COMMENTS OF THE UTILITY SOLID WASTE ACTIVITIES GROUP, THE EDISON ELECTRIC INSTITUTE AND THE NATIONAL RURAL ELECTRIC COOPERATIVE ASSOCIATION ON EPA'S PROPOSED AMENDMENT TO THE DISPOSAL REQUIREMENTS FOR LARGE PCB CAPACITORS IN CHEMICAL WASTE LANDFILLS (44 Fed. Reg. 66851, NOVEMBER 21, 1979)

The Utility Solid Waste Activities Group (USWAG), the Edison Electric Institute (EEI), and the National Rural Electric Cooperative Association (NRECA) are pleased to submit these comments on EPA's proposed amendment to the PCB disposal requirements, extending the date for disposal of large PCB capacitors in chemical waste landfills until thirty days after an approved Annex I incinerator is operational for general use. (44 Fed. Reg. 66851 (November 21, 1979)).

USWAG is an informal consortium of approximately 65 electric utility operating companies, EEI and NRECA. EEI is the national association of investor-owned electric power companies. Its members provide approximately 77% of the total electric generating capacity of the United States. NRECA is the national association of rural electric cooperatives. Its membership totals in excess of 1,000 and serves 25 million people in 46 states. A complete list of USWAG members appears as Attachment A to these comments.

USWAG agrees that there is a need to extend the January 1, 1980 cutoff date for disposal of PCB capacitors in chemical waste landfills. To that extent, USWAG supports EPA's proposal.

However, USWAG believes that the deadline proposed by EPA, i.e., "thirty days after EPA has announced an approved Annex I incinerator is operational for general use for the disposal of large PCB capacitors," is needlessly vague and largely impractical.

First, it is unclear what is meant by "operational for general use." This could be interpreted to require nothing more than that a facility has an EPA permit to operate. Such an interpretation would simply ignore the very real possibility that start-up problems associated with actual day-to-day operations will cause shutdowns or other delays. Moreover, a 30-day period is an insufficient time frame in which utilities can reasonably plan and arrange for transportation to the incineration facility.

Second, extension of the deadline until 30 days after only one incinerator is approved, as proposed by EPA, will in no way insure that adequate disposal facilities for capacitors are available. In fact, it seems quite clear that the El Dorado, Arkansas incinerator will not even be able to meet the demands placed on it just by disposal of liquid PCB wastes, let alone by disposal of PCB capacitors.

For these reasons USWAG believes that landfill disposal of large PCB capacitors should be continued, at a minimum, until July 1, 1981.

DISCUSSION

Earlier this fall, USWAG petitioned under Section 21 of the Toxic Substances Control Act to effect an extension of the landfill disposal deadline. That petition has been placed in the record of this proceeding. 44 Fed. Reg. at 66852. We will not repeat many of the points made in that filing. Rather, these comments will respond to the data requests made by EPA in the notice and will focus on the issues raised by EPA's actual proposal.

I. DATA REQUESTED IN THE PROPOSAL

EPA specifically requested responses to five questions:

(1) How many large PCB capacitors are disposed of monthly?

(2) How many large PCB capacitors will remain in use after January 1, 1980?

(3) How long would it take industry to begin sending large PCB capacitors to incinerators?

(4) What cost and space limitations would industry face if it were not able to dispose of large capacitors at all, for example, for six months?

(5) How many large PCB capacitors are leaking at the time of disposal?

To assist EPA in obtaining accurate data on each of these points, USWAG, through its member association the Edison Electric Institute, conducted two surveys of over 100 electric

utility companies. The results of these surveys are summarized below, together with other relevant data that USWAG has been able to obtain from other sources.

(1) Number of PCB Capacitors Disposed of Monthly

Based on responses received from over 60 utility companies representing slightly under 50% of the total U.S. electric generating capacity, nearly 4,800 large PCB capacitors are disposed of by these companies on a monthly basis. The Electric Power Research Institute (EPRI) has estimated that on an industry-wide basis over 26,000 large high voltage and large low voltage PCB capacitors will require disposal each month.[1/]

(2) Number of Large PCB Capacitors Remaining In Use After January 1, 1980

Based on responses from 49 utility companies representing 43% of the total U. S. electric generating capacity, slightly over one million large PCB capacitors will remain in service at these companies after January 1, 1980.[2/]

1/ The EPRI number includes the large numbers of PCB capacitors used by rural electric companies which do not generate their own power but which transmit and distribute electric power.

2/ If one includes all capacitors in use in the United States, including rural cooperatives, we roughly estimate that 7-9 million PCB capacitors will be in use after January 1, 1980.

(3) Time Needed for Industry To Start Sending Capacitors To Incinerators

The time necessary is largely a factor of the availability of transportation to Arkansas and the ability of the incinerator facility to handle incoming shipments. Some information on the latter factor is available (see Section II, below). Given the brief comment period, however, USWAG was unable to obtain pertinent data concerning the transportation question. Accordingly, we can give no precise response to EPA's third inquiry. It is our belief, however, that transportation arrangements will not be available on call and that other issues such as those relating to liability and insurance will slow the transport of large PCB capacitors.

