EXECUTIVE SUMMARY†

Polychlorinated Biphenyls Analysis in Bituminous Materials

George E. Hoag, Assistant Professor

Stanley E. Alexander, Graduate Assistant

Project 82-1

JHR 84-161 October 1984

†Based upon final report, JHR 84-160, August 1984.

This research was sponsored by the Joint Highway Research Advisory Council of the University of Connecticut and the Connecticut Department of Transportation and was carried out in the Civil Engineering Department of the University of Connecticut.

Conclusions and Recommendations

A method for the efficient extraction of PCBs from asphalt pavement and asphalt oil and subsequent analysis by electron-capture gas chromatography was developed. Recovery efficiencies of PCBs from asphalt oil and asphalt pavement using the test method were 99.5 percent and 94.8 to 99.7 percent, respectively.

Most asphalt pavement core samples contained Aroclor 1242. One set of asphalt pavement cores contained both Aroclor 1242 and Aroclor 1260. The maximum asphalt pavement PCB concentration measured in this research was 314 ug/Kg of Aroclor 1242 in sample B7P5521, Box 7 - Pole 5521. In this sample, the binder PCB concentration was 6.24 mg/Kg.

All samples of surface seal-coats (i.e. mixtures of cutter and aggregate) contained Aroclor 1242. The maximum PCB concentration in the seal-coats was 670 ug/Kg. This sample had a cutter PCB concentration of 9.97 mg/Kg as Aroclor 1242.

Soil samples taken from areas under asphalt pavement and in road-runoff zones contained Aroclor 1242 ranging from 28 ug/Kg to 95 ug/Kg. All samples contained PCBs. These results, although only preliminary, do indicate that PCBs are strongly retained in the asphalt matrix and do not significantly leach out under ambient environmental conditions.

The significance of the PCB analyses conducted in this study is that none of the asphalt pavements, binders or cutters, received from the Connecticut DOT, are PCB wastes, as defined in the Toxic Substances Control Act (TOSCA). The lower cut-off level of PCBs that are to be regulated under TOSCA is 50 ppm on a dry weight basis (i.e. PCB Waste, by definition). The highest PCB level measured any sample received for analysis in this study was 670 ug/Kg (ppb).

(i.e. 0.670 ppm) as Aroclor 1242 (dry weight basis). It can be seen that the levels of PCB detected in this study are only about 1/100 of the 50 ppm standard.

If it is assumed, however, that all of the PCBs in the asphaltic products sampled, originated in the asphaltic portion of the sample, the concentrations are significantly greater. The highest concentration in the hexane-extracted asphalt oil was 9.97 mg/Kg as Aroclor 1242. This is still well below the TOSCA level for a PCB waste (i.e. 50 mg/Kg).

Because this research did not address the sources of PCBs in bituminous materials, the origin of the PCBs in the samples analyzed cannot be determined. There is a possibility that waste oil, contaminated with PCBs at concentrations greater than 50 mg/Kg, was added to some of the products tested and only because of dilution were the PCB levels observed in this study less than 50 mg/Kg. This hypothesis, however, cannot be confirmed with information presently available.

It is recommended that additional research be initiated addressing the sources of PCBs in asphaltic and bituminous materials in order that their presence be minimized.

Future work should investigate the PCB content of soils near a highway containing PCBs. Ideally, the site should be located in a non-urban and non-industrial location to minimize other sources of PCBs.

Finally, work should be initiated that investigates the leachability of PCBs from asphaltic and bituminous materials by a variety of materials such as acidic rainfall and anthropogenic organic compounds in highway runoff.

INTRODUCTION

Concern has been expressed that polycholorinated biphenyls (PCBs) and possible other toxic substances may have been improperly disposed of in fuel and waste oils, subsequently finding their way into bituminous materials in Connecticut.[1] Because PCBs are soluble in hydrocarbon solvents and oils, the high cost of disposal and the present non-hazardous classification of waste oil in Connecticut, their presence in bituminous materials is possible. PCBs are known to be ubiquitous in the environment. It is also possible, therefore, for trace PCB contamination in bituminous materials to be the result of background PCB levels from non-specific sources.

The purpose of this research project is two-fold: 1. To develop a qualitative and quantitive method of PCB analysis in bituminous materials, and 2. to determine whether PCBs are present in bituminous materials from selected sampling sites in Connecticut.

