is an investment casting facility located in a small industrial park in suburban Detroit, MI. PCBs are a constituent of the wax mold compound used to fashion intricate shapes which are to be cast. Figure 6 is a typical chromatogram of a soil sample extract taken from this location. Aroclor 1260 is present in many of the soil samples. Decachlorobiphenyl is absent in the soils. Figure 7 shows the concentrations of Aroclor 1260 observed in the vicinity of Valcast Corp. No distribution pattern is evident. The one observed concentration of 18 ppm Aroclor 1242 appears to be anomalously high, however, replicate analysis yielded values of 16 ppm and 19 ppm, respectively. Aroclor 1242 was not detected in any other soil samples from this area.

A small drainage ditch passes adjacent to the north boundary of the Valcast facility. This ditch serves to remove stormwater runoff in the vicinity and receives discharged cooling water from Valcast and other local small industries. Analysis of the Valcast cooling water at the point of discharge and of water in the drainage ditch failed to detect PCB levels greater than the detection limit of 0.1 µg/l. Two bottom sediment samples taken from this drainage ditch, however, had concentrations as follows:

Aroclor 1242	2.3 ppm	9.4 ppm
Aroclor 1260	6.7 ppm	8.9 ppm
Decachlorobiphenyl	0.09 ppm	0.11 ppm

Three grab samples of water and bottom sludge were taken from the sanitary sewer system about 1/4 mile down stream of the Valcast facility.

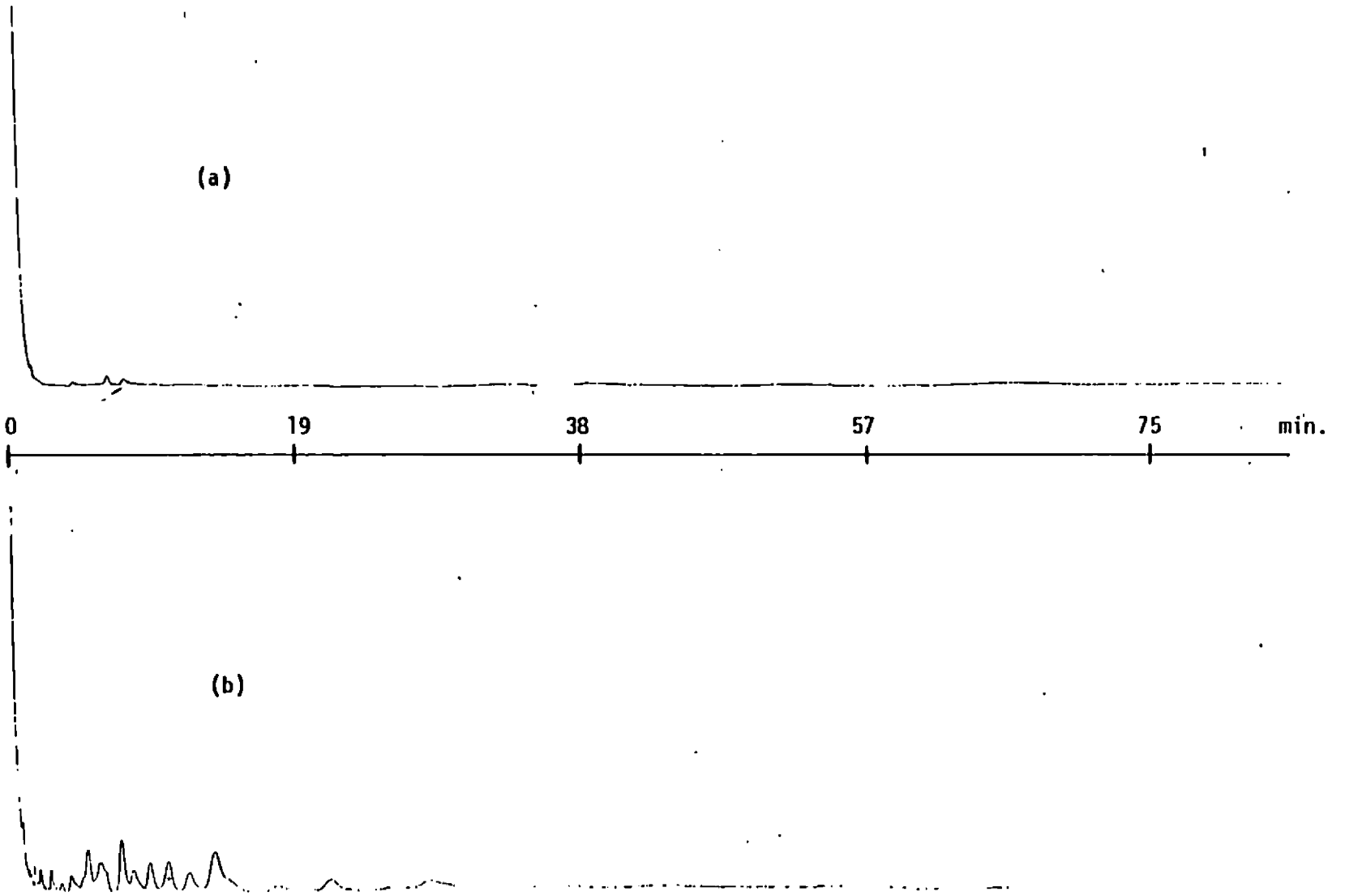


Figure 6. Typical chromatograms of soil samples taken in the vicinity of Valcast Corp., Troy, Michigan--(a) <0.01 ppm, (b) 0.014 ppm Aroclor 1260

ACM CC6463

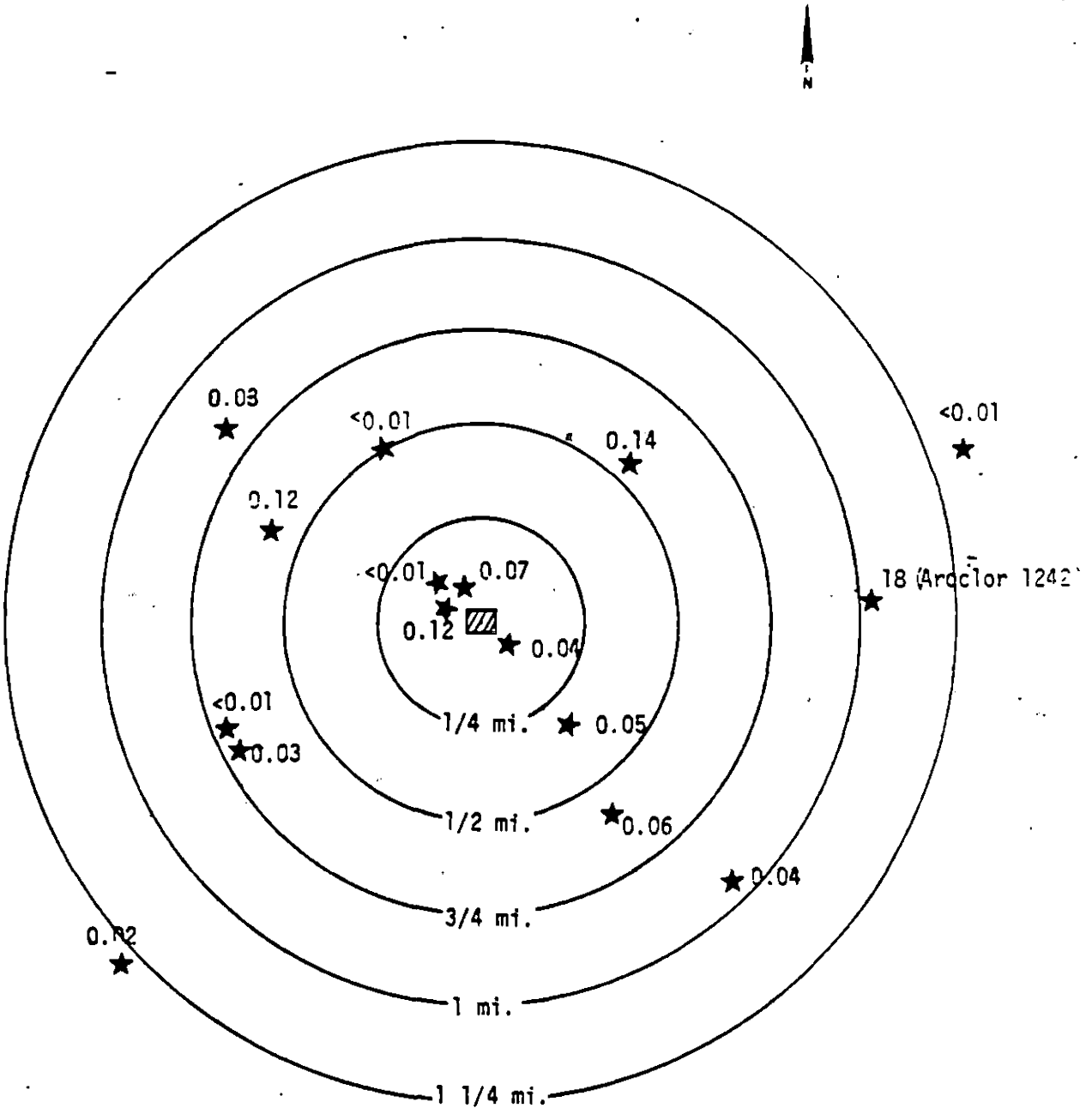


Figure 7. Concentration of Aroclor 1260 in soil as a function of distance from Valcast Mfg. Co. Concentrations are expressed in ppm.

ADM CCe4c4

Table 5. ANALYTICAL RESULTS OF SAMPLES TAKEN FROM THE SANITARY SEWER SYSTEM OF TROY, MICHIGAN, AT INTERSECTION OF ELLIOT AND EXECUTIVE DRIVE.

Date	Time	Type Sample	Aroclor 1260	Decachlorobiphenyl
23 Feb 75	1530	water	<0.1 µg/l	<0.01 µg/l
22 Feb 75	1815	water	<0.1 µg/l	<0.01 µg/l
23 Feb 75	1145	water	7.0 µg/l	4.1 µg/l
22 Feb 75	--	bottom sludge	0.11 ppm	0.034 ppm

This sewer system serves numerous small industries in the area. Results of the analysis of these samples are tabulated in Table 5. It appears that some Aroclor 1260 and decachlorobiphenyl are finding their way into the sewer system. Insufficient information is available to identify the source of these PCBs.

Data from Vicinity of Monsanto Co., Sauget, IL.

Aroclors have been produced by Monsanto Co. at the Sauget, Illinois site since prior to 1957. PCB mixtures ranging from 16 percent chlorine to 68 percent chlorine have been produced over the years. Production of the higher percent chlorine mixtures has been voluntarily reduced since 1970 and lower substituted isomers have been introduced. Polychlorinated terphenyls and chlorinated benzenes have also been produced at this facility. It is reported (Papageorge, 1975) that terphenyl production was suspended in 1971.

