SUMMARY OF POLYCHLORINATED BIPHENYL, POLYCHLORINATED DIBENZO-P-DIOXIN AND DIBENOFURAN LEVELS IN BLOOD SAMPLES TAKEN FROM RESIDENTS OF CRYSTAL SPRINGS, MISSISSIPPI

Richard A. Parent [1], Joseph A. Palausky [2], M. Coreen Hamilton[3], and William L. Barclay[4]

[1]Consultox Ltd., PO Box 1239, Damariscotta, ME 04543
[2]Terrachem, 8600 Shawnee Mission Parkway, Suite305, Shawnee Mission, KS 66202
[3]Axys Analytical Services Ltd., PO Box 2219, Sidney, BC, Canada V8L 3S8
[4]Southwest Research Institute, PO Drawer 28510, San Antonio, TX 78228

Introduction

Nearly 1000 blood or serum samples have been collected over the last two years to complement a large study of dust and soil samples from properties proximate to a facility known to be contaminated with polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDFs). The blood serum or whole blood samples have been analyzed by multiple techniques and at multiple facilities.

In the beginning of the study, a screening method using an electron capture detector (ECD) was used to establish an initial baseline. Based on these initial screens an apparent elevation of PCBs in serum samples defined as serum levels >3ppb, was observed. In order to further evaluate the nature of the elevated results, definitive analyses for PCBs and PCDD/PCDFs by high-resolution mass spectrometry (HRMS) using USEPA Methods 1668A[1] and 1613B[2] were performed. The criteria chosen for normal background, that is <3ppb, was considered a conservative choice at the time and is even more conservative currently since the apparent normal background levels continue to decrease. Currently, it would appear to be around 1ppb.

The evaluation of contaminants at Crystal Springs, MS is a work in-progress. The objective of this paper is to present background information for techniques as well as preliminary summary findings on levels observed thus far in the study. Sampling of the exposed population continues and future efforts will include soil sampling and dust sampling data.

Materials and Methods

Screening analyses for PCBs were conducted at Pacific Toxicology Laboratories (PacTox) in Woodland Hills, California and Southwest Research Institute (SWRI) in San Antonio, Texas. Both laboratories used protein precipitation followed by organic solvent extraction and silica gel cleanup. Extracts at SWRI were also processed through acid partitioning with concentrated sulfuric acid. For analysis, PacTox analyzed extracts using electron capture detection and a modified version of the Webb-McCall method[3] while SWRI used an ECD method based on USEPA SW-846 Method 8082[4]. The techniques provide detection limits for total PCBs at concentrations of 2 ppb (SWRI) and 3 ppb (PacTox) on a serum basis with measurable and acceptable accuracy.

Definitive HRMS analyses were conducted at Midwest Research Institute (MRI) in Kansas City, Missouri and Axys Analytical Services (Axys) in Sidney, British Columbia. MRI performed analyses based on whole blood while Axys performed analyses on serum only. Extraction was performed at both laboratories using protein precipitation followed by organic solvent extraction, similar to the screening technique but because extracts were to be analyzed for PCDD/PCDFs as well as PCBs, the cleanup was more intensive. For cleanup, MRI used a Fluid Management Systems (FMS) Inc. Power Prep™ automated system that included silica, alumina, and AX-21 carbon columns. Axys used gel permeation chromatography (GPC) followed by silica for PCBs and silica, alumina, and carbon for PCDD/PCDFs. At both laboratories, HRMS analyses were conducted according to USEPA Methods 1668A and 1613B.