(4) Cost and Space Limitations If No Disposal Method Is Available For Large PCB Capacitors

Based on more than 60 responses, 63% of the surveyed utility companies have less than six months of available storage capacity for large PCB capacitors, and approximately half of these have less than three months of available storage capacity. More importantly, most utilities will require between four and twelve months to complete construction of expanded storage facilities.[3/]

3/ If adequate incineration facilities are not available in the immediate future, even these expanded storage facilities may be inadequate. As discussed in Part II, the El Dorado incinerator, even if fully operational, may be

Footnote continued --

While a wide cost range was estimated by the respondents to provide an additional six months storage capacity for PCB capacitors, 61% of the responding utilities estimated their costs to be between $10,000 and $50,000. Overall, the average estimated cost was $34,000 per utility.

(5) Number of Large PCB Capacitors Leaking At Time of Disposal

The actual percentage of capacitors leaking at the time of disposal varies greatly from utility to utility. Based on responses from approximately 60 utility companies, we estimate that, on the average, approximately 40% of all large PCB ca-capacitors are leaking at the time of disposal and thus are disposed of only after they have been placed in a secondary container. 4/

II. CAPACITY OF THE EL DORADO, ARKANSAS INCINERATOR

It is our understanding that the ENSCO facility in El Dorado, Arkansas is the only incinerator tested to date for

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Footnote continued --

incapable of meeting the monthly disposal demands for capacitors. In such an event, utilities will be forced to expand their storage facilities continually as more and more capacitors rapidly accumulate.

4/ Our surveys did not provide a basis for determining the exact nature of the leaks. A small percentage of the leaks probably result from rupture of the casing. The majority of leaks, we believe, result from broken bushings.

disposal of PCB capacitors. In addition to that capability, the incinerator also is equipped — and has been tested — to burn PCB liquids. The limitations on the facility's disposal capacity raise serious doubt that a minimally adequate disposal mechanism will be available when the incinerator is "operational for general use," absent some alternative disposal method.

The estimated disposal capacity of the El Dorado incinerator is 28,000 gallons of liquid PCBs per month and 6,000 large PCB capacitors per month.[5/] This capacity will be totally inadequate to meet not only the initial needs but even the monthly needs of the utility industry.

The Electric Power Research Institute has estimated that from 1978 until 1996, 587,000 gallons of PCB liquids from utility-owned PCB Transformers will require disposal each year. Since the lack of an approved incinerator has prevented the disposal of PCB liquids since February 1978, there are already over one million gallons of liquid PCBs awaiting incineration. Thus it is expected that some 1.76 million gallons (1.174 million gallons currently in storage plus 587,000 gallons requiring

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5/ This assumes that EPA permits the incinerator to operate 24 hours/day at the feed rate at which the test burn was conducted. Test burn feed rate was 1000 pounds of PCB capacitors and 500 pounds of PCB oil per hour. This corresponds to a feed rate of 8.33 capacitors per hour and 38.8 gallons of oil per hour.

disposal in 1980) will require incineration in 1980. Given the capacity of the facility, if nothing but dielectric fluids were burned at El Dorado it would not be possible even to keep pace with the annual disposal requirements, let alone eliminate the inventory that will be on hand when the incinerator is approved.

Moreover, excluding the vast quantities of fluids requiring incineration, the 26,000 large PCB capacitors requiring disposal each month would also greatly exceed the estimated capacity of the incinerator. In fact, even if only leaking capacitors were incinerated, the material available for disposal (estimated at 11,000/month assuming 40% leakage) would exceed the incinerator's capacity. Clearly, the El Dorado incinerator will not alleviate the current need for landfill disposal of PCB capacitors.

Not only does the El Dorado, Arkansas facility lack adequate incineration capacity, but its location also poses serious transportation difficulties. There are no major interstates or highways running into the town. Nor is there a major rail route into El Dorado.[6/] Given the volume of the material for disposal, it seems inconceivable that the current transportation routes into the town will be sufficient to

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6/ A rail siding is located at the facility, but scheduled service into El Dorado is limited.

handle the influx of trucks carrying capacitors and drums of fluids from all across the United States.

Moreover, at the present time, there is not sufficient storage capacity at the incinerator to store the large quantities of materials that will be shipped to the incinerator. If this incinerator is the only approved disposal site, the tremendous demand on the facility and the corresponding need for the scheduling of transportation of capacitors and fluids to the site will pose significant logistical problems. It is by no means clear when these logistical difficulties will be solved in order to permit the incinerator to operate at its estimated capacity -- a capacity still far short of the expected demand.

III. SAFETY OF CHEMICAL WASTE LANDFILLS

At the present time, large PCB capacitors are disposed of in chemical waste landfills. In the majority of cases, capacitors are non-leaking at the time of disposal with the capacitor casing itself preventing leakage of PCBs into the environment. In those cases where capacitors are leaking at the time of disposal, the capacitors are placed in containers specifically constructed according to Department of Transportation specifications to prevent the leakage of hazardous waste. Thus, before any capacitor is placed in a chemical waste landfill, measures are taken to insure that PCBs are unlikely to leak into the landfill.

Further, a study sponsored by EPA indicates that PCBs are highly unlikely to migrate through the soil of a chemical waste landfill.[7/] PCBs were, in fact, found to be immobile in earth materials commonly used in chemical waste landfills. Thus, even if PCBs would at some future date leak from a capacitor casing or container, it is highly unlikely that the PCBs would be able to migrate further.