BACKGROUND

Polychlorinated biphenyls are a group of synthetic aromatic clorinated organic compounds which have found widespread use because of their general thermal stability, resistance to acids, bases and oxidants.[2] Common industrial applications include transformer cooling oils, capacitor dielectric fluids, heat transfer and hydraulic oils, dedusting agents, plasticizers in rubber, adhesives, wax extenders, carbonless reproducing paper, and inks.

PCB PRODUCTION

Between 1929 and 1977 about 1.9 billion pounds of PCB were produced in the United States.[2] In 1979, the Environmental Protection Agency (EPA) banned their manufacture and limited their use under provisions of the Toxic Substances Control Act (TOSCA). While they are no longer chemically manufactured, it was estimated that in 1982, 750 million pounds were still in use, 500 million pounds were in the environment and 150 million pounds were exported.[3]

Of the 500 million pounds of PCBs in the environment, 300 million pounds were in landfills, 50 million pounds have been degraded and 150 million pounds remained in the air, water and sediments.[4]

The major manufacturer of PCBs in the U.S. was Monsanto. They marketed PCBs under the Aroclor^{R} trade name.[2] Aroclor products are characterized by the name Aroclor followed by a four-digit number (e.g. Aroclor 1242), where the first two-digits (e.g. 12) represent a chlorinated biphenyl and the last two digits (e.g. 42) represent the percent chlorine by weight present. Monsanto produced approximately 10 various Aroclor mixtures. The current and former uses of PCB and the Aroclor grade are listed in Table 1.[5,6]

Each Aroclor mixture contains many individual clorinated biphenyls. For example, 32 individual chlorinated biphenyls have been identified in the Aroclor 1242, while in Aroclor 1260, 36 compounds have been identified.[2]

TABLE 1

Current and Former PCB Use and Specific Aroclors Used

Current PCB Use	Aroclors Used
Electrical Capacitors	1221, 1254
Electrical Transformers	1242, 1254, 1260
Vacuum Pumps	1248, 1254
Gas-transmission Turbines	1221, 1242

Former PCB Use	
Hydraulic Fluids	1232, 1242, 1248, 1254, 1260
Plasticizer in Synthetic Resins	1248, 1254, 1260, 1262, 1268
Adhesives	1221, 1232, 1242, 1248, 1254
Plasticizer in Rubbers	1221, 1232, 1242, 1248, 1254, 1268
Heat Transfer Systems	1242
Wax Extenders	1242, 1254, 1268
Dedusting Agents	1254, 1260
Pesticides, Extenders, Inks	1254
Lubricants, Cutting Oils	1254
Carbonless Reproducing Paper	1242

PCB STANDARDS

Aquatic Standards

The environmental Protection Agency has promulgated regulations for PCBs in drinking water supplies. To insure the maximum protection of human health from the potential carcinogenic effects of PCB exposure through ingestion of contaminated water and aquatic organisms, the ambient water concentration should be zero.[7] For protection of freshwater aquatic life (i.e. stream standard for PCBs) the maximum allowable 24-hour average PCB concentration is 0.014 ug/1.

Commercial Standards

Under Subchapter R of the Toxic Substances Control Act (CFR 40.761.1), Part 761, Standards for Polychlorinated Biphenyl Manufacturing, processing, distribution in commerce, and use prohibitations have been established. In subpart A,761.1(b), in reference to the regulated levels of PCBs, it is stated that,

"...the terms PCB and PCBs are used in this rule to refer to any chemical substances and combination of substances that contain 50 ppm (on a dry weight basis) or greater..."[8] of additional importance it is also stated that,

"Any chemical substances and combination of substances that contain less than 50 ppm PCBs because of any dilution, shall be included as PCB and PCBs unless otherwise specifically provided."[8]

In summary, unless a product has been specifically given a PCB standard, the standard that makes PCB a toxic waste, subject to the regulations of TOSCA, is 50 ppm, in the most concentrated constituent of a waste material.

