# INFORMATION TO USERS

# POLYCHLORINATED BIPHENYLS, DIOXINS AND FURANS

# IN AMBIENT AIR DURING THE SMITHVILLE PCB INCINERATION PROJECT

BY

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THESIS

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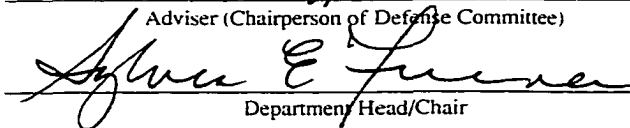
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at Chicago

This thesis is dedicated to my wife, Patricia Rooney. To say that the thesis would not have been completed without her support, financial and emotional, is an understatement. It is as much hers as mine in terms of the sacrifices made. I love you Pat!

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WJM

# TABLE OF CONTENTS

# TABLE OF CONTENTS (continued)

# LIST OF TABLES

## LIST OF TABLES (continued)

# LIST OF FIGURES

# LIST OF EQUATIONS

# LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| ' | Feet |
| " | Inches |
| $1^\circ$ | Primary |
| $2^\circ$ | Secondary |
| 2378TOT | Sum of 2, 3, 7, 8 PCDD/DF compounds |
| $\alpha$ | Size of probability of creating a Type 1 error (rejecting a true null hypothesis |
| A | Face area |
| AA | Atomic Absorption (spectrometry) |
| AA | Ambient Air |
| AAQC | Ambient Air Quality Criteria/Criterion |
| AAQS | Ambient Air Quality Standard |
| acm | Actual cubic meter |
| ADJRSQ | Adjusted r-squared |
| ADM | Air Dispersion Model(s)/Modeling |
| Ah | Arylhydrocarbon hydroxylase |
| $a_{ij}$ | Fractional amount of emission of species $i$ from source $j$ |
| Allantemp | Temperature in °C at Allanburg Station |
| AM | Ambient Air |
| $a_n$ | Parameter in calculation of $D_n$ (Equation 13) |
| ANOVA` | Analysis of variance |
| APCS | Air Pollution Control System |
| AR | Ambient Air |