Finally, the Annex II requirements for chemical waste landfills (40 C.F.R. § 761.41, 44 Fed. Reg. 31553 (May 31, 1979)) insure that even in the highly remote possibility that PCBs did escape from a chemical waste landfill, these chemicals would be quickly detected. Landfill operators are required to have both groundwater monitoring wells and leachate collection systems which permit the early detection of any leakage of PCBs into the environment.

Thus, chemical waste landfills provide an environmentally safe disposal method for PCB capacitors.

IV. USWAG PROPOSALS

In its petition to the Agency requesting an extension of the deadline, USWAG suggested that the deadline be extended

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7/ Griffin, DeWalle, Chian, Kim and Au, Attenuation of PCBs by Soil Materials and Char Wastes in Management of Gas and Leachate in Landfills (S.K. Banerji ed. 1977) (Sponsored by University of Missouri and Cincinnati Office of EPA). (See Attachment B).

to July 1, 1981. We continue to believe that the deadline must be extended until at least that date.

The El Dorado, Arkansas incinerator will not be approved for use, at the earliest, until sometime in the first six months of 1980. Even if the results from the test burn are favorable (a fact we still do not know), EPA has stated that local public hearings will be held prior to final approval. Therefore, it seems unlikely that the incinerator will become operational prior to mid-1980.

Given the vast quantities of liquid PCBs requiring disposal and the difficult logistical and transportation problems remaining to be solved, it is likely that the El Dorado incinerator will be unable to handle even a small percentage of the capacitors requiring disposal each month. In light of these problems, a July 1, 1981 cutoff date seems most reasonable. This date will insure that the incinerator has been in operation for at least one year and that a sizeable portion of stored liquid PCBs will have been destroyed. By then, also, the logistical and transportation problems will have been studied and possibly, resolved, permitting the orderly and efficient disposal of PCBs. Moreover, by that time, an additional liquid PCB incinerator in Texas may be in operation to ease the demand on the El Dorado facility.

In light of these facts and those previously addressed in USWAG's petition, EPA's proposal to permit continued disposal

only until 30 days after an incinerator is operational for disposal of capacitors is unrealistic. This short timetable could well result in numerous problems and confusion as vast quantities of accumulated liquids and capacitors containing PCBs descend on El Dorado. In addition, the uncertainty of the cutoff date will preclude utilities from planning their disposal efforts in an orderly and economic fashion. Ultimately, it would result in needless expenditures for new storage facilities for capacitors, despite the fact that such equipment could be safely disposed of in chemical waste landfills. The environment would gain little, if anything, from such an approach; the utility's customers would incur additional needless cost.

Accordingly, USWAG urges that the time during which large PCB capacitors can be disposed of in a chemical waste landfill be extended at least until July 1, 1981. If, however, EPA adopts its current proposal, EPA must give assurance it will not prematurely announce that the El Dorado incinerator is operational for general use. A realistic start-up period should be reflected in that decision, as well as a determination that the facility is, in fact, technically capable of handling large PCB capacitors on a day-to-day basis. This is particularly necessary since no test burn of large capacitors was made this fall. Finally, the incinerator should be declared "operational for general use" only after it is

demonstrated that the facility is capable of handling the expected demand for capacitor disposal and the associated logistical, transportation and storage problems associated with the incinerator have been solved. USWAG seriously doubts these criteria can be met prior to July 1, 1981. Furthermore, they must be met in order that there be a realistic, practical and economic approach to the disposal of large PCB capacitors in an Annex I facility. In the interim, the disposal of such equipment in a chemical waste landfill provides an environmentally sound solution to a significant problem and that disposal should be continued.[8/]

Respectfully submitted,

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8/ Since leaking capacitors are fully enclosed within a secondary container, we see no reason to distinguish between capacitors that do and do not leak at the time of disposal.

ATTACHMENT A

MEMBERS OF THE UTILITY SOLID WASTE ACTIVITIES GROUP

Edison Electric Institute
National Rural Electric Cooperative Association
Appalachian Power Company
Atlantic City Electric Company
Baltimore Gas & Electric Company
Central Hudson Gas & Electric Corporation
Central Illinois Light Company
Central Illinois Public Service Company
Central & South West Corporation
- Central Power & Light Company
- Public Service Company of Oklahoma
- Southwestern Electric Power Company
- West Texas Utilities Company

Columbus & Southern Ohio Electric Company
Commonwealth Edison Company
Consolidated Edison Company of New York, Inc.
Duke Power Company
Duquesne Light Company
Florida Power & Light Company
Gulf States Utilities
Houston Lighting & Power Company
Illinois Power Company
Indiana & Michigan Electric Company
Indianapolis Power & Light Company
Iowa-Illinois Gas & Electric Company
Iowa Power & Light Company
Iowa Public Service Company
Kentucky Power Company
Los Angeles Department of Water & Power
Middle South Services, Inc.
- Arkansas Power & Light Company
- Louisiana Power & Light Company
- New Orleans Public Service, Inc.
- Mississippi Power & Light Company