Of course, there is a degree of subjective reasoning which may be applied when interpreting these regulations. For example, if waste oil, contaminated with PCBs greater than 50 ppm (on a dry weight basis) is added to an asphalt binder (e.g. AC-20) and the resulting concentration is 5 ppm (on a dry weight basis) in the AC-20, is the AC-20 now a PCB toxic wastes? If the AC-20 is blended with an aggregate to make an asphalt cement now a PCB toxic waste? According to the letter of the law, perhaps the answer to this question is yes.

However, if the waste oil cannot be sampled (e.g. years after the asphalt was made) then how can it be proved, without reasonable doubt, that the waste oil did indeed contain PCBs at a concentration greater than 50 ppm. The answer is simply that it cannot be determined. Therefore, unless a representation sample of waste oil (i.e. in this example) can be obtained, then an asphalt pavement sample with a PCB concentration less than 50 ppm can not be termed a PCB waste.

PCB ANALYSIS OF ASPHALT PAVEMENT CORES

Two sets of asphalt pavement cores were received from Connecticut DOT. This first set of cores analyzed were labeled as follows:

Box 1, Location 1 = B1L1

Box 2, Location 2 = B2L2

Box 3, Location 3 = B3L3

Box 4, Location 4 = B4L4

Box 5, Pole 5523 = B5P5523

Box 6, Pole 5851 = B6P5851

Box 7, Pole 5521 = B7P5521

The second set of cores were received in October 1983, and were labeled as follows:

Core 0 = SSTC0

Core 1 = SSTC1

Core 2 = SSTC2

Core 3 = SSTC3

Core 4 = SSTC4

Core 5 = SSTC5

Results from the analysis of the first set of cores are given in Table 2. Replicates of B2L2 were run and it is evident that the recovery of binder was significantly variable; 2.94 percent and 4.76 percent binder. This probably results from the small sample size used and the subsequent error because of aggregate content in the samples. Of the seven cores received, three were found to contain Aroclor 1242 ranging from 2.48 mg/Kg to 6.24 mg/Kg. The results of the second set of cores analyzed for PCB and binder content and are found in Table 3.

In these cores, both Aroclor 1242 and 1260 were found. PCB were also found in all samples. Average Aroclor 1242 content in the binder and pavement was 1.76 mg/Kg and 55 ug/kg, respectively.

Average Aroclor 1260 content in the binder and pavement was 1.81 mg/Kg and 55 mg/Kg, respectively. Binder content averaged 3.08 percent.

It should be noted it was reported that cores from the first two sets (i.e. Table 2 and Table 3 results) were taken from the same location, however, results in Table 2 were obtained by chipping pavement from the bottom of the core and results in Table 3 were from asphalt chipping from the top of cores. It is interesting that the top of the core contained both Aroclor 1242 and 1260, while the bottom of the cores contained only Aroclor 1242.

A third set of asphalt samples were received from the Connecticut DOT which consisted of scraping from a surface-coating treatment consisting of small peastone size gravel in oil.

The code to same names and reported locations are as follows:

Rt. 21A = CT. Rte. 21, 0.5 mi. N. of Rte. 12, southbound lane

Rt. 21B = CT. Rte. 21, 1.0 mi. N. of Rte. 12, northbound lane

Rt. 21C = CT. Rte. 21, 1.5 mi. N. of Rte. 12, northbound lane

Rt. 169A = CT. Rte. 169, 0.5 mi. N. of Rte. 44, northbound lane

Rt. 169B = CT. Rte. 169, 1.0 mi. N. of Rte. 44, northbound lane

Rt. 169C = CT. Rte. 169, 1.5 mi. N. of Rte. 44, northbound lane

Rt. 272A = CT. Rte. 272, Drakeville 0.30 mi. into project

Rt. 272B = CT. Rte. 272, Drakeville 0.60 mi. into project

Rt. 272C = CT. Rte. 272, Drakeville, end of project

Rt. 197A = CT. Rte. 197, 0.5 mi. E of Rt. 169, eastbound lane

Rt. 197B = CT. Rte. 197, 1.0 mi. E of Rt. 169, eastbound lane

Rt. 197C = CT. Rte. 197, 2.0 mi. E of Rt. 169, eastbound lane

Rt. 61A = CT. Rte. 61, Morris, 1.0 mi. into project

Rt. 61B = CT. Rte. 61, Morris 2.0 mi. into project

Rt. 61C = CT. Rte. 61, Bethlehem, 3.0 mi. into project

Rt. 61D = CT. Rte. 61, Bethlehem, (library)