A typical chromatogram of a soil sample taken in the vicinity of the Monsanto facility is shown in Figure 8 along with the chromatogram of several other PCBs run under the same instrument conditions. This particular soil sample contains 11 ppm Aroclor 1242, 9.3 ppm Aroclor 1260 and 1.0 ppm decachlorobiphenyl. Lighter chlorinated Aroclor mixtures are likely present as well. The instrument conditions employed, however, do not give adequate separation of these mixtures to permit accurate quantification. The presence of decachlorobiphenyl at the concentrations observed is interesting. Decachlorobiphenyl has been reported as a component of only one Aroclor mixture, Aroclor 1268 (Hutzinger, Safe and Zitko, 1974). Whether it may be a component of any of the terphenyl mixtures or biphenyl/terphenyl mixtures or a by-product is not known.

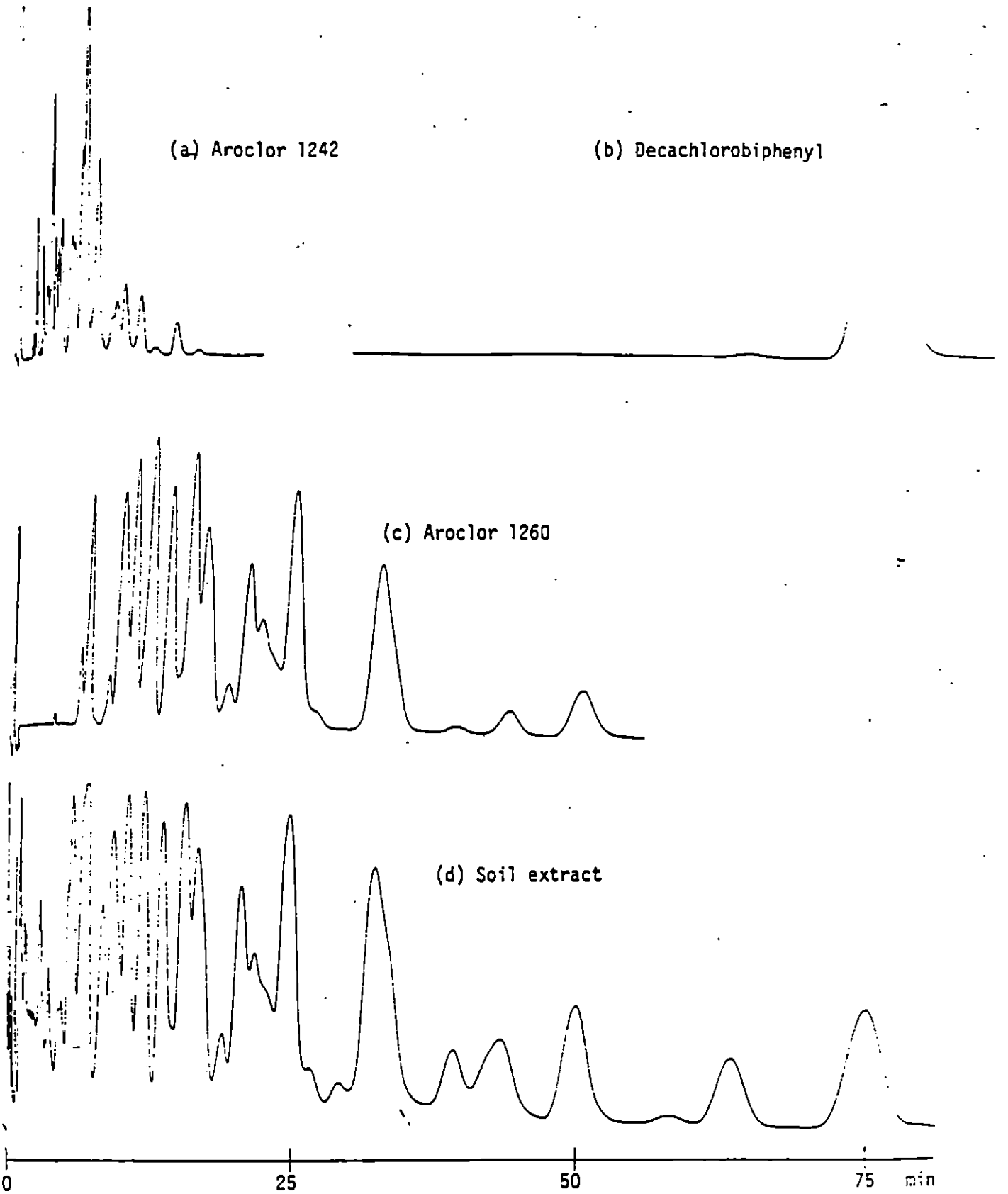


Figure 8. Typical chromatograms of standard Aroclors, decachlorobiphenyl and a soil sample taken in the vicinity of Monsanto Co., Sauget, Illinois.

The measured soil concentration of Aroclor 1242, Aroclor 1260 and decachlorobiphenyl in the vicinity of the Monsanto facility are depicted in Figures 9, 10 and 11, respectively. Figure 12 shows the long-term average wind direction in the area. The distribution of all PCBs analyzed appears to be higher near the plant site and generally decreasing with distance from the site. Furthermore, there is evidence that generally higher concentrations are present in the soils located to the southeast. This corresponds to the predominant wind direction and may suggest an airborne transport of the PCBs from the facility.

One 15 cm deep core sample was taken 1/2 mile southwest of the Monsanto site. Analysis of the bottom 11 cm of this soil yielded PCB concentrations basically equivalent to the top 4 cm.

A 24-hour composite sample from the influent and the effluent of the Sauget village sewage treatment plant taken beginning 0800 on February 17, 1975, was provided by plant personnel. The Monsanto Co. jointly owns this facility. Analysis of these samples were as follows:

	Aroclor 1242	Aroclor 1260	Decachlorobiphenyl
influent	6.8 µg/l	8.7 µg/l	<0.01 µg/l
effluent	4.5 µg/l	4.7 µg/l	<0.01 µg/l

The treatment plant effects a reduction of 34 percent Aroclor 1242 and 46 percent Aroclor 1260. No decachlorobiphenyl was detected.

ALP CCE4CE

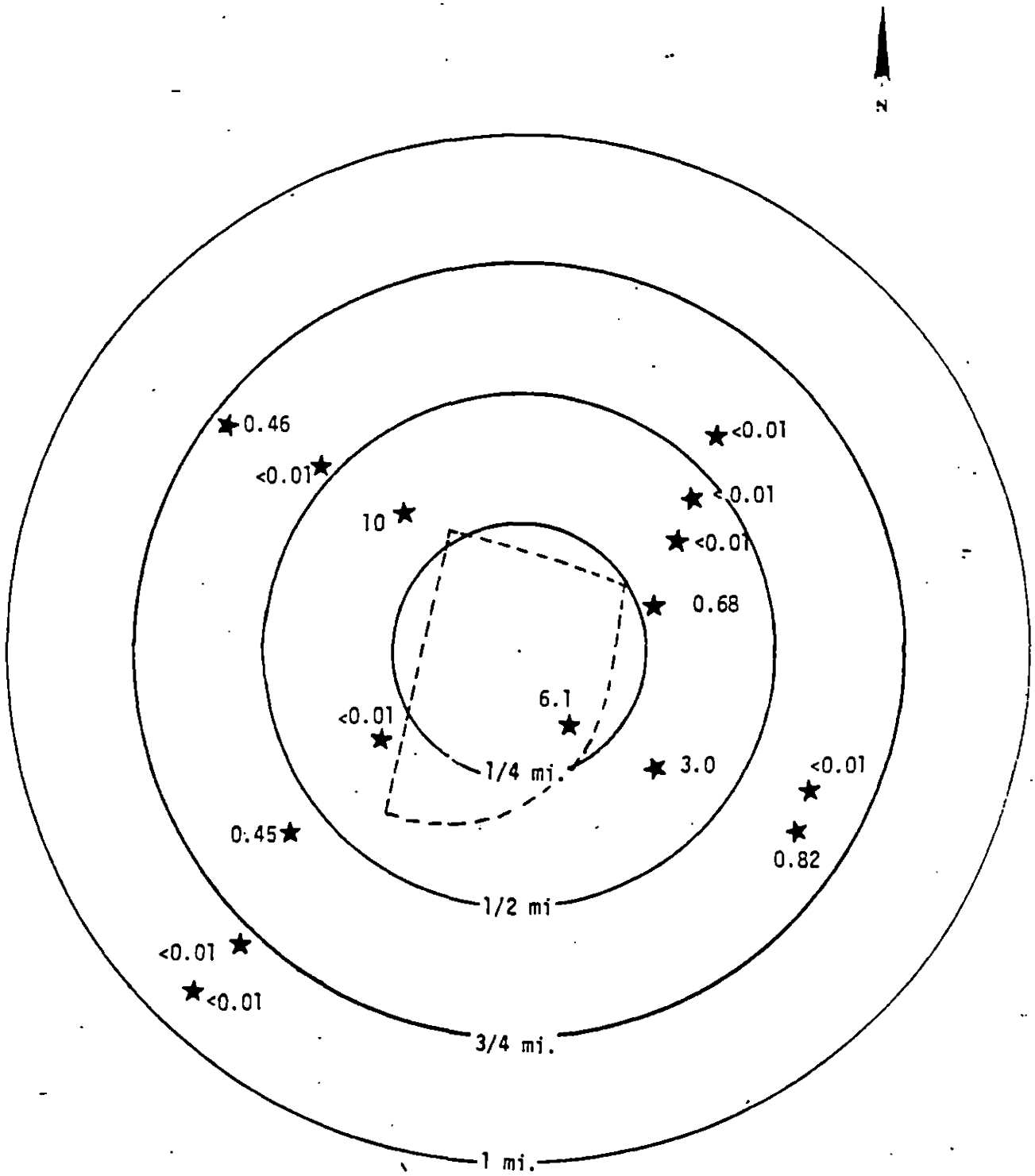


Figure 9. Concentration of Aroclor 1242 in soil as a function of distance from Monsanto Mfg. Co. Concentrations are expressed in ppm.