Monongahela Power Company
New England Power Company
Niagara Mohawk Power Corporation
Northern Indiana Public Service Company
Northern States Power Company
Ohio Power Company
Ohio Valley Electric Company
Oklahoma Gas & Electric Company
Pacific Gas & Electric Company
Pennsylvania Power & Light Company
Philadelphia Electric Company
Potomac Electric Power Company
Public Service Electric & Gas Company
Public Service Company of Indiana, Inc.
Southern California Edison Company
Southern Company Services, Inc.
- Alabama Power Company
- Georgia Power Company
- Gulf Power Company
- Mississippi Power Company

Tampa Electric Company
Texas Utilities Generating Company
The Cleveland Electric Illuminating Company
The Detroit Edison Company
The Potomac Edison Company
Union Electric Company
Virginia Electric & Power Company
West Penn Power Company
Wisconsin Electric Power Company
Wisconsin Power & Light Company
Wisconsin Public Service Corporation

ATTACHMENT B

ATTENUATION OF PCB's BY SOIL MATERIALS AND CHAR WASTES

by

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ATTENUATION OF PCB's BY SOIL MATERIALS AND CHAR WASTES

by

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ABSTRACT

Adsorption of polychlorinated biphenyl (PCB) isomeric mixtures containing 42 and 54 percent chlorine by montmorillonite clay and soil and the relative mobility of these compounds through soil media were determined by both gas chromatography and ^{14}C labeling techniques. Adsorption by these earth materials was found to be strong with more than 90 percent removal from solution at concentrations approaching the water solubility of the compounds tested.

PCB's were found to be immobile in earth materials when measured by the soil thin-layer chromatography technique. R_f values for PCB's were found to be zero to 0.02 for all amounts of PCB's tested (42-206 ng). Dicamba, a pesticide with high mobility, was used as an internal standard and yielded R_f values of 0.80 to 1.00.

Gas chromatographic analytical procedures that allowed improved quantitative measurement of PCB's in aqueous solutions were developed. The overall perchlorination procedure for conversion of isomeric mixtures of PCB's to the fully chlorinated biphenyl by digestion with $SbCl_5$ was successfully reduced from approximately 20 steps to about 10 steps. The speed of the analyses was improved and interference from bromine was removed. Reproducibility of the overall perchlorination with 80 ng biphenyl in sealed glass tubes was determined to be 0.32 percent relative standard deviation.

INTRODUCTION

Polychlorinated biphenyls (PCB's) are used in a wide range of industrial applications such as electrical insulation, fire-resistant and heat transfer fluids, hydraulic fluids, high temperature and pressure lubricants, sealants, expansion media, adhesives, plasticized paints, lacquers, varnishes, pigments, paper coatings, waxes, and as constituents in elastomers. They were largely ignored as environmental contaminants until Jensen (1) and Widmark (2) identified them in 1966. PCB's did not attract much concern as hazardous chemicals until the incidents of contaminated cooking oil in Japan in 1968 and of contaminated chicken feed in the United States in 1971 (3). Laboratory studies with animals have shown that PCB's can cause enlargement of the liver, induction of hepatic microsomal enzymes, reproductive failures, gastric disorders, skin lesions, and tumors in birds and mammals (3). The 2000 afflicted Japanese people in the "Yusho" incident of 1968 experienced lesions of the skin, facial swelling, and neurological disorders that were similar to the results reported in the animal studies (4).

Fish and other aquatic organisms tend to accumulate PCB's in lipid-rich tissues and organs. Predators at the top of the food chain may accumulate PCB's to levels of more than 10^7 times that of the ambient water (4). Man usually resides at the top of the various food chains and, due to the biological magnification, may ingest large amounts of PCB's even though only trace amounts are present in the ambient waters.

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PCB's have, therefore, been considered as a significant hazard to human health as well as the environment.

PCB's have been manufactured in the United States since 1929; it has been estimated that more than 400,000 tons have been produced since that time. The sole U.S. manufacturer of PCB's is the Monsanto Company located near East St. Louis, Illinois. Since 1971, Monsanto voluntarily has restricted its sales of PCB's to only "closed" systems, such as PCB-containing insulating fluids used in electrical transformers and capacitors. These two applications account for essentially all the current use of PCB's in the United States (3). On October 5, 1976, Monsanto announced that it would cease to manufacture and distribute PCB's by October 31, 1977. A timetable set by the U.S.-EPA has called for a gradual phasing out of PCB manufacturing by January 1, 1979, and a ban on all PCB processing or distribution in commerce by July 1, 1979 (6). These steps have significantly reduced the introduction of PCB's into the environment.

Unfortunately, approximately one-half million pounds of PCB's are still imported into the U.S. each year from foreign manufacturers and millions of pounds of PCB's still exist causing the environmental levels to remain quite high. For example, two tributaries of Lake Michigan have PCB levels that consistently exceed 100 ppt. This has contributed to PCB levels between 4 and 10 ppt in certain parts of the lake. The present U.S.-EPA recommended water quality criteria is less than 1 ppt and the high PCB levels have caused great concern to the residents of Chicago, who draw their drinking water from the lake (4).