Results from the analysis of the above samples are reported in Table 4. Aroclor 1242 was the only PCB, if any, found in these samples. The average PCB content in the binder pavement of the Rt. 21 samples was 4.99 mg/Kg and 542 ug/kg,

TABLE 2

Binder and PCB Content of Asphalt Cores

Sample Code	Concentrate Volume	PCB Mass Detected	Asphalt Oil Extracted	Initial Sample Mass	PCB Concentration in Oil	PCB Type	PCB Concentration in Pavement	Binder Content in Asphalt
	(ml)	(ug)	(g)	(g)	mg/kg	Aroclor	ug/kg	percent
B2L2(a)	10	6.90	1.145	24.070	6.02	1242	286.	4.76
B2L2(b)	10	7.18	1.652	56.110	4.34	1242	128.	2.94
B1L1(a)	10	ND	1.01	17.264	ND	--	ND	5.83
B1L1(b)	10	ND	0.97	18.630	ND	--	ND	5.21
B3L3	10	ND	0.83	18,860	ND	--	ND	4.40
B4L4	10	ND	0.79	17.570	ND	--	ND	4.50
B6P3523	10	ND	0.95	18.550	ND	--	ND	5.12
B6P5851	10	2.28	0.918	18.910	2.48	1242	120.	4.86
B6P5521	10	5.49	0.88	17.441	6.24	1242	314.	5.09

TABLE 3

Binder and PCB Content of Asphalt Cores, Second Set

Sample Core	Concentrate Volume ml	PCB Type Aroclor	PCB Detected ug	Asphalt Oil Extended g	Initial Sample Mass g	PCB Concentration in Oil as Aroclor 1242 mg/kg	PCB Conc in Pavement as Aroclor 1242 ug/kg	PCB Type	PCB Detected ug	PCB Conc in Oil as Aroclor 1260 mg/kg	PCB Conc in Pavement as Aroclor 1260 ug/kg	Binder Content in Pavement percent	Total PCB Concentration in Oil mg/kg	Total PCB Concentration in Pavement ug/kg
SSTC0	10	1242	6.37	2.709	65.521	2.35	94.0	1260	4.01	1.48	59.0	4.13	3.83	153
SSTC1	8	1242	4.14	1.973	65.812	2.10	63.0	1260	12.0	6.08	183.	3.00	8.18	246
SSTC2	10	1242	3.30	1.982	65.069	1.66	49.0	1260	0.95	0.48	14.0	2.96	2.14	63.0
SSTC3	10	1242	1.73	1.915	63.649	0.91	27.0	1260	1.43	0.75	22	3.00	1.66	49.0
SSTC4	10	1242	2.24	1.609	71.283	1.39	31.0	1260	2.30	1.43	33	2.26	2.80	64.0
SSTC5	10	1242	4.10	1.917	61.738	2.14	66.0	1260	1.16	0.61	19	3.11	2.75	85.0

TABLE 4

PCB and Binder Content of Surface Coating Treatment Samples

Sample Code	Concentrate Volume	PCB Type	PCB Detected	Asphalt Oil Extracted	Initial Sample Mass	PCB Concentration in Oil	PCB Concentration in Pavement	Binder Content
	ml	Aroclor	ug	g	g	mg/ug	ug/kg	percent
Rt 21A	10	1242	11.15	2.151	26.890	5.18	414.	8.00
Rt 21B	10	1242	INT*	1.563	28.870	--	--	5.41
Rt 21C	10	1242	19.10	1.916	28.500	9.97	670.	6.72
Rt 169A	10	1242	6.76	1.992	28.640	3.39	236.	6.96
Rt 169B	10	1242	7.66	1.902	28.870	4.03	265.	6.59
Rt 169C	10	1242	8.82	1.724	29.200	5.11	302.	5.90
Rt 272A	10	1242	3.93	2.294	28.800	1.71	79.0	7.97
Rt 272B	10	1242	8.46	1.66	28.880	5.09	293	5.75
Rt 272C	10	1242	4.88	2.137	28.445	2.28	171.	7.51
Rt 197A	10	1242	2.49	2.164	30.870	1.15	80.0	7.01
Rt 197B	10	1242	8.55	1.828	29.569	4.67	289.	6.18
Rt 197C	10	1242	6.90	1.268	28.697	5.44	240.	4.42
Rt 61A	10	1242	3.67	2.768	29.308	1.32	125	9.45
Rt 61B	10	1242	5.81	1.778	28.093	3.26	207.	6.33
Rt 61C	10	1242	ND**	1.959	28.357	ND	ND	6.91
Rt 61D	10	1242	ND	2.868	30.087	ND	ND	9.53