ACM CC84c5

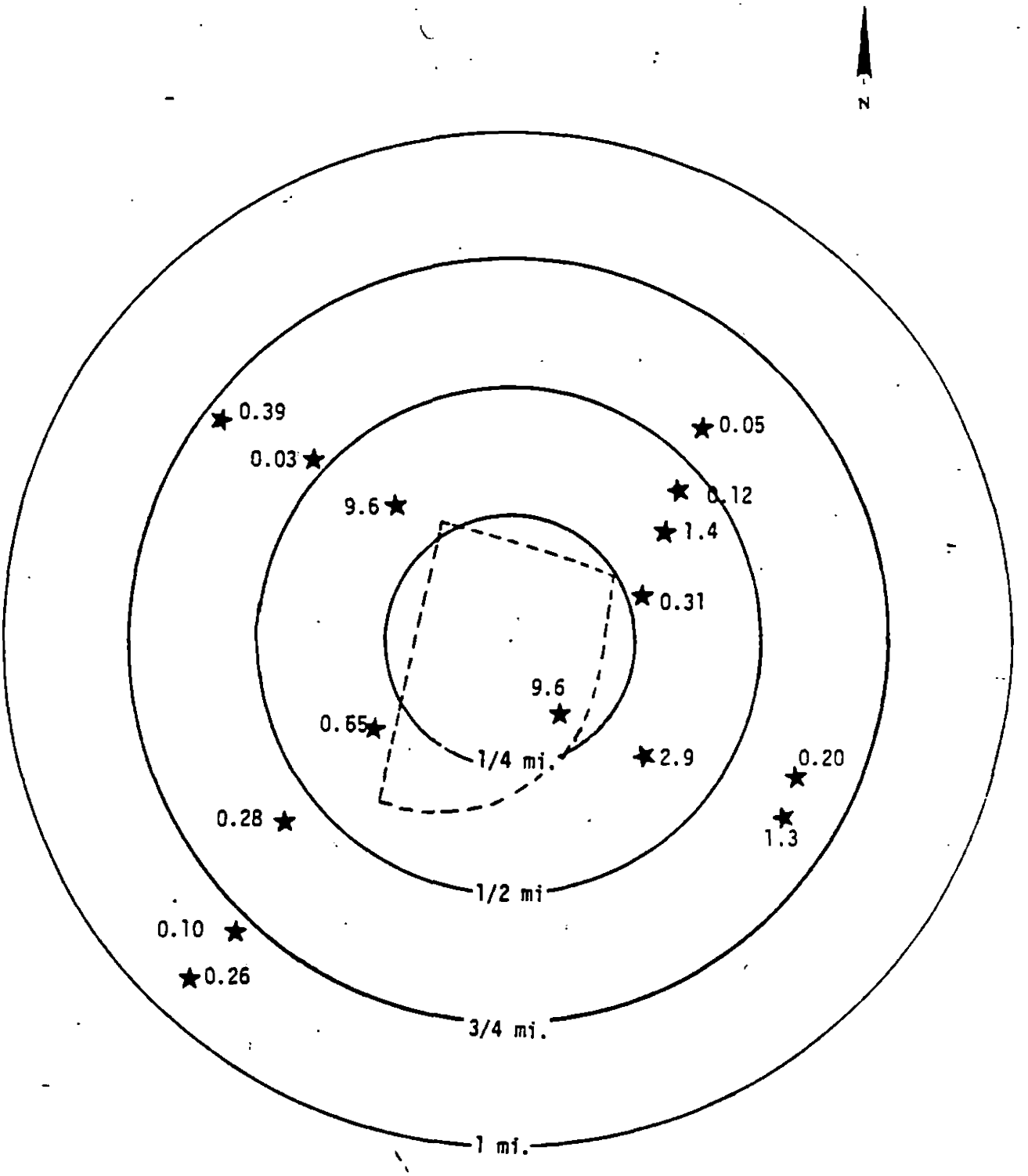


Figure 10. Concentration of Aroclor 1260 in soil as a function of distance from Monsanto Mfg. Co. Concentrations are expressed in ppm.

ACM CC6470

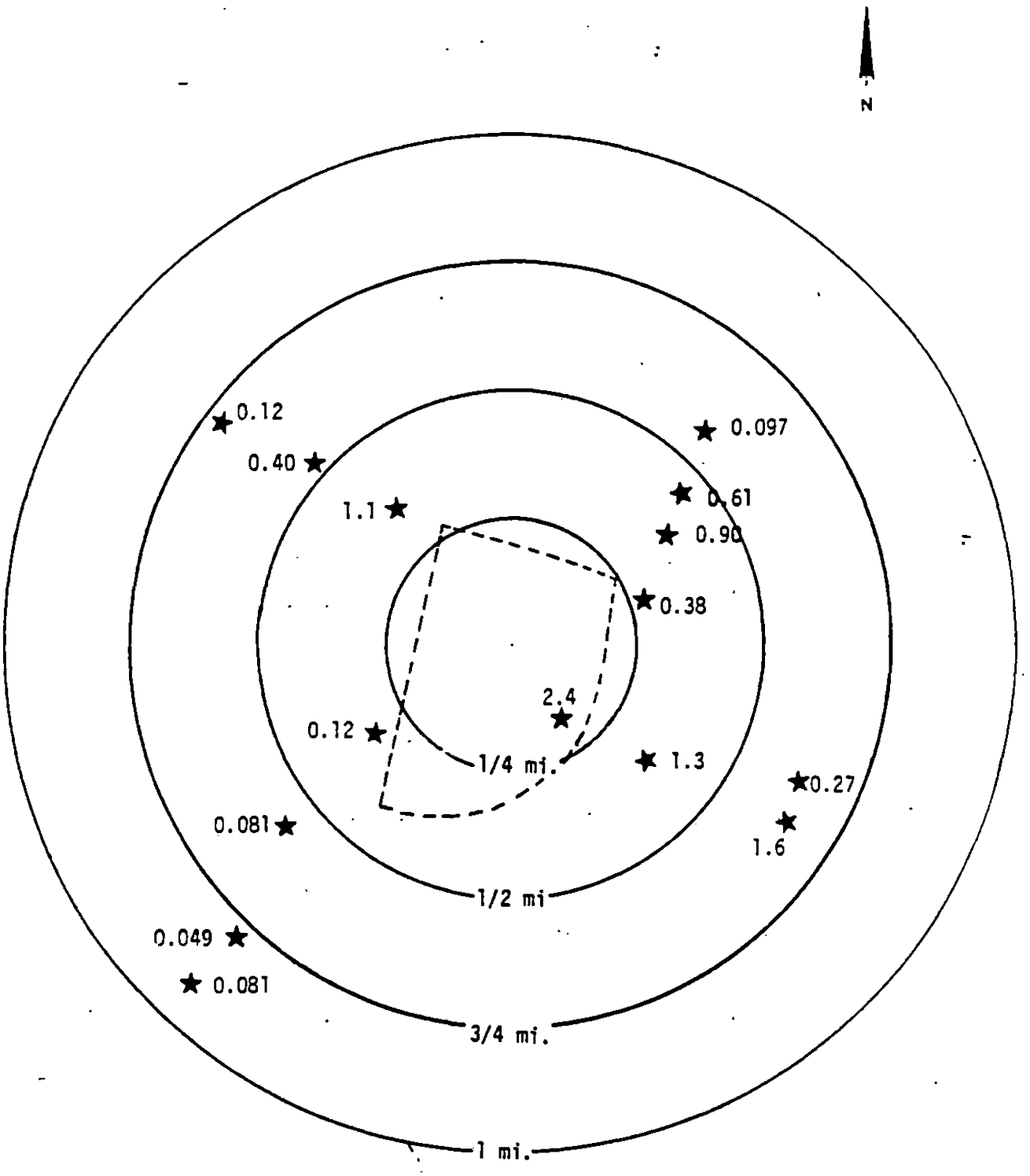


Figure 11. Concentration of decachlorobiphenyl in soil as a function of distance from Monsanto Mfg. Co. Concentrations are expressed in ppm.

ADM CC6471

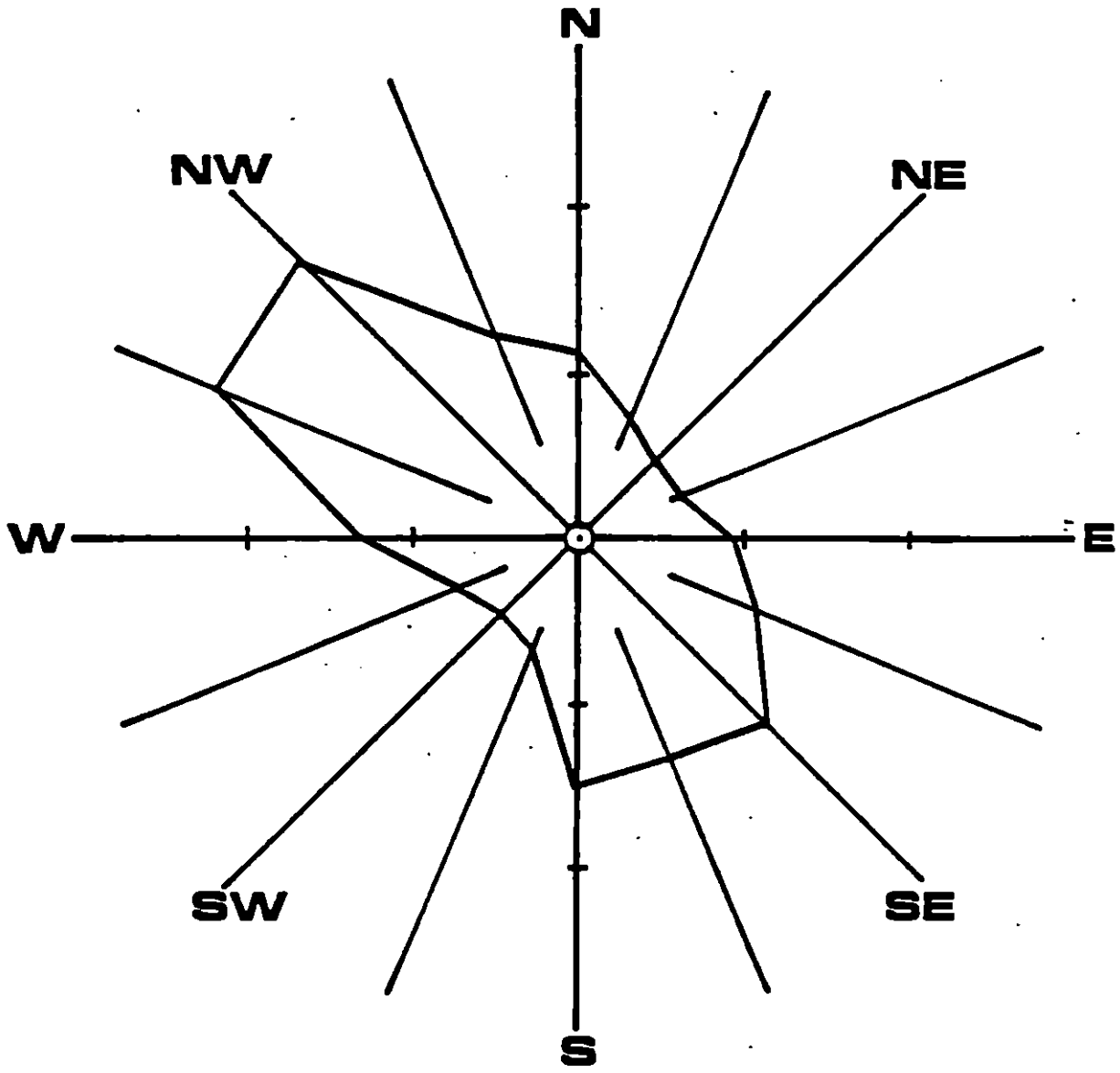


Figure 12. Ten Year Averaged Wind Rose for St. Louis, Missouri, January through March, 1951-1960.