Many companies discard their old electrical equipment in unapproved places and thus discharge the PCB's into the atmosphere and waterways. One problem of disposal involves the high costs and fees for transporting PCB wastes to regional incinerators or approved landfills vs. simply discarding the wastes. Incineration is considered the safest method for disposal of PCB wastes. However, this method is extremely costly and has some operating difficulties. PCB's do not burn readily and, under improper operating conditions, can be vaporized during incineration. Thus, incineration may turn out to be the major source of PCB's reentering the environment. In addition, large electrical transformers and capacitors, the major source of waste PCB's, cannot be satisfactorily incinerated.

Thus, land disposal is the only reasonable alternative for waste PCB's. Although landfill disposal appears to be the most acceptable alternative, little information is presently available concerning the possibility of ground-water contamination by leaching PCB's from landfills. Lidgett and Veddem (7) analyzed waters around a sanitary landfill for PCB's and found the contamination levels to be below their detection limit of 4 ppb. Similarly, Robertson and Li (8) failed to detect PCB's in ground water using GC/Mass Spectrometry techniques. Tuckar, Litsenagi, and Mass (9) studied the leaching of Aroclor 1016 from various types of soils and concluded that PCB's are not readily leached from soil by percolating water.

The paucity of information available shows no evidence that ground waters have become contaminated by PCB's. However, many surface waters do contain PCB's and the mechanism of transport in the biosphere and the mechanism of attenuation in soil are still unknown. Data on the factors affecting PCB attenuation by earth materials would provide a rational basis for future disposal site selection and design.

BACKGROUND

The research reported here is supported in part by Grant R-804684-01, from the U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Cincinnati, OH 45268.

The purposes of the present project are:
a) To conduct an extensive literature review of pertinent information on the adsorption of hazardous organic compounds;
b) To measure the adsorption capacity of selected earth materials for pure PCB's and PCB wastes;
c) To quantitatively evaluate the effects of pH, biological degradation, photodecomposition, volatilization, time, and adsorbent structure on adsorption of PCB's;
d) To use this data to develop a mathematical model that will allow prediction of PCB adsorption and mobility; and
e) To further develop analytical procedures that will allow improved quantitative measurement of PCB's contained in aqueous solutions.

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PCB Materials

Polychlorinated biphenyls (PCB's) is a generic term applied to certain mixtures of synthetic organic compounds. These compounds are mixtures of very closely related isomers and homologs that contain two phenyl rings with 10 possible chlorine attachments. The biphenyl structure is shown in Figure 1. PCB's are made by substituting chlorine atoms for one or more of the hydrogen atoms at the numbered positions of the biphenyl structure. These compounds are chemically and thermally stable, very resistant to microbial degradation, and are highly persistent in the environment.

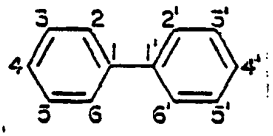

Fig. 1. BIPHENYL STRUCTURE: Positions 2 to 6 and 2' to 6' indicate ten possible positions for chlorine substitution. Different amounts of chlorine substitution form the various PCB's.

The PCB materials chosen for study were the pure Aroclors 1242 and 1254 (42 and 54% substituted chlorine, respectively) supplied by the Monsanto Company, and the ^{14}C labeled compounds were prepared by New England Nuclear Corporation. Gas chromatographic traces of the ^{14}C labeled compounds were identical to those of the pure Aroclors 1242 and 1254, respectively. Therefore, it was assumed that there were no significant differences in the respective compounds and that the ^{14}C labeled and pure Aroclors would behave similarly in studies of adsorption, mobility, and microbial degradation.

A used capacitor fluid was also obtained for study. The fluid was drained from a burned out 50 KVA capacitor manufactured by Westinghouse in 1966 and originally contained Aroclor 1242. This capacitor was supplied by Illinois Power Company and was scheduled to be landfilled. We believe this fluid is representative of the type of PCB wastes that are normally disposed of in landfills.

Adsorbents

Earth materials, representing a wide range in characteristics, have been selected as adsorbents. The materials being studied are: Ottawa silica sand; Panther Creek southern bentonite clay; the soils, namely Bloomfield ls, Ave sic, Cisne sil, Flanagan sil, Catlin sil, Drummer sicl, Weir sic, a calcareous loam till; and two coal chars. The chars were selected because of their high adsorption capacity for organic compounds. They are a waste product of many coal conversion processes and thus have potential use as a liner material for disposal sites accepting organic wastes.

Analytical Development

In general, PCB's are determined quantitatively by comparing gas chromatographic (GC) response patterns of a multicomponent environmental sample with commercial PCB's (Aroclors) or a mixture of Aroclors. This technique is limited by the sensitivity and reproducibility of comparisons of the large number of peaks produced by the various PCB isomers. The procedure is further complicated because the various components of water soluble PCB's contained in environmental samples are not likely to have the same composition as those in the original Aroclor used as a reference compound. For practical reasons, the quantization is usually done by integration of the major peaks while ignoring the minor peaks. This can cause some error, depending on how well the mixture of isomers in an unknown sample compares to a standard.

Because of these problems, we have developed procedures that allow improved quantitative measurement of PCB's in aqueous samples. The main thrust of our studies have been to improve previous procedures whereby isomeric mixtures of PCB's were converted to the fully chlorinated biphenyl, decachlorobiphenyl (DCB), by digestion with $SbCl_5$. This procedure has the advantage of converting all the PCB's to a single peak for improved quantitation. The electron capture GC detector is many times more sensitive to DCB than it is to PCB's; thus, the conversion to DCB improves the sensitivity and lowers the detection limit for PCB's.