| | |
|---|---|
| ARB | Air Resources Branch |
| AS | Ash |
| ASME | American Society for Mechanical Engineering |
| ASTA | Automated Short Term Adsorber |
| atm | Atmosphere(s), unit of pressure, 1 ATM = 101325 Pa |
| ave. | Average |
| ave. temp. | Average temperature |
| ave. tempC | Average temperature in degrees Celsius |
| AWFSO | Automatic Waste Feed Shut-Off |
| b | Slope intercept |
| BCC | Bioaccumulative Chemicals of Concern |
| BKHEX | Cyclohexane |
| bldg | Building |
| BWI | Biomedical Waste Incineration |
| BZ | Ballschmiter Congener Number |
| B1HEXA | Hexane |
| B12TMB | 1,2,4-Trimethylbenzene |
| B2BENZ | Benzene |
| B2EBNZ | Ethylbenzene |
| B2ISPR | 2-Methyl-1,3-Butadiene |
| B2MXYL | M+P-Xylene |
| B2OXYL | O-Xylene |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| B2TOLU | Toluene |
| B23TMB | 1,3,5-Trimethylbenzene |
| c | Parameter in Junge-Pankow Adsorption in Equation (2) |
| $c_{ik}$ | Concentration for species $_i$, sample $_k$ in Equation (11) |
| $c_i$ | Concentration for species $_i$, in Equation (12) |
| C | Average air concentration |
| $^{\circ}C$ | Degrees Celsius |
| $C_{at\,x}$ | Concentration at distance $x$ |
| $C_a$ or $C_{air}$ | Air Concentration |
| C of A(s) | Certificate(s) of Approval |
| C of A (Air) | Certificate of Approval (Air) |
| C of A (Site) | Certificate of Approval (Site) |
| C of A (System) | Certificate of Approval (System) |
| C of C | Chain of Custody |
| CAD | Collisionally Activated Dissociation |
| CADD | Computer Aided Drafting and Design |
| calc. | Calculated or calculation(s) |
| CB | Chlorobenzene |
| CC | Clausius-Clapeyron |
| CDF | Chlorodibenzofuran |
| CDN | Canada |
| CDUT | Cadmium |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| CE | Combustion Efficiency |
| CEM | Continuous Emissions Monitor(ing) |
| CEPA | Canadian Environmental Protection Act |
| CEV | Ceiling Exposure Value |
| cfm | Cubic feet per minute |
| CFU | Carbon Filtration Unit |
| CI | Confidence Interval |
| Cl | Chlorine |
| Cl4DD1 | 2, 3, 7, 8-TeCDD |
| Cl4DF1 | 2, 3, 7, 8-TeCDF |
| Cl5DD1 | 1, 2, 3, 7, 8-PeCDD |
| Cl5DF1 | 1, 2, 3, 7, 8-PeCDF |
| Cl5DF2 | 2, 3, 4, 7, 8-PeCDF |
| Cl6DD1 | 1, 2, 3, 4, 7, 8-HxCDD |
| Cl6DD2 | 1, 2, 3, 6, 7, 8-HxCDD |
| Cl6DD3 | 1, 2, 3, 7, 8, 9-HxCDD |
| Cl6DF1 | 1, 2, 3, 4, 7, 8-HxCDF |
| Cl6DF2 | 1, 2, 3, 6, 7, 8-HxCDF |
| Cl6DF3 | 2, 3, 4, 6, 7, 8-HxCDF |
| Cl6DF4 | 1, 2, 3, 7, 8, 9-HxCDF |
| Cl7DD1 | 1, 2, 3, 4, 6, 7, 8-HpCDD |
| Cl7DF1 | 1, 2, 3, 4, 6, 7, 8-HpCDF |

| | |
|---|---|
| Cl7DF2 | 1, 2, 3, 4, 7, 8, 9-HpCDF |
| Cl8DD1 | OCDD |
| Cl8DF1 | OCDF |
| CL | Confidence Limit |
| cm | Centimeter |
| CMB | Chemical Mass Balance |
| *CN* | MOE LIS Sample Type for PCB in Air Analysis by Ortech |
| CO | Carbon Monoxide |
| $CO_2$ | Carbon Dioxide |
| Conc. | Concentration |
| Contbldg | Containment building source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, no weighting |
| Contbld1 | Containment building source contribution in ambient air samples by CMB modeling, SAS Proc Reg, weighting for 10% precision |
| Contbld2 | Containment building source contribution in ambient air samples by CMB modeling, SAS Proc Reg, weighting for 20% precision |
| cos | Cosine |
| cot | Cotangent |
| CP | Chlorophenol |
| CRUT | Chromium |
| CUUT | Copper |
| CV | Coefficient of variation |