Scale: 1" = 5% Calm Winds = 2.0%

ALP CCc47c

REFERENCES

Environmental Protection Agency (1973). Method for Polychlorinated Biphenyls (PCB's) in Industrial Effluents. NERC, Cincinnati, OH.

Environmental Protection Agency (1974). Analysis of Pesticide Residues in Human and Environmental Samples. Pesticides and Toxic Substances Effects Laboratory, Research Triangle Park, N.C.

Hutzinger, O.; Safe, S.; and Zitko, V. (1974). The Chemistry of PCB's. CRC Press, Cleveland, OH. 269 p.

Murphy, P.G. (1972). Sulfuric acid for the cleanup of animal tissues for analysis of acid-stable chlorinated hydrocarbon residues. JAOAC 55:6; 1360-1362.

Papageorge, W.B. (1975). Personal communication. Manager, Product Acceptability, Specialty and Process Chemicals, Monsanto Industrial Chemicals Co., St. Louis, MO.

Selikoff, I.J. (1972). ed. PCBs - Environmental Impact. Environ. Res. 5:3; 249-362.

U.S. Government Interdepartmental Task Force on PCBs (1972). PCBs and the Environment. NTIS document COM-72-10419.

CONCLUSIONS

1. The distribution of Fenclor DK suggests that this compound may be transported to soils in the vicinity of Yates Mfg. Co. by way of airborne emissions.

2. Aroclor 1260 is present in urban Chicago soils. There is no evidence Yates Mfg. Co. is the source of this soil contamination.

3. Detectable, but lower levels, of Aroclor 1260 are present in soils in Troy, Michigan. There is no evidence Valcast Corp. is the source of the soil contamination. No decachlorobiphenyl (or Fenclor DK) was detected in soils in the area.

4. Significant quantities of Aroclor 1242 (18 ppm) were observed in a single soil sample taken in a residential area near Valcast Corp. The importance of this single data point should not be over-emphasized. However, Aroclor 1242, Aroclor 1260 and decachlorobiphenyl were also detected in drainage ditch sediments at much higher concentrations than the observed PCB levels for soils in the area.

5. The drainage ditch sediments near Valcast Corp. contained detectable levels of decachlorobiphenyl. Its source is unknown. A number of small industries are located in the immediate vicinity, any of which could be the source as well as intermittent discharge, leakage or runoff from the Valcast site or facility.

6. One of three grab samples taken over a period of time from the sanitary sewer system near Valcast Corp. contained detectable levels of Aroclor 1260 (7.0 µg/l and decachlorobiphenyl (4.1 µg/l). The other two samples were below detection limits of 0.01 µg/l and 0.001 µg/l, respectively. Sewer sludge contained both Aroclor 1260 and decachlorobiphenyl. These

materials are apparently discharged to the sewer system on an intermittent basis. The source is unknown.

7. Decachlorobiphenyl is relatively abundant compared to the other PCBs in soils in the vicinity of the Monsanto facility. Decachlorobiphenyl is not reported to be a major component of any of the Aroclor mixtures. It may be a by-product associated with Aroclor production which is eliminated or greatly reduced in the commercial preparations by refinement at the Monsanto facility and may, therefore, find its way into the environment at this location.

8. Aroclors 1242 and 1260 were also present in soils near the Monsanto plant. There appears to be a tendency for higher PCB levels close to the plant with decreasing concentration with distance. There is some evidence that higher soil concentrations exist along the northwest to southeast axis which corresponds to the dominate wind direction at this location. This suggests airborne transport of the PCBs from the plant with subsequent deposition, of at least the heavier isomers of PCB, on nearby soils.

9. PCBs are present in Sauget, Illinois wastewaters. The sewage treatment plant removes less than 50 percent of the Aroclor 1242 and Aroclor 1260. Decachlorobiphenyl is not present in these wastewaters.

10. Aroclor 1260 was found to be present in the soils of all three sites sampled. This product is currently used in electrical transformer fluids and has been used in the past in hydraulic fluids, plasticizers and dedusting agents (Hutzinger, Safe and Zitko, 1974). Aroclor 1242

was found in comparable concentration near the Monsanto facility and in drainage ditch sediments near Valcast. This product has consistently been the most heavily produced by Monsanto of all the PCB mixtures.

11. Decachlorobiphenyl may be more widely spread than would be anticipated by projection from Monsanto production figures for Aroclors.

SUGGESTIONS FOR CONTINUED STUDY OF PCBs

1. Conduct total PCB analysis employing the perchlorination technique of selected samples on hand. Determine what fraction of the total PCB present has been quantified as Aroclors 1242 and 1260 and decachlorobiphenyl.

2. Conduct polychlorinated terphenyl (PCT) analysis of selected samples on hand.

3. Assess PCB and PCT levels in various urban and non-urban soils and stream sediments.

4. Conduct analysis of airborne and precipitation-borne PCB and PCT in the vicinity of known users.

5. Evaluate PCB and PCT levels in and near dumps and landfills in the air, water, soil and groundwaters.

6. Investigate the potential for chlorination of biphenyl at normal wastewater and drinking water treatment levels.

7. Investigate the possibility of chlorinated dibenzofuran, dioxin and naphthalene contamination of various foreign and domestic PCB products.

8. Evaluate the rate of degradation of PCBs in the environment.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D C 20460

September 23, 1975

Dr. Robert E. Keller
Manager, Applied Sciences
Monsanto Industrial Chemicals, Inc.
800 North Lindbergh Blvd.
St. Louis, Mo. 63166

Dear Dr. Keller:

In reference to our Las Vegas conversation, the following are attached:

1. "Environmental Levels of PCB's"
2. PCB data from the Sauget, Illinois area.

If possible, I would be interested in having a copy of the PCB list of references you had compiled. Call if I can be of further help. My phone number is 202-755-6956.

Sincerely yours,

Vincent J. DeCarlo

Vincent J. DeCarlo,
Chief, Monitoring and Information
Systems Branch
Office of Toxic Substances

ACM CC8442

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
NATIONAL WATER QUALITY LABORATORY
6201 Congdon Boulevard
Duluth, Minnesota 55804

February 25, 1972

Dr. Scott Tucker
Monsanto Company
Organic Chemicals Division
1700 South Second Street
St. Louis, Missouri 63177

Dear Dr. Tucker:

On May 22 and 23, 1972, there will be an informal inter-agency work session on PCB's in the environment, to be held at the Holiday Inn at Duluth, Minnesota. Our objectives are to assess the present state of knowledge and effort, and to identify additional study need priorities. You (or in some cases, a member of your agency) are invited to participate. A copy of the proposed agenda and time schedule is enclosed.

Please let us know by April 1, 1972, if you will attend. Additional information will be sent later regarding reservation times and places.

Very truly yours,

Donald I. Mount

Donald I. Mount, Ph.D.
Director

Encl.

PLAINTIFF'S EXHIBIT 927

ACM CC8478

INTERAGENCY MEETING ON PCB's IN THE ENVIRONMENT

Monday Morning, May 22, 1972

WELCOME — Donald I. Mount, Ph.D.

ARRANGEMENTS AND ANNOUNCEMENTS

STATE OF THE ART

Presentation of present efforts by attendees.

THE OUTLOOK

EPA ENFORCEMENT

Monday Afternoon

THREE CONCURRENT SESSIONS ON NEEDS

This session, after its discussion regarding regulation, will split with attendees going to the session of their choice, either B or C.

A. Regulation — Head and Srini

Use of isomer measurements quantification of PCB's
Residue tolerances, etc.
Oil-sediment regulations
Discharge permit usefulness
Etc., etc.

B. Analytical — Donaldson and Veith

Separation of isomer and aroclors
Clean-up
Precision accuracy
Positive identification
Labeled compounds
Monitoring needs
- Sensitivity
- Type sample
- Preservation

C. Biological Effects - Duke and Schoettger

Additional toxicity studies
Aquatic
Terrestrial
Residue studies and half-life
Food chain studies
Interaction with pesticides

Monday Evening

INTEREST GROUP — Informal Meetings (about 3)

Tuesday Morning, May 23, 1972

PRESENTATION BY EACH OF THREE WORK GROUPS

Head, Donaldson and Duke

MEETING SUMMARY AND IDENTIFICATION OF NEEDS AND PRIORITIES

ACP CCE4EC

Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

January 14, 1976

Mr. Robert D. Kleopfer
USEPA Region VII Laboratory
25 Funston Road
Kansas City, Kansas 66115

Dear Mr. Kleopfer:

Per our phone conversation of 1-14-76, I am sending you a copy of ASTM Method D-3304, which was developed from analytical methodology provided by Monsanto. I am also enclosing a copy of my presentation at the National Conference on Polychlorinated Biphenyls in Chicago on November 19, 1975. This paper describes the properties and composition of PCB mixtures. The text I recommended as a reference for further information is listed as reference 1 in the paper.

I hope this information is useful to you.

Sincerely,

James P. Mieure

J. P. Mieure, Ph.D.
Research Group Leader

ss
Enclosures(2)

bcc: R. E. Keller
J. C. Weber
D. Wood

ACM CC8461

PLAINTIFF'S EXHIBIT 928

OPTIONAL FORM NO. 10
MAY 1962 EDITION
GSA FPMR (41 CFR) 101-11.6

UNITED STATES GOVERNMENT

Memorandum

ENVIRONMENTAL PROTECTION AGENCY
National Water Quality Laboratory
6201 Congdon Boulevard
Duluth, Minnesota 55804

TO : See Below

DATE: May 2, 1972

FROM : Director, NWQL,
Duluth, Minnesota

SUBJECT: Interagency Meeting on PCB's in the Environment

The progress for the "Interagency Meeting on PCB's in the Environment" scheduled for May 22 and 23, 1972 to be held in Duluth, Minnesota has now been finalized. The program remains essentially the same as the one which was announced earlier and a copy is enclosed. Starting time will be 9:00 a.m., May 22, 1972 in the Conference Room at the Duluth Holiday Inn.