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CURRENT STUDIES OF PCB ATTENUATION AND ANALYTICAL DEVELOPMENT

PCB Mobility

The technique of determining pesticide mobility in soils by soil thin-layer chromatography was introduced in 1968 by Helling and Turner (10). Since the introduction of the technique, the mobility of a large number of pesticides in a variety of soils has been tested (11, 12, 13). Soil thin-layer chromatography, or soil TLC, is a laboratory method that uses soil as the adsorbent phase and water as the developing solvent in a TLC system. The system is relatively simple and yields quantitative data on the mobility of organic compounds in soils that appear to correlate well with trends noted in the literature (10). The results reported here are mobility data for Aroclor 1242 and 1254 on TLC plates made from sand, clay, three soils, and a coal char. Dicamba, a pesticide of known high mobility, was used as an internal standard.

The soil sample was slurried with water until moderately fluid, and then was applied with a spreader to clean glass plates 20 cm by 20 cm square. The soil was spread to a thickness of 0.3 mm and then air dried. A horizontal line was scribed 12 cm above the base to stop water movement; vertical lines were scribed 2 cm apart to separate the various treatments. The compounds were spotted 2 cm from the base and leached 10 cm with water. The activity of the ^{14}C labeled compound varied between 11,000 and 44,000 dpm. The plates were immersed in 0.5 cm of water in a closed glass chamber and were removed when the wetting front reached the horizontal line. Leaching was thus ascending chromatography. The soil plate was then removed and air dried. A piece of 8 x 10 inch medical X-ray film was placed in direct contact with the soil plate for approximately one week. The resultant autoradiograph indicated the relative movement of the compound, which was measured as the frontal R_f of the spot or streak.

Figure 2 shows the results of PCB and Dicamba mobility on Catlin soil plates. The figure is a composite of data from two plates illustrating the low mobility of the two PCB's at four concentrations and the excellent replication of the Dicamba mobility. The amounts of PCB spotted in each lane is labeled on the figure and ranged from 42 to 206 ng. It is clear that at all four amounts PCB's remained at the origin, were immobile in Catlin soil, and the Dicamba had an R_f of between 0.85 and 0.90. The R_f is defined as the distance the compound moved relative to the distance the water front moved, that is, the Dicamba moved 85 to 90 percent of the distance the water front moved on the plate. The two PCB's had R_f values of zero.

The R_f values obtained for Aroclor 1242 and 1254, and for Dicamba on TLC plates made with several earth materials are presented in Table 1. The results clearly indicate that the two PCB's tested are highly immobile in these test systems. R_f values of zero to 0.02 were obtained for all the materials tested, even the pure silica sand. Dicamba was shown to be highly mobile in these tests with R_f values ranging from 0.20 in the clay to 1.00 in the sandy materials.

Adsorption Studies

Equilibrium adsorption studies were carried out by shaking known volumes of PCB solutions with varying weights of earth materials at a constant temperature of 25°C. Figure 3 shows representative results for adsorption of Aroclor 1242 and 1254 by montmorillonite clay. Weights of clay varied from 0.01 to 0.5 g per 10 ml of solution. Blanks containing no clay were carried through the experiment. The data in Figure 3 indicates that more than 50 percent of the PCB's were removed in the blanks (no clay). The reaction was carried out in sealed centrifuge bottles so that volatilization and losses during separation of the solid from the liquid phase were minimized. Since PCB's are highly resistant to microbial degradation, the results are interpreted as adsorption of the PCB's onto the glass walls of the centrifuge bottle. This strong adsorption by the glass container is consistent with the observation that PCB's were immobile on the silica sand TLC plates described above. Adsorption by 0.5 g of clay is nearly complete with less than 1 ppb remaining in solution. It was concluded that PCB's are strongly adsorbed by earth materials. This conclusion is consistent with the high degree of immobility observed in the soil TLC study.

Analytical Procedure Development

Little effort has been made to derivatize

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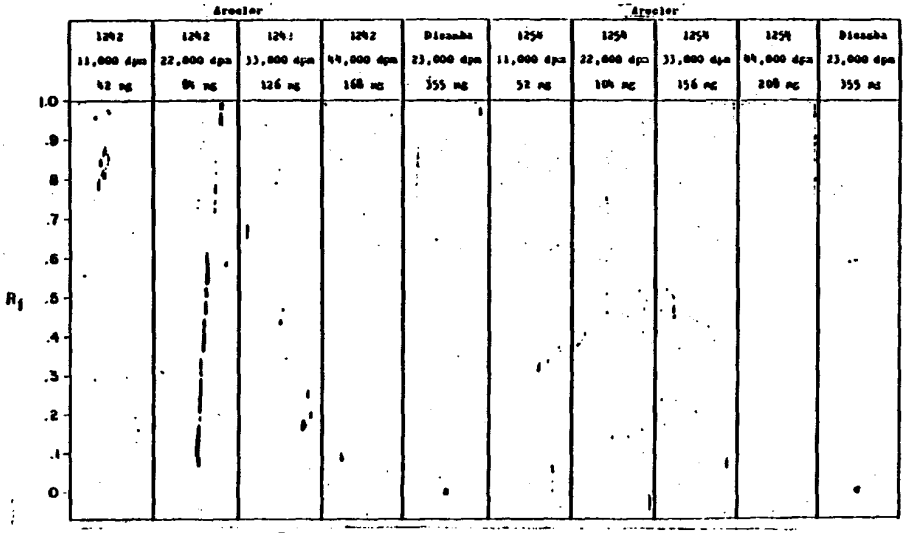

Fig. 2. PCB and Dicamba mobility in water on Catlin silt soil thin-layer chromatography plates.