Results and Discussion

In an effort to evaluate the compiled data from four laboratories, summary statistics were first calculated. Overall summary results for 743 individuals are reported in Table 1. This table is divided by screening and definitive HRMS results. The screening information includes the total number of samples analyzed, frequency of detection above the 2 or 3 ppb detection limit, and statistics on serum PCB concentration for all detections above the detection limit. The definitive HRMS information includes the total number of samples analyzed by this technique, the serum and lipid total PCB concentration in ppb, the lipid total World Health Organization (WHO) toxic PCBs and 2,3,7,8-substituted PCDD/PCDFs in parts per trillion (ppt), and the toxic equivalency quotient for WHO toxics, 2,3,7,8 substituted PCDD/PCDFs and their total (DF/P TEQ). The data in Table 1 indicates that the data set is very heterogeneous and requires further evaluation beyond the scope of this presentation.

Table 1. Study Summary Statistics

	Total samples=743	**Average**	**Range**	**ST. DEV**
Screen	**Screen analyses=657**			
	Detections =286			
	Serum Total PCB (ppb)	4.3	2.0-67	4.6
HRMS	**HRMS analyses=198**			
	Serum Total PCB (ppb)	13	0.2-162	25
	Lipid Total PCB (ppb)	1966	30.2-25200	3600
	Lipid Toxic PCB TEQ (ppt)	19.1	1.4-188	23
	Lipid 2378-PCDD/PCDFs (ppt)	1073	0-4560	790
	Lipid D/F TEQ (ppt)	32.0	2.21-216	24
	Lipid DF/P TEQ (ppt)	50.6	5.2-234	37

Sampling for the study has been conducted over a two year time period. Table 2 presents a summary by age (decades) and gender of the participants with the number of participants appearing in each category indicated in the table. Care must be used when reviewing this information. For example, in the >80 age group, no males participated and the three samples of female blood were analyzed by HRMS while only 2 were analyzed by screening techniques. Tables 3, 4, and 5 present an evaluation similar to that presented in Table 1 but based on age and gender of participant.

Table 2. Demographic Summary

	Age of Donor	<10	>10	>20	>30	>40	>50	>60	>70	>80	>90
	Total samples	31	103	95	123	165	123	59	40	3	1
Screen	Total Screen Analyses	30	99	88	101	132	112	57	36	2	1
	Female	12	50	48	64	84	64	35	20	2	1
	Male	18	49	40	37	48	48	22	16	NA	NA
HRMS	Total HRMS analyses	3	7	8	28	55	52	26	15	3	1
	Female	0	4	4	19	31	33	16	9	3	1
	Male	3	3	4	9	24	19	10	6	NA	NA

Table 3. Data Summary by Age

	Age of Donor	<10	>10	>20	>30	>40	>50	>60	>70	>80	>90
	Total number of samples	31	103	95	123	165	123	59	40	3	1
Screen	No. of individual samples	30	99	88	101	132	112	57	36	2	1
	No. of Detections	3	6	10	28	74	88	46	28	2	1
	Average serum conc. (ppb)	4.4	3.1	2.4	2.5	3.4	4.3	6.3	5.8	3.6	10.7
HRMS	HRMS (No. of samples)	3	7	8	28	55	52	26	15	3	1
	Average serum conc. (ppb)	1.3	1.8	1.9	12	9.1	11.8	17.9	33.3	26.5	80.9
	Average PCB/lipid basis (ppb)	205	355	319	1699	1401	1712	2960	4982	3153	11100
	Average PCB/lipid TEQ (ppt)	8.63	4.96	6.52	8.19	14.1	18.6	38.9	39.1	30.6	46.0
	Average 2378-D/F lipid (ppt)	518	419	503	686	890	1268	1352	1905	1415	4427
	Average D/F lipid TEQ (ppt)	30.0	14.8	11.0	21.0	26.4	34.4	43.6	49.9	62.8	216
	Average DF/P lipid TEQ (ppt)	38.7	19.8	17.5	29.1	40.6	53.2	82.4	88.4	93.4	202