For the presentation of present efforts by attendees it is requested that one individual present the efforts of his group or laboratory. Presentations should be limited to ten minutes or less and be strictly informal. We would expect presentations from the following groups:

1. Fish Pesticide Laboratory
2. Southeast Water Laboratory
3. Perrine Primate Laboratory
4. Chamblee Toxicology Laboratory
5. Monsanto
6. Justice Department
7. Great Lakes Fisheries Laboratory
8. National Marine Water Quality Laboratory
9. Analytical Quality Control Laboratory
10. Gulf Breeze Laboratory
11. National Water Quality Laboratory
12. Food and Drug Administration
13. Patuxant Wildlife Research Center, and
14. Department of Fisheries and Wildlife, Michigan State University.

If other individuals desire to make a presentation of important findings or facts, please contact John I. Teasley, National Water Quality Laboratory, Duluth, Minnesota 55804.

For Monday evening a group dinner is being planned preceded by a cocktail hour and followed by the interest group discussion. This will be an excellent time to meet other attendees to discuss mutual problems.

Buy U.S. Savings Bonds Regularly on the Payroll Savings Plan

ACM CC8462

Those who do not have accommodations in Duluth as yet can obtain them directly at the Duluth Holiday Inn (please specify the National Water Quality Laboratory PCB Meeting), or if you desire, contact John Teasley who will make the necessary arrangements for you. Likewise, if possible, a schedule of your arrival time in Duluth would be helpful.

Don

Donald I. Mount, Ph.D.

Attachment:
Program (2 pgs)

TO:
Mr. William T. Donaldson)
Dr. Ronald Webb)
Dr. Leo Azarraga) Southeast Water Laboratory, Athens, Georgia
Mr. George Baughman)

Dr. Thomas Duke)
Dr. Del Nimmo)
Mr. Albert Wilson) Gulf Breeze Laboratory, Gulf Breeze, Florida
Mr. John Couch)

Dr. Richard Schoettger) Fish Pesticide Laboratory,
Dr. David Stalling) Route #1, Columbia, Missouri 65201

Mr. August Curley, Chamblee Toxicology Laboratory, Chamblee, Georgia 30341
Dr. Henry F. Enos, Perrine Primate Laboratory, Perrine, Florida 33157

Mr. William Papageorge) Monsanto, St. Louis, Missouri 63166
Dr. Scott Tucker)

Dr. Gilman Veith, University of Wisconsin, Madison, Wisconsin 53706
Dr. Elizabeth Anderson, Environmental Protection Agency, Washington, D.C. 20460
Dr. John Buckley, Environmental Protection Agency, Washington, D.C. 20460
Dr. Jerry Burke, Food and Drug Administration, Washington, D.C.

Dr. Stan Hegre) National Marine Water Quality Laboratory
Dr. Peter Rogerson) West Kingston, R.I.

Dr. Howard Johnson, Michigan State University, East Lansing, MI 48823
Mr. William Potter, Food and Drug Administration, Minneapolis, Minnesota
Mr. Wayne Willford, Great Lakes Fisheries Laboratory, Ann Arbor, MI 48107
Dr. John Hesse, Michigan Department of Natural Resources, Lansing, MI 48895

Mr. Jim Lichtenberg) Analytical Quality Control Laboratory, Cincinnati, OH
Mr. Tom Bellar)

INTERAGENCY MEETING ON PCB's IN THE ENVIRONMENT

Monday Morning, May 22, 1972

WELCOME — Donald I. Mount, Ph.D.

ARRANGEMENTS AND ANNOUNCEMENTS

STATE OF THE ART

Presentation of present efforts by attendees.

THE OUTLOOK

EPA ENFORCEMENT

Monday Afternoon

THREE CONCURRENT SESSIONS ON NEEDS

This session, after its discussion regarding regulation, will split with attendees going to the session of their choice, either B or C.

A. Regulation — Walpole and Srini

Use of isomer measurements quantification of PCB's
Residue tolerances, etc.
Oil-sediment regulations
Discharge permit usefulness
Etc., etc.

B. Analytical — Donaldson and Veith

Separation of isomer and aroclors
Clean-up
Precision accuracy
Positive identification
Labeled compounds
Monitoring needs
- Sensitivity
- Type sample
- Preservation

ACM CC6465

C. Biological Effects - Duke and Schoettger

Additional toxicity studies
- Aquatic
  Terrestrial
Residue studies and half-life
Food chain studies
Interaction with pesticides

Monday Evening

INTEREST GROUP — Informal Meetings (about 3)

Tuesday Morning, May 23, 1972

PRESENTATION BY EACH OF THREE WORK GROUPS

Walpole, Donaldson and Duke

MEETING SUMMARY AND IDENTIFICATION OF NEEDS AND PRIORITIES

RECEIVED
DEC 29 1975
J.W.H.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

December 22, 1975

OFFICE OF THE
ADMINISTRATOR

Dear Mr. Hanley

For at least five years, the Federal Government and the manufacturing industry have been aware that polychlorinated biphenyls (PCBs) pose a threat to human health and the environment. Last month, at EPA's National Conference on Polychlorinated Biphenyls in Chicago, leading experts clearly documented the fact that PCBs are pervasive in the environment, are causing disruption and economic harm to commercial fishing in many areas and are creating a serious potential health hazard to the public. While certain voluntary measures have been initiated in the past, the widespread and persistent occurrence of PCBs underscores the failure of existing practices to adequately control the escape of PCBs into the environment.

Today I announced a broad EPA program of regulatory and non-regulatory actions to reduce the levels of PCBs in the environment. My statement, (which is enclosed), stated that we must, as a society, accept and work toward a goal of totally eliminating the production, importation and use of PCBs as rapidly as possible. Toward that end, I am asking you, as a principal member of the PCB industry, to commit yourself to a deliberate and expeditious search for alternatives.

I recognize that this effort will not be easy. A careful examination and balancing of the environmental consequences of alternatives will be required. The economic impacts of the changeover will have to be considered. I also recognize that such an effort cannot be accomplished overnight. Nevertheless, I have confidence that American industry has the capacity to solve this difficult task, and I solicit your full cooperation and participation in this effort.

So that we can begin this undertaking as soon as possible, I am inviting you and other representatives of your industry to meet with me on January 14 to discuss this undertaking and work towards the development of plans on how it can be accomplished as smoothly and rapidly as possible.

I have also asked representatives of the principal users of PCB-containing transformers and large capacitors to meet with me on January 22 to discuss ways that we can effectively manage and control PCBs in current use. I am enclosing a copy of my letter to these companies. At our meeting on January 14, we might also discuss some of the matters outlined in that letter.

ACM 008467

PLAINTIFF'S EXHIBIT 930

I am looking forward to meeting with you at EPA in Room 1112, 1921 Jefferson Davis Highway, Crystal Mall #2, Arlington, Virginia, on January 14, from two to five in the afternoon. If you have any questions concerning the arrangements for this meeting, you may contact Dr. I. E. Wallen, (202) 755-6956.

Sincerely yours,

Russell E. Train

Russell E. Train
Administrator

Mr. John W. Hanley
President
Monsanto Chemical Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166

Enclosures

ADM CCE46t

Monsanto

SPECIALTY CHEMICALS DIVISION

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

Dear Customer:

Monsanto will stop accepting polychlorinated biphenyl ("PCB") waste returns effective August 31, 1977. We now have substantial volumes of PCB waste on hand which must be incinerated along with our production unit's residue before the incinerator is decontaminated and shutdown later this year. For this reason we are not able to accept any significant volumes between now and August 31st.

The American National Standards Institute's publication ANSI C107.1 -1974 lists the following firms as having incineration facilities capable of handling PCB's.

Chem-Trol Pollution Services, Inc.
P.O. Box 200
1550 Balmer Road
Model City, New York 14107
Phone: 716-754-8231

Rollins Environmental Services, Inc.
P.O. Box 2349
Wilmington, Delaware 19899
Phone: 302-656-8541

It is, of course, your responsibility to determine the adequacy of the incineration facility for the disposal of PCB waste and its compliance with applicable laws and regulations.

Sincerely,

James A. Alley

James A. Alley
Industry Specialist
Dielectrics

tmc

[redacted]
File

Monsanto

bcc: K. W. Easley
R. A. Stohr
E. T. Mollica
W. C. Hammann
R. C. Isham

JUL 30 1977

JUL 5 1977

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

June 30, 1977

Mr. George F. Wirth, Chief
Special Chemicals Branch
Office of Toxic Substances (WH-557)
U.S. Environmental Protection Agency
Washington, D.C. 20460

Dear Mr. Wirth:

Enclosed is a letter we are sending to our customers notifying them that we will stop accepting polychlorinated biphenyl ("PCB") waste returns effective August 31, 1977.

Our incinerator was built to dispose of our PCB production unit's residue and to assist our customers to dispose of their waste. This incinerator was designed to handle only "straight" PCBs or those contaminated with an organic solvent such as trichlorobenzene. As stated in our letter, we now have substantial volume of PCB waste on hand which must be disposed of, along with our production unit's residue and whatever residue remains from the shut down and decontamination of our PCB production facility.

This action is in line with Monsanto's announcement to shut down our PCB manufacturing unit and exit the business by October 31, 1977. If you have any questions, please let me know.

Sincerely,

J. Coleman Weber
Manager
Product Acceptability
Specialty Chemicals Division

JCW:rd
Enclosure

cc: J. A. Alley

PLAINTIFF'S EXHIBIT 932

Monsanto

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone 314 694-1000

August 4, 1978

Office of Toxic Substances (TF-794)
Environmental Protection Agency
401 "M" Street, S.W.
Washington, D. C. 20460

ATTENTION: Ms. Joni T. Repasch

Dear Ms. Repasch:

On June 7, 1978, the EPA published a proposed rule in 43 Federal Register beginning on page 24,802 covering Manufacturing, Processing, Distribution in Commerce, and Use Bans of Polychlorinated Biphenyls (PCB's). This letter sets forth Monsanto Company's comments on the proposed rule. Please include these comments, with the attachment, in the official record of this proceeding.

Our comments are divided into two parts. The first part provides general comments which focus on the EPA's proposed maximum concentration of 50 ppm and the justifiable need for a heat transfer system use authorization. The second part sets forth specific language and recommendations related to these matters, and to certain other matters in specific sections of the proposed rule.