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Table 1: Mobility of Aroclors 1242 and 1254 and Dicamba in Earth Materials as Measured by Soil Thin-Layer Chromatography.

Earth Material	Compound		
	Aroclor 1242	Aroclor 1254	Dicamba
	R_f		
Silica sand	.02	.02	1.00
Bloomfield Ia	.01	.01	1.00
Ava silt	.00	.00	1.00
Catlin silt	.00	.00	.86
Montmorillonite	.00	.00	1.00
Coal Char (1200°F)	.00	.00	.86

the PCB residue to a single compound for quantification. The attempted derivatives were biphenyl and decachlorobiphenyl (DCB). The former derivative could be obtained by catalytic hydrogenation of PCB's (14, 15). The main disadvantage of this approach is that the derivative, biphenyl, is determined with flame ionization detector (FID) on GC, which decreases the sensitivity of the detection system.

Procedures have been established to convert PCB's to perchlorinated PCB, DCB, by Armour (16). In brief, an extracted PCB residue with 0.2 to 0.3 ml antimony pentachloride in ~0.1 ml chloroform was subjected to heating at 170° for 4 to 15 hours. The reaction vessel used was 10 OD mm × 150 mm (internal volume ~7.5 ml) resealable glass tubes; heat was applied to one third of the tube length during the reaction. At the end of the heating the excess $SbCl_5$ was decomposed with 6N HCl, followed by hexane extraction of DCB for GC analysis. Overall perchlorination reaction requires approximately 20 steps.

The procedure has been subjected to further study by Trotter (17) and the limitations on the use of $SbCl_5$ for perchlorination of PCB's were discussed. Commercially available $SbCl_5$ is contaminated with traces of Br, likely as antimonybromotetrachloride. The presence of the Br contaminants is believed to be the source of bromononachlorobiphenyl (BNCB), which was a likely competing product with DCB during perchlorination.

Based on the above information, our efforts have been directed toward modification of the perchlorination procedure by:
1) Increasing the amount of solvent used during perchlorination.
2) Removing the Br interference.
3) Reducing the overall number of reaction steps.

The gas chromatographic column used in this study consisted of a 1 m ID × 1.83 m glass column packed with 4% SE 30/6% OV-210 on 80/100 mesh chromosorb WHP. The column temperature was held isothermally at 250°C. The detector used was a Hewlett Packard linear ^{63}Ni electron capture (ECD) with nitrogen as a carrier gas. The attenuation of the gas chromatograph was set at 1 × 4 with which full-scale recorder deflection was observed with 100 ng DCB.

For the gas chromatographic quantification, Mirex was used as an internal standard. Reproducibility of gas chromatographic quantitation of DCB with Mirex as an internal standard will be discussed in the later part of this section.

By increasing the amount of perchlorination solvent, loss of extracted PCB's can be avoided during concentration of the extracts (18). Also, a larger volume of solvent will maintain refluxing inside the reaction vessel resulting in complete mixing of PCB's and the perchlorinating reagent, $SbCl_5$.

When 2 ml of a mixture containing equal amounts of $CHCl_3$ and $SbCl_5$ was heated overnight at a heating block temperature of 220°C, interfering gas chromatographic peaks were observed. The interfering GC peaks may result from a reaction between the $SbCl_5$ and the $CHCl_3$, or between $SbCl_5$

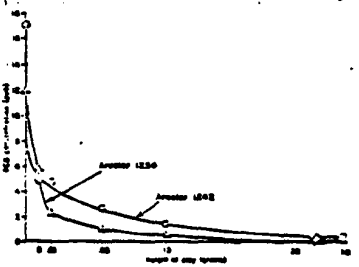

Fig. 1. Adsorption of Aroclor 1242 and 1254 by montmorillonite at 25°C.

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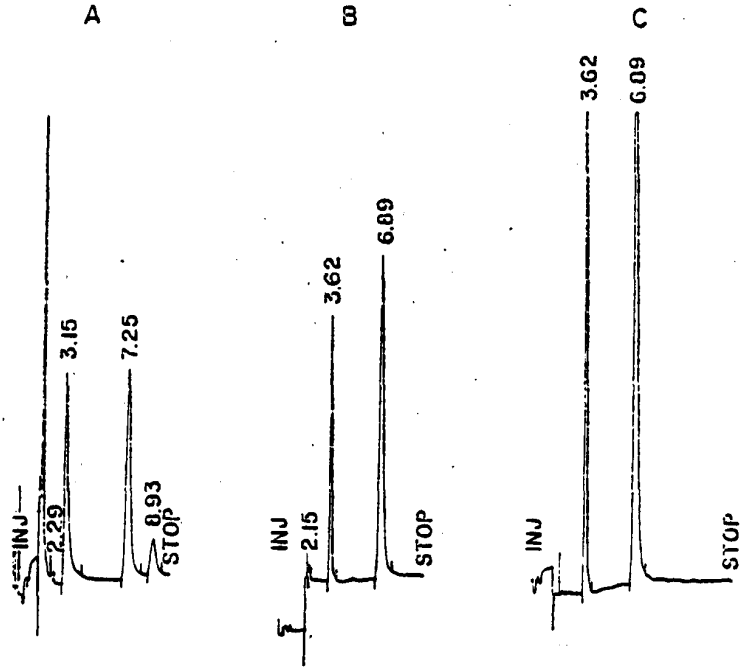