*INT - Interference, not possible to qualitate at low level.
**ND - None detected.

respectively. The Rt. 21 sample with an interference was not quantified and was not averaged as a result. This was the only sample received which was not quantified because of an interference not able to be removed. Rt. 169 samples averaged binder and pavement PCB concentrations of 4.18 mg/Kg and 268 mg/Kg, respectively. It was observed that the PCB concentration increased with distance in a northerly direction away from Rt. 44. Rt. 272 samples had average PCB concentrations in the binder and pavement of 3.03 mg/Kg and 181 ug/Kg, respectively. PCB concentrations in the binder in the Rt. 197 samples increased with distance in an easterly direction from Rt. 169. Of the Rt. 61 samples, two had none detected levels of PCBs and the two closest to the beginning of the project had 1.32 mg/Kg and 3.26 mg/Kg Aroclor 1242 concentrations.

Analysis of Soil Samples Under and Near Asphalt Pavements

Several soil samples were obtained by removing a pavement core and sampling soild from the area immediately below from which the core was taken. Additionally, soil samples were taken from a catch basin which received runoff from an asphaltic pavement and at point where the catch basin drained into a small pond.

Soil samples were coded with respect to the following locations:

Rt. 6AS - Route 6, 150' south of Rt. 64 intersection
Rt. 6BS - Route 6, 140' south of Rt. 64 intersection
Rt. 64AS - Route 64, 150' east of Rt. 6 intersection
Rt. 64BS - Route 64, 160' east of Rt. 6 intersection
Rt. 6CB - Route 6, catch basin, west side of road, 150 south of Rt. 64 intersection
Rt. 6PD - pond sediment sample, at entrance to pond from above catch basin

Examination of Table 5 indicates that the levels of PCB found in all samples were quite low. The highest PCB concentration in the soil samples from under the asphalt pavement cores was 95 ug/Kg of Aroclor 1242. Sediment from both the catch basin and the pond sediment were also quite low at 67 ug/Kg and 50 ug/Kg of Aroclor 1242, respectively. Aroclor 1260 was not detected in any of these samples.

TABLE 5

PCB RESULTS FROM SOIL

SAMPLES ADJACENT TO ASPHALT PAVEMENTS

Sample Code	Concentrate Volume (ml)	PCB Mass ug	PCB Type Aroclor	Sample Mass g	PCB Concentration in soil ug/Kg
Rt. 6AS	7	1.844	1242	66.6275	28
Rt. 6BS	7	5.845	1242	61.6667	95
Rt. 64AS	8	2.444	1242	72.4806	34
Rt. 64BS	8	4.214	1242	54.7707	77
Rt. 6CB	7	3.990	1242	59.2036	67
Rt. 6PD	8	4.722	1242	94.3765	50

REFERENCES

1. Perricone, L.P., "Toxic Wastes in Bituminous Liquids," Memorandum to Dr. Charles E. Dougan, Director of Research, Bureau of Planning and Research, State of Connecticut, Department of Transportation, December 22, 1984.

2. Hutzinger, O., Sate, S., and Zitko, V., The Chemistry of PCBs, CRC Press, Cleveland, OH., 1974.

3. Miller, S., "The Persistant PCB Problem," Environmental Science and Technology, 16, 2, 1982.

4. Federal Register, V. 41(64): Thursday, April 1, 1976, p. 14134.

5. Thruston, A., PCB Newsletter, No. 3, July 1971.

6. Panel of Hazardous Trace Substances, Polychlorinated Biphenyls-Environmental Impact, Environmental Research, 5.249, 1972.

7. "Ambient Water Quality Criteria for Polychlorinated Biphenyls," Office of Water Regulations and Standards, United States, EPA, EPA 440/5-80-068, October 1980.

8. Federal Register, 42CFR710, Toxic Substances Control Act, P.L. 94-469.