GENERAL COMMENTS

The proposed immediate, mandatory removal from service of heat transfer systems containing fluids whose PCB concentration equals 50 ppm or greater is not justified in view of the lack of any significant risk to health or the environment. To require industry immediately to remove from service and drain all these systems or to replace the systems entirely to meet a 50 ppm concentration level is an arbitrary mandate and will generate a substantial, immediate risk of injury and environmental harm from spillage and result in an abrupt, massive buildup of PCB contaminated fluid without available disposal facilities or time to develop orderly plans to

carry out the disposal. Furthermore, the EPA cites no evidence in the preamble of any environmental or health hazard to support the proposed reduction in the regulated concentration of PCB's in a PCB mixture under Section 761.2(w) from 500 ppm to 50 ppm, nor does the May, 1978 EPA Support Document-Draft Voluntary Environmental Impact Statement upon which the proposed rules are based support this reduction. Therefore, Monsanto strongly recommends the EPA withdraw this proposed reduction.

Yet even with the withdrawal of the 50 ppm concentration, it is imperative that an authorization be granted for continued use of heat transfer systems containing residual PCB's. The evidence conclusively establishes that the heat transfer system use activity meets the requirements for granting an authorization to allow continued operation, and Monsanto requests the EPA to grant such an authorization. On page 42 of the EPA Support Document, the EPA states that before it grants an authorization for continuation of a non-totally enclosed use activity the following two requirements must be met:

(1) the activity authorized must not pose an unreasonable risk of injury to health or the environment, and

(2) the ban would cause major and extensive economic disruptions.

Regarding the first requirement, an analysis of potential PCB exposure from various sized PCB contaminated heat transfer systems is illustrative of the insignificant risk of injury to health or the environment posed by authorizing continued use of these systems. The highest risk area for leakage in these systems is in the pump seals, but inspection maintenance for pump seals is also emphasized because of user awareness of this risk. A pump seal failure would be rapidly detected by inspectors or automatic monitoring devices and loss of fluid would be unlikely to exceed from 1% to 5% of the total fluid volume in the system.

For example, a 500 gallon system containing 1% volume of PCBs has a total PCB content equal to 60 pounds, and a leak of 5% of the total fluid (which is unlikely) would release only 3 pounds of PCB's. Similarly, a 10,000 gallon system containing a PCB contamination of 500 ppm has a total PCB content of 60 pounds, and a leak of 5% of the total fluid (again unlikely) would release only 3 pounds of PCB's. A leakage of 3 pounds of PCB's is below the EPA's designated harmful quantity for PCB spills into navigable waters (10 pounds) under 40 CFR 118.4 issued pursuant to the Federal

Water Pollution Control Act and, in Monsanto's opinion, does not create a significant risk to health or the environment. Furthermore, the above examples are worst case situations because they assume no spill prevention program (for example, diking) or effluent control program in effect. If such programs were in effect it would be highly unlikely for any amount of PCB's approaching 3 pounds to escape into the environment.

The proposed immediate, mandatory removal of these systems from service also meets the standards for the second requirement for an authorization by resulting in substantial, widespread economic disruption. Since the EPA states in the preamble and the Support Document that it lacks information necessary to evaluate the impact of the ban on the heat transfer system use activity, the following information is presented which is generally consistent with the specific information requests in 43 FR 24810 relative to hydraulic die-casting systems, and which clearly and conclusively demonstrates this economic impact:

1. Number of systems contaminated. It is estimated that when the sale of PCB heat transfer fluids was discontinued in 1972 there were 450 heat transfer systems using this fluid. This estimate is based on (a) the current level of new systems introduction, (b) the ten year period (1962-72) during which PCB heat transfer systems were specified, and (c) the total volume of 20 million pounds of PCBs sold for heat transfer systems from 1962 through 1971 as reported by the 1972 Interdepartmental Task Force on PCBs COM-72-10419 pages 6 and 7.

2. The average liquid volume of the systems. It is estimated that about one-half of all PCB contaminated heat transfer systems have less than a 500 gallon liquid volume. Systems greater than 500 gallon volumes are estimated to average about 2,000 gallons. These estimates are based upon a review of systems filled in 1977 and 1978 and upon the average system size of Monsanto units converted in the 1970-72 period - a typical cross section of the industry pattern.

3. The range of liquid volume. Heat transfer systems of greater than 10,000 gallons are unusual. Small experimental pilot plant units may contain 50 gallons.

4. Fluid top-off. Heat transfer fluids are designed to be thermally stable within the recommended temperature range of operation and to operate at low pressure. Accordingly, routine top-off is minimal. Average top-

off may be higher because of fluid removal from parts of the system when maintenance is performed on other components of the system such as pumps, valves and heaters or in the event a system malfunction causes a thermal degradation of the fluid. Monsanto's experience indicates that some systems may require no top-off for three to five years; other systems may require a top-off of 50% in one year if major maintenance programs requiring drainage are undertaken. However, systems are not routinely drained.

5. Efforts to reduce PCB contamination. We estimate that greater than 90% of the plants operating with PCB heat transfer systems converted to alternative non-PCB fluids in 1970-72. Some of those converting drained and refilled the system with non-PCB fluid; some drained, flushed and refilled; some drained, chemically cleaned and refilled; and other dismantled and discontinued use of liquid systems. We estimate that these efforts have generally resulted in current system PCB levels in the industry ranging from around 100 ppm to several thousand ppm. Recovery from heat transfer systems would generally be expected to be greater than 90%. Note that for the purposes of these comments the term "recovery" is defined as the percentage of total system fluid volume extracted from the system by draining.

6. Servicing fluids to remove PCB's from systems. Following is a review and analysis of the potential success of three methods the EPA has considered for PCB removal:

   (a) Drain and refill. If small systems (500 gallons or less) are drained and refilled with a non-PCB fluid, a 98-99% recovery of dissolved PCB's can be expected. This service method will not, however, remove PCB absorbed by the heat transfer system walls. In the case of systems larger than 500 gallons a 90-99% recovery can be expected depending upon the complexity of the piping layout and heat exchanger design.

   (b) Distillation is of questionable efficiency in separating and removing PCB's from heat transfer fluid due to the similarity in boiling ranges of PCB's and non PCB heat transfer fluids. The boiling ranges for these respective fluids are as follows:

PCB		
	Therminol FR 1	617°F - 690°F
	Therminol FR 2	644°F - 707°F

Non-PCB	Therminol 55	635°F - 734°F
	Therminol 66	643°F - 668°F

(c) Carbon treatment experiments to remove PCB's are currently being conducted to investigate the carbon treatment removal method, but no data are presently available.

7. Present PCB levels in systems - We estimate the range of PCB concentration levels in heat transfer systems to be from about 100 ppm to about 30,000 ppm.

8. Cost of new systems - The cost of a new system could result in a large dollar expenditure compared to the much lower cost of replacing fluid. Replacing a heat transfer system may well mean totally rehabilitating a plant because these systems are integral parts of the users' plants, and replacement of heat transfer systems is impossible without replacement of reactors, coolers and heat exchangers. Such replacement would usually require a multimillion dollar expenditure. Further, the costs of lost production would be extraordinarily high in terms of lost wages, lost sales and product shortages which could impact a wide area of other manufacturing industries using finished products during the length of time required to replace each system. Thus the immediate, mandatory removal of these systems from service would result in substantial, widespread economic disruption in industries using heat transfer systems and the products produced from processes using such systems.

9. Cost of draining and refilling systems - We estimate the cost of draining and refilling systems would be from $10 million to $30 million, depending upon authorized PCB level, and based upon the model of an average 2,000 gallon system and the estimated 450 systems in the industry. For example, PCB reduction to a concentration level of 500 ppm in a 2,000 gallon system, with a current 1% PCB volume (10,000 ppm) and assuming a 90% fluid recovery, would result in a marginal removal cost of approximately $220 per pound. It is estimated that to reduce from a 500 ppm level to a 50 ppm level would require a marginal removal cost of about $30,000 per pound. Starting with a PCB content in the 2,000 gallon system of 240 pounds, draining the system (90% recovery) would leave 200 gallons of fluid containing 2 gallons of PCB's or 24 pounds. This quantity should, when the system is refilled with 2,000 gallons of flushing fluid, result in a PCB concentration of 1500 ppm. A

second draining and refilling with flushing fluid should initially drop PCB's to 2.4 pounds or 150 ppm, but this amount would shortly increase as PCB's are released from the surface walls into the fluid. Once a proper concentration has been obtained to assure the concentration remains below 500 ppm, the flushing fluid would be drained and the system refilled with non-PCB heat transfer fluid.

The direct cost estimates of flushing and draining, excluding costs associated with lost production and resulting disruption of supply to consumers, are as follows:

(a)	Flushing fluid - 2x2,000 gallons at $2.00 per gallon	$8,000
(b)	New fill of non-PCB heat transfer fluid - 2,000 gallons at $8.00 per gallon	$16,000
(c)	Disposal of initial drained fluid and 2 flushing fluid changes - 6,000 gallons at $2.26 per gallon	$16,000
(d)	Labor and overhead - 4 men 10 to 15 days	$12,000
	Total	$52,000

This estimate assumes that only two flushings are required and that draining and flushing proportionately reduces PCB concentration level without a major breakdown of the system involving gasket replacement or rewelding which could easily double or triple costs. Based upon this estimate, the cost of removal of 235 pounds would give a marginal removal cost of $220 per pound to achieve a residual level below 500 ppm. To achieve a level of 50 ppm it is likely that at least two further drain and flush procedures and chemical cleaning would be required. At $50,000 per procedure, the final 1.6 pound removal would carry a marginal removal cost of at least $30,000 per pound.

The above information relative to environmental and health injury and economic impact is clear evidence which meets the two requirements necessary to support the grant of a use authorization for heat transfer systems containing residual PCB's. Accordingly, Monsanto recommends the proposed rules be revised to authorize for a period of 5 years the continued use and servicing of all 500 gallon capacity or less heat transfer systems used and serviced in a manner other than a totally enclosed manner to the extent these systems contain 1% or less by volume of PCB's, provided users attain this 1%

PCB volume within one year after the effective date of the rule. For systems with greater than 500 gallon capacity, Monsanto recommends the EPA authorize for 5 years continued use and servicing of these systems in a manner other than a totally enclosed manner to the extent they contain a PCB concentration of 500 ppm or less, provided users attain this 500 ppm PCB concentration within 2 years after the effective date of the rule. These transition time periods would permit an orderly reduction of PCB levels during which disposal of fluids by incineration could be planned, thereby avoiding spillage and buildup of PCB contaminated fluid inventories awaiting disposal. Please note that proposed language for this use authorization is set forth as new Section 761.31(h) on pages 10-11 of these comments.