Fig. 4. Gas chromatography traces for PCB analysis. A) Interferences caused by Sr and incomplete perchlorination. B) Complete perchlorination showing disappearance of Sr interferences. C) Analysis of actual water sample using perchlorination procedure.

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and the C_4H_9OK that is present in $CHCl_3$ as a preservative. Further, the use of CH_2Cl_2 gave a similar result. However, CCl_4 did not react with $SbCl_5$ under the given reaction conditions.

A close examination of the distributions of the reaction products DCB and BNCB reveals that the halogenation steps are reversible. When a mixture of 0.5 ml of $SbCl_5$ and 80 ng of biphenyl in 1 ml of CCl_4 was reacted at 220°C for different periods of time, the distribution of these products also changes. BNCB is believed to be formed from the reaction between biphenyl and $SbCl_4$, which is present as an impurity in $SbCl_5$. The ratios of DCB and BNCB vs. reaction times are given in Table 2.

Table 2: Effect of Reaction Time on Formation of DCB and BNCB.

Reaction time	% of DCB Formed	% of BNCB Formed
4 hours	83	17
8 hours	93	7
25 hours	96	4

It is clear that a longer reaction time favors the formation of DCB over BNCB and indicates that the initial formation of BNCB is a kinetically controlled reaction. Further reaction time shifts the unstable BNCB to the more stable compound DCB—that is, it is a thermodynamically controlled reaction. Figure 4A shows that when the reaction is incomplete the BNCB peak appears at 8.6 on the GC trace. When the reaction is complete, BNCB does not appear on the GC trace (Fig. 4B). Thus interference from BNCB can be eliminated by complete reaction in the perchlorination step. Furthermore, the appearance of the BNCB peak indicates that complete perchlorination is not achieved in the particular sample.

The overall perchlorination procedure of PCB's was successfully reduced to approximately 10 steps by modifying the usual methods of liquid-liquid extraction and evaporation of the solvent. This new technique now only requires 15 to 20 minutes to prepare a finished sample after perchlorination of PCB's. The detailed procedure is shown in Figure 3. It was found that the sample reaction temperature must be at least 180°C for more than 16 hours to achieve complete reaction and destruction of BNCB. In our studies, this procedure required a heating block temperature of 240°C. Figure 4C shows a typical GC trace for a water sample processed by the procedure shown in Figure 3.

PCB ANALYTICAL PROCEDURE

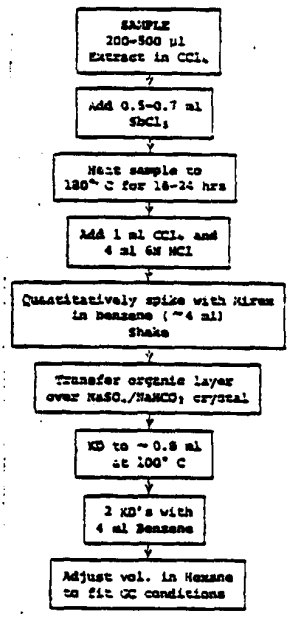

Fig. 3. Schematic block diagram of procedures used in PCB analysis by perchlorination with $SbCl_5$.

The reaction step was initially carried out in glass sealed tubes and excellent reproducibility was obtained. Table 3 shows representative results from four runs where a relative standard deviation of 0.32 percent was obtained. However, the glass sealed tubes were subject to explosion and created a safety hazard to workers in the laboratory. Therefore, the glass tubes were replaced with the teflon plugged reaction tubes shown in Figure 6; the teflon plugged tubes were more convenient and safer to use. However, Table 3 shows that

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Table 3: Perchlorination of Biphenyl to DCB.

Sample	Glass Sealed	Teflon Sealed
1	58.7	69.1
2	58.8	72.8
3	59.0	74.8
4	59.4	66.8
	RSD = 0.52%	RSD = 5.0%

much more variability in the data was obtained. The relative standard deviation from replicate samples is 5 percent. This accuracy is satisfactory for most routine analysis, but we are working to find ways to improve this procedure further.

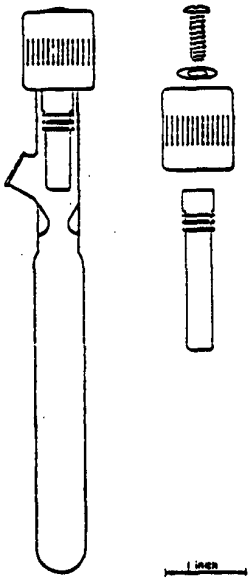

Fig. 6. Teflon plugged reaction vessel used in perchlorination reaction.

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