Table 4. Data Summary for Female Participants by Age

	Age of Donor	<10	>10	>20	>30	>40	>50	>60	>70	>80	>90
	Total number of samples	12	53	51	80	99	70	36	23	3	1
Screen	No. of individual samples	12	50	48	64	84	64	35	20	2	1
	No. of Detections	2	4	6	15	48	48	31	16	2	1
	Average serum conc. (ppb)	3.5	3.0	2.6	2.4	3.2	4.1	5.2	6.5	3.6	10.7
HRMS	HRMS (No. of samples.)	0	4	4	19	31	33	16	9	3	1
	Average serum conc. (ppb)	NA	2.2	2.3	4.8	9.4	10.7	15.1	45.0	26.5	80.9
	Average PCB/lipid basis (ppb)	NA	338	391	734	1426	1478	2373	6826	3153	11100
	Average PCB/lipid TEQ (ppt)	NA	5.76	7.70	8.7	12.9	19.0	41.2	53.1	30.6	46.0
	Average 2378-D/F lipid (ppt)	NA	489	592	685	914	1341	1721	2321	1415	4427
	Average D/F lipid TEQ (ppt)	NA	19.4	10.0	18.4	24.7	36.8	50.6	60.1	62.8	216
	Average DF/P lipid TEQ (ppt)	NA	25.2	17.7	27.1	37.8	55.7	91.8	109	93.4	202

Table 5. Data Summary for Male Participants by Age

	Age of Donor	<10	>10	>20	>30	>40	>50	>60	>70	>80	>90
	Total samples	19	50	44	43	66	53	23	17	NA	NA
Screen	No.of individuals samples	18	49	40	37	48	48	22	16	NA	NA
	No. of Detections	1	2	4	13	26	40	15	12	NA	NA
	Average serum conc. (ppb)	6.2	3.3	2.1	2.6	3.7	4.4	8.6	4.8	NA	NA
HRMS	HRMS (No. of samples)	3	3	4	9	24	19	10	6	NA	NA
	Average serum conc. (ppb)	1.3	1.3	1.6	27	8.6	14	22	16	NA	NA
	Average PCB/lipid basis (ppb)	205	377	247	3737	1371	2101	3939	1664	NA	NA
	Average PCB/lipid TEQ (ppt)	8.63	3.88	5.34	7.17	15.5	18.0	35.0	13.8	NA	NA
	Average 2378-D/F lipid (ppt)	518	327	413	688	864	1147	660	969	NA	NA
	Average D/F lipid TEQ (ppt)	30.0	8.73	11.9	26.4	28.3	30.3	30.5	26.9	NA	NA
	Average DF/P lipid TEQ (ppt)	38.7	12.6	17.3	33.5	43.8	49.0	64.9	41.0	NA	NA

The purpose of this presentation is to report on this preliminary data without providing an analysis of its implications. Obviously, there appear to be numerous individuals of various age groups who show elevated PCB and PCDD/PCDF levels both on a wet-weight and lipid basis. TEQs for PCDD/PCDFs alone and in combination with PCBs are also above what is considered normal in an "unexposed" population, if such a population exists. Going further with this study, we have examined individual congeners for the PCBs and individual homologs for the PCDD/PCDFs and have compared the values with the recently published CDC NHANES survey data[5] and find elevations of selected individual homologs with definite patterns. While this study is a work-in-progress, we intend to provide this additional information coupled with soil and dust data when we have completed the data collection phase of this program.

References

[1] USEPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS, December 1999.
[2] US EPA Method 1613 (1994) Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B.
[3] R.G. Webb and A.C McCall, "Quanttitative PCB Standards for Electron Capture Gas Chromatography", J. Chrom. Sci., Vol 11, 366-373 (1973)
[4] USEPA, "Test Methods for Evaluating Solid Waste (SW-846)", Third Edition. December 1996.
[5] "Second National Report on Human Exposure to Environmental Chemicals", Centers for Disease Control and Pevention, Atlanta, GA, NCEH Publ.# 02-0716, January, 2003

Acknowledgement

The authors would like to recognize David Nutt and Associates for financial and moral support in pursuit of this rather extensive investigation.