Specific Suggested Changes in the Proposed Rules

Sec. 761.2(w) "PCB mixture." In addition to the proposed arbitrary 50 ppm concentration, the definition includes any material, no matter how dilute in PCB concentration, if the material is contaminated by a substance containing a PCB concentration of 50 ppm or greater. For example, if a gallon of heat exchange fluid containing 500 ppm PCB were diluted to 1,000 gallons with a non-PCB flushing fluid (final concentration 0.5 ppm PCB), the resulting flushing fluid when drained would still be arbitrarily considered a PCB mixture. We recommend the definition be changed to read:

> (w) "PCB Mixture" means any combination of chemical substances which contains 500 ppm (0.050 percent on a dry weight basis) or greater of a PCB chemical substance. This definition includes, but is not limited to, dielectric fluid and contaminated solvents, oils, waste oils, heat transfer fluids, other chemicals, rags, soil, paints, debris, sludge, slurries, dredge spoils, and materials contaminated as a result of spills.

Sec. 761.2(bb) "Manufacture 'for Commercial Purposes.'" We recommend for clarification the addition of the following subsection to the definition, which is consistent with the discussion by the EPA set forth in column 1, 43 FR 24805:

> (3) As the desired product. Inadvertent manufacture as a by-product in the manufacture of another chemical is not "manufactured for commercial purposes."

Sec. 761.2(cc) "PCB Sealant, Coating, or Dust Control Agent." This term is defined based on the state of the

analytical art. In complex mixtures such as waste oils, analysis for PCB is not sensitive because of background interference. We recommend that a concentration level be set related to the toxicological properties of PCB's and the demonstrated injury risk associated with human and environmental exposure. Such a concentration would, among other things, avoid a moving target definition depending upon the sophistication of the analytical equipment used.

Sec. 761.2(dd) "Process 'for Commercial Purposes.'" We recommend the addition of the following subsection to the definition. This is consistent with the discussion in column 1, 43 FR 24805 and our proposed modification of section 761.2(bb).

> (3) for means other than PCB removal. Processing which removes PCB from the material to be used for commercial purposes does not constitute "processing for commercial purposes."

Sec. 761.2(ff) "Significant Exposure." This term is defined based on the state of the analytical art. We believe that significant exposure should be, as discussed above relative to Section 761.2(cc), a specific concentration related to the toxicological properties of PCB's and to injury risk associated with human or environmental exposure. We recommend, consistent with the 1977 American Conference of Governmental and Industrial Hygenists publication of Threshold Limit Values for Chemical Substances in the Workplace, that this section be amended to read as follows:

> (ff) "Significant Human Exposure" means any exposure of humans to PCB chemical substances or PCB mixtures in excess of 0.5 mg/cu. meter TWA for a 40 hour week by an applicable analytical method.

Sec. 761.1(gg) "Small Quantities for Research and Development." The definition of this term is unjustified and arbitrary. No data are presented in the preamble by the EPA that use in research has posed any measurable risk of injury to health or harm to the environment. Monsanto has no evidence of any adverse effect of PCB's in laboratory use. We suggest as an alternative replacing section 761.2(ff) with the following wording taken in part from the TOSCA Inventory Reporting Regulations, 42 FR 64576, section 710.2(y):

> (gg) "Small Quantities for Research and Development" means any quantity of PCB chemical substance or PCB mixture manufactured or processed only for purposes of scientific experimentation or analysis of chemical

> research on, or analysis of, PCB's, including research or analysis for the development of a product that (1) are no greater than reasonably necessary for such purposes, and (2) are used by, or directly under the supervision of, a technically qualified individual(s).

It would also seem appropriate to include as new section 761.2(kk) the definition of "Technically Qualified Individual" based upon section 710.2(aa) of the TOSCA Inventory Reporting Regulations.

Sec. 761.2(hh) "Totally Enclosed Manner." This term is defined with reference to section 761.2(ff) and, consistent with our recommended changes above to that section, we suggest section 761.2(hh) be changed to read:

> (hh) "Totally Enclosed Manner" means any manner that will ensure any exposure of human beings or the environment to PCB chemical substances will be insignificant.

Sec. 761.2(jj) "Applicable Analytical Method." We propose the following new definition of this term:

> (jj) "Applicable Analytical Method" means a method (other than the perchlorination procedure) which distinguishes PCB Chemical Substance as defined in section 761.2(t) from all other materials.

The basis for exclusion of the perchlorination procedure is discussed more fully in the attached letter dated March 15, 1976 from J. Coleman Weber of Monsanto to Dr. I. E. Wallen of the EPA.

Section 761(kk) "Technically Qualified Individual." We proposed a new definition for this term with the following wording taken from Section 710.2(aa) of the TOSCA Inventory Reporting Regulations, 42 FR 64576:

> (aa) "Technically Qualified Individual" means a person (1) who because of his education, training, or experience, or a combination of these factors, is capable of appreciating the health and environmental risks associated with the chemical substance which is used under his supervision, (2) who is responsible for enforcing appropriated methods of conducting scientific experimentation, analysis, or chemical research in order to minimize such risks, and (3) who is responsible for the safety assessments and clearances related to the procurement, storage, use, and disposal of the chemical substance as may be appropriate or required

within the scope of conducting the research and development activity. The responsibilities in clause (3) of this paragraph may be delegated to another individual, or other individuals, as long as each meets the criteria in clause (1) of this paragraph.

Section 761.31(f) Hydraulic die casting systems-use. The same considerations that support a use authorization for hydraulic die casting systems apply to other industrial hydraulic systems as well. Therefore, we recommend that all references in this section to the words "hydraulic die-casting system" be changed to "industrial hydraulic system."

Section 761.31(h) Heat transfer systems - use. We recommend this new use authorization as follows:

(h) Heat Transfer Sytems - Use. Heat transfer systems containing PCB mixtures may be used and serviced in a manner other than a totally enclosed manner until five years after the effective date of this rule subject to the following conditions:

(1) One year after the effective date of this rule no heat transfer systems of 500 gallon capacity or less may contain fluid whose PCB mixture volume is greater than 1%.

(2) Two years after the effective date of this rule no heat transfer systems of greater than 500 gallon capacity may contain fluid whose concentration of PCB mixture exceeds 500 ppm.

(3) Ninety days after the effective date of this rule each person who owns a heat transfer system containing residual PCB's above the authorized levels shall report to EPA, and retain records of, the number of such systems he owns, the volume capacity of each such system, and the PCB volume or concentration, as appropriate, of the fluid contained in such systems. This report shall be sent to the Pesticides and Toxic Substances Enforcement Division (EN-342), Environmental Protection AGency, 401 M Street S.W., Washington, D. C. 20460. Each person who owns such a system shall also keep a current record of the dates of each draining or refilling and the measured PCB concentration or volume, as appropriate, of the fluid in the refilled systems on those dates for each system. If any such system is

sold, the transaction and the parties thereto shall be reported to EPA by the Seller. At its discretion, EPA may require the submission of a copy of a person's current record.

(4) Each report submitted to EPA under paragraph (h)(3) of this section shall contain the certification found in §761.31(b)(2).

(5) Each person who owns a heat transfer system containing residual PCB's above the authorized levels shall develop and implement a plan for the control of PCB exposures and contamination in accordance with Annex VII.

Your favorable consideration of the above comments is respectfully requested.

Sincerely,

W. R. Corey
Director, TOSCA Administration

March 18, 1976

Dr. E. E. Wallen
Environmental Protection Agency
Office of Toxic Substances
401 M Street S.W.
Washington, DC 20460

Dear Dr. Wallen:

Monsanto has a concern over the validity of the perchlorination technique used by EPA and others to measure and/or confirm polychlorinated biphenyls in environmental materials.

In our investigation of the perchlorination method, we have found that such chemicals as biphenyl, alkylated biphenyl, and many other substituted biphenyls, interfere with the perchlorination technique. It also appears that various petroleum components may interfere. If these chemicals were present in environmental materials that were being tested for PCB's using the perchlorination method, erroneously high PCB concentrations would be reported.

A recent article in the Journal of the AOAC (Vol.58, No.3, 1975) points out two other limitations of the perchlorination procedure:

1. High and variable reagent blanks, which cause erroneously high findings.

2. Formation of bromononachlorobiphenyl, which causes low recoveries.

A copy of the article is attached.

ACM CC6502

Since these limitations can lead to significant errors in determining trace levels of PCB's in environmental samples, we suggest that EPA carefully review the validity of the perchlorination technique. Results that have been obtained using this technique may not be valid.

If any other information is needed, please let us know.

Sincerely,

J. Coleman Weber
Manager, Product Acceptability

mah

cc: Dr. A. C. Trakowski
Environmental Protection Agency

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be protected by copyright

Limitation on the Use of Antimony Pentachloride for Perchlorination of Polychlorinated Biphenyls

WILLIAM J. TROTTER and SUSAN J. V. YOUNG
Division of Chemistry and Physics, Food and Drug Administration, Washington, DC 20204

Two contaminants are present in commercially available antimony pentachloride ($SbCl_5$) used to perchlorinate polychlorinated biphenyls (PCBs) to decachlorobiphenyl (DCB). DCB is found in the $SbCl_5$ perchlorination reaction blank in which no PCBs were added. Bromononachlorobiphenyl (BNCB) is found after use of $SbCl_5$ to perchlorinate PCBs. Levels of DCB found in the $SbCl_5$ reaction blanks from various distributors ranged from 8 to 972 ng DCB/ml $SbCl_5$. The relationship of the formation of BNCB to amounts of various PCB Aroclors perchlorinated is examined.

Polychlorinated biphenyl (PCBs) residues are extracted, cleaned up, and detected by methods similar to those used for organochlorine pesticides. PCB residues are quantitatively determined by comparing the gas-liquid chromatographic (GLC) response of the multicomponent residue and commercial PCBs (Aroclors®) or a mixture of Aroclors producing a GLC response pattern similar to that of the residue (1). This approach is limited because the multicomponent PCB residue may not have the same proportional composition as the Aroclor or Aroclors used as the quantitation reference. Residues can be composed of mixtures of chlorobiphenyl components from more than 1 Aroclor. Metabolic and other environmental factors complicate the description of the PCB residue composition.

There has been considerable work to develop methods to convert the multicomponent PCBs to a single derivative on which to base the residue determination. Procedures have been reported to catalytically dechlorinate PCBs with hydrogen over palladium or platinum to biphenyl, cyclohexylbenzene, and bicyclohexyl (2, 3). A principal disadvantage with that procedure is that the hydrocarbon product is determined with a GLC flame ionization detector, resulting in low sensitivity. Attempts have been made to convert PCBs to the fully chlorinated decachlorobiphenyl (DCB) (3–5). Armour (6) reported optimum conditions for perchlorinating PCBs with antimony pentachloride ($SbCl_5$). The method provides a qualitative confirmatory procedure for PCB determination. The GLC electron capture detector response is enhanced because total PCBs are manifested as a single peak for DCB. In measuring the single peak for DCB the analyst is not faced with analytical judgments such as baseline correction, method of integration, or discrimination between PCBs and non-PCB components. However, it is necessary to be aware that the various Aroclors give rise to different equivalents of DCB and that the nonchlorinated biphenyl (also used as a fungicide) is perchlorinated by $SbCl_5$ to DCB. Nonetheless, using the perchlorination derivatization can reinforce the residue value determined by measuring a multicomponent PCB residue.

During attempts to apply the perchlorination derivatization in determining low residue levels of PCB and make use of the increased electron capture response to DCB, 2 contaminants were indicated which led to erratic recoveries of DC

Experimental

Reagents and Apparatus

(a) *Antimony pentachloride.*—Hooker Chemical, Niagara Falls, NY 14302 (received in glass bottle with lead-lined cap); Matheson Coleman & Bell (MCB), Norwood, OH 45212 (reagent grade); B&A (Allied Chemical), Morristown, NJ 07 (reagent grade, 99%); Research Organic-Inorganic Chemical (ROC-RIC), Belleville, NJ 07 (99.99%); and J. T. Baker Chemical, Phillipsburg, NJ 08865 (Baker Analyzed Reagent).

(b) *Gas chromatograph.*—Searle-Analytic (Des Plaines, IL 60055) Model 5360 with 6' × 4 mm glass column containing 1% OV-101 on 80–100-mesh Chromosorb W (HP). Operating conditions: column flow, 60 ml nitrogen/min; column, 200°; detector, 202°C; injector, 225°C; pinched-out electron capture detector with titanium tritide detector voltage (constant dc) adjusted to obtain one-half full scale recorder deflection for 0.7 pg DCB when full scale deflection is 1×10^{-9} amp.

(c) *Mass spectrometer.*—Varian MAT CH-5 (Varian Associates, Springfield, NJ 07081) CH5-DF mass spectrometer (MS) coupled to Varian Aerograph 2740

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chromatograph via all-glass system using Watson-Biemann 2-stage separator. GLC operating conditions: 6' × 4 mm id glass column containing 3% OV-1 on 80–100 mesh Chromosorb W (HP); column flow, 60 ml helium min; column 240°C. MS operating conditions: electron energy, 70 ev; emission current, 300 μa; multiplier voltage, 2.2 kv.

Results and Discussion

A peak identical to that of DCB was found in the reaction blank for the Armour perchlorination procedure (6) with the described GLC operating conditions. The identification of DCB was confirmed by GLC-MS of a hexane extract of a hydrolyzed sample of $SbCl_5$ which had not been subjected to the perchlorination procedure. Various quantities (0.2–2.0 ml) of $SbCl_5$ from the 5 commercial sources were examined to determine the presence of DCB. $SbCl_5$ alone was carried through the perchlorination reaction (6) except that no $CHCl_3$ was present with $SbCl_5$ in the reaction vessel. DCB was determined by GLC. Table 1 lists the amounts of DCB found.

After perchlorinating PCBs with $SbCl_5$, a secondary peak with a GLC retention time relative to DCB of 1.31 was observed similar to that reported by Huckins *et al.* (7). This later eluting peak is seen in Fig. 1, the chromatogram from the 0.2 ml $SbCl_5$ (Hooker Chemical) perchlorination of 0.50 μg Aroclor 1221. This peak was found when $SbCl_5$ from each supplier was used. The peak was determined by GLC-MS to be due to bromononachlorobiphenyl (BNCB). BNCB was assumed to be a competing product with DCB arising from a small amount of $SbCl_3Br_2$ in $SbCl_5$, so parameters relating to possible limitations of the perchlorination procedure were studied. Various quantities (0.5–10 μg) of Aroclors 1221, 1242, 1254, and 1260 in $CHCl_3$ were perchlorinated. Recoveries of DCB and estimates of the relative amounts of BNCB formed are given in Table 2. Calculation of the relative

Table 1. DCB (ng/ml) formed from various amounts of $SbCl_5$

Supplier	$SbCl_5$, ml 0.2	1.0	2.0	Av.
Hooker Chemical	37	44	47	43
ACB	35	42	38	38
G&A	960	1042	913	972
MOC-RIC	12	13	12	12
J. T. Baker	9	7	7	8

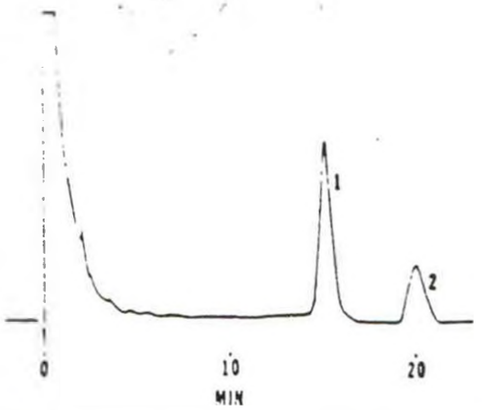

FIG. 1—Electron capture GLC curve from the 0.2 ml $SbCl_5$ (Hooker Chemical) perchlorination of 0.50 μg Aroclor 1221; 0.51 ng equivalent Aroclor 1221 injected. Peak 1 represents 0.31 ng DCB. Peak 2 represents 0.20 ng BNCB.

amounts of BNCB product formed was based on comparison of the electron capture GLC peak height of BNCB with that of a DCB reference.

The amount of DCB determined in the reaction blank was directly proportional to the amount of $SbCl_5$ used (Table 1). This indicates $SbCl_5$ was the source of the DCB and that contamination from other possible sources during the perchlorination was negligible. The procedure for perchlorinating PCBs specifies the use of 0.2 ml $SbCl_5$. $SbCl_5$ producing 5–972 ng $SbCl_5$/ml in the reaction blank would add 0.5–65 ppb. based on a 3 g sample.

DCB produced in the reaction blank was assumed to come from PCB contamination of $SbCl_5$. In an effort to locate the origin of this contamination, $SbCl_5$ bottle closures were investigated. GLC analysis of hexane, in which the plastic caps were soaked for 4 days, did not reveal PCBs. Hooker Chemical, the sole domestic source of $SbCl_5$, supplied $SbCl_5$ in glass bottles with lead-lined caps. This bulk supplier of $SbCl_5$ indicated that the production of chlorine in carbon anode half-cells with linseed oil or other organic binders forms certain organic compounds; however, the destructive oxidative environment in the electrolytic cells would make the production of PCB unlikely as a result of this pathway. On the other hand, antimony metal is commonly obtained as a metallurgical by-product by carbon reduction of its oxide; therefore,

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Table 2. DCB and BNCB from perchlorination of various Aroclors with 0.2 ml $SbCl_5$[a]

Aroclor	Amt, μg	DCB recd, %	BNCB[b] recd, %	DCB + BNCB[b] combined rec, %
1260	10	86	0	86
1254	10	84	0	84
1242	10	88	4	92
1221	10	67	16	83
1260	4	81	0	81
1254	4	80	0	80
1242	4	78	8	86
1221	4	70	18	88
1260	0.5	89	2	91
1254	0.5	78	6	84
1242	0.5	72	10	82
1221	0.5	60	19	79

[a] Hooker Chemical $SbCl_5$.

[b] Quantity calculated by comparison of electron capture GLC response to BNCB vs. response to DCB reference standard.

it is conceivable that PCBs could be associated with the antimony metal employed in the $SbCl_5$ process. No heat transfer systems containing PCBs are used in either the chlorine or $SbCl_5$ production facilities, and $SbCl_5$ does not come into contact with plastics in the manufacturing operation or in shipping containers (Hooker Chemical and Plastics Corp., 1974, private communication).

Two parameters (various quantities and various Aroclors) were studied in relationship to the production of BNCB as a competing product of DCB during the perchlorination of PCBs. BNCB was calculated by comparison of the electron capture GLC response to BNCB vs. the response to DCB. Several factors are considered: (1) In this reaction bromination is kinetically favored over chlorination. With perchlorination of lower amounts of PCBs the relative yield of BNCB to DCB is greater because the chlorinating agent is the limiting quantity in contaminated $SbCl_5$. (2) Bromination occurs to a greater degree for a given quantity of the less chlorinated PCBs such as Aroclors 1221 and 1242 rather than for 1254 and 1260. This likely is due to a greater number of reactive sites and less steric hindrance. (3) In the range of PCBs and chlorinated (0.5–10 μg) in the above study, it is likely that with lower amounts of PCBs or less chlorinated Aroclors the decrease in DCB recovery is principally due to the increase in BNCB formed.

One of the major advantages of perchlorination in determining minute quantities of PCBs is the inherent increase in effective GLC detector response. Contaminated $SbCl_5$, as described here, would preclude its use in many of these cases.

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Monsanto

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July 27, 1978

Office of Toxic Substances (TS-794)
Environmental Protection Agency
401 M Street, S. W.
Washington, D. C. 20460

Attention: Ms. Joni T. Repasch

Dear Ms. Repasch:

This notification is sent to you in accordance with instructions contained in the June 7, 1978 issue of the Federal Register in connection with proposed rules for the Manufacturing, Processing, Distribution and Commerce, and Use Bans of Polychlorinated Biphenyls.

The instructions require that requests to participate in the hearing, to be conducted August 21, 1978, are to be sent to the above address by July 31, 1978. Monsanto Company does not at this time plan to present testimony at the hearing. We do, however, desire to participate in the hearing in every other respect, including the questioning of witnesses which do testify. We are, therefore, hereby giving notice to this effect.

Thank you for including this notification in the record of this proceeding.

Yours very truly,

Phocion S. Park
Environmental Counsel

jf

PLAINTIFF'S EXHIBIT 935

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March 16, 1978

Mr. Ben Lemlich
Office of Toxic Substances (TS-788)
Environmental Protection Agency
401 M Street S.W.
Washington, D.C. 20460

Dear Mr. Lemlich:

Confirming our telephone conversation of March 14, 1978, you approved our proposed modifications to the M_L and M_S labels for PCB's. The M_L change involved the "A toxic environmental..." statement where "with" in the second line dropped to the third line, "Regulations" to the fourth line and "contact" to the fifth line. The M_S change concerned the "for proper disposal..." statement where "information" was moved to the first line and "U.S. Environmental" to the second line with all copy centered right and left. These modifications afford maximum, overall type size utilization with adequate word spacing in the area defined for these labels by the regulations published in the Federal Register dated February 17, 1978.

Based upon your approval, we are proceeding to have labels produced in order to achieve the earliest possible compliance.

Yours truly,

Kenneth E. Smith, Jr.
Labeling Supervisor