| | |
|---|---|
| $C_w$ | Aqueous concentration |
| CWML | Chemical Waste Management Ltd. |
| $\Delta$ | *Delta* (change) |
| DAS | Data Acquisition System |
| DCB | o-, m-, or p-Dichlorobenzene |
| DecaPCB | Decachlorobiphenyl |
| deg. | Degree |
| Dev. | Deviation |
| DF | Degrees of Freedom |
| Dia. | Diameter |
| DiPCB | Dichlorobiphenyl |
| $D_{jik}$ | Atmospheric dispersion term in Equation (11) |
| DL | Detection Limit |
| DM | Deputy Minister's Office of MOE |
| $D_n$ | LAR coefficient in Equation (13) |
| Dome | Dome source contribution in ambient air samples by CMB modeling, SAS Proc Reg, no weighting |
| Dome1 | Dome source contribution in ambient air samples by CMB modeling, SAS Proc Reg, weighting for 10% precision |
| Dome2 | Dome source contribution in ambient air samples by CMB modeling, SAS Proc Reg, weighting for 20% precision |
| DR | Daily Report |
| DRE | Destruction and Removal Efficiency, see Equation (10) |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| dscm | Dry standard cubic meter at 25 °C and 101.325 kPa |
| E | East |
| E | Exponent when used for scientific notation (power of 10) |
| EA | Environmental Assessment |
| EAB | Environmental Assessment Board |
| EC | Environment Canada |
| ECD | Electron Capture Detector(s) |
| ECNI | Electron Capture Negative Ionization |
| e.g. | *Exempli gratia* (for example) |
| $E_{jk}$ | Emission rate term in Equation (11) |
| EMM | Environmental Monitoring Manual |
| EMP | Environmental Monitoring Program |
| ENSCO | Ensco Environmental Inc. |
| ENT | Effluent Neutralization Tank |
| EPA | Ontario's Environmental Protection Act |
| est. | Estimate |
| et al. | *Et alii* (and others) |
| exp | Exponent |
| F | The F statistic |
| °F | Degrees Fahrenheit |
| fb or FB | Field Blank |
| FC | MOE LIS Sample Type Code |

| | |
|---|---|
| Fcrit | Critical value of the F statistic |
| FEUT | Iron |
| fg | Femtogram |
| $fg/m^3$ | Femtogram ($10^{-15}$ g per cubic meter) |
| FPAC | Federal Provincial Advisory Committee |
| Fract | Relative fraction |
| FRP | Fiberglass Reinforced Plastic |
| g | Gram(s) |
| g/bldg | Gram(s) per building |
| g/day | Gram(s) per day |
| $g/m^2$ | Gram(s) per meter squared |
| $g/m^2 \cdot h$ | Gram(s) per meter squared per hour |
| $g/m^3$ | Gram(s) per cubic meter |
| GC | Gas Chromatography |
| GC-ECD | Gas Chromatography-Electron Capture Detection |
| GC-HECD | Gas Chromatography-Hall Electrolytic Conductivity Detection |
| GC-MS | Gas Chromatography-Mass Spectrometry |
| GFF | Glass Fiber Filter |
| gmol | Gram-mole |
| g/s | Gram(s) per second |
| g/yr | Gram(s) per year |
| h | Hour |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| H | Henry's Law Constant |
| $\Delta H_{vap}$ | Enthalpy of Vaporization |
| ha | Hectacre(s) |
| HBB | Hexabromobiphenyl |
| HCB | Hexachlorobenzene |
| HCH | Hexachlorocyclohexanes |
| HCl | Hydrochloric Acid |
| $h_e$ | Equivalent emission height |
| HECD | Hall Electrolytic Conductivity Detection |
| HexaPCB | Hexachlorobiphenyl |
| HeptaPCB | Heptachlorobiphenyl |
| HG | MOE LIS Sample Type Code |
| hgt | Height |
| Hi-Vol | High Volume Air Sampler |
| $H_o$ | Null Hypothesis |
| HpCDD | Heptachloro-dibenzo-p-dioxins |
| HpCDF | Heptachloro-dibenzofurans |
| hr | Hour |
| HRGC | High Resolution Gas Chromatography |
| HRMS | High Resolution Mass Spectrometers |
| HV4 | MOE LIS Test Group Code |
| HV | MOE LIS Test Group Code |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| HxCDD | Hexachloro-dibenzo-p-dioxins |
| HxCDF | Hexachloro-dibenzofurans |
| HWI | Hazardous Waste Incineration |
| HYSPLIT | Hybrid Single Particle Lagrangian Integrated Trajectory |
| i | Ranking |
| I | Factor used for dispersion coefficient calculation (Equation 19) |
| IADN | Integrated Atmospheric Deposition Network |
| IARC | International Agency for Research on Cancer |
| id or ID | Identification |
| i.e. | *id est* (that is) |
| INORG | Inorganics |
| IOMC | Inter-Organization Programme for the Sound Management of Chemicals |
| ISC | Industrial Source Complex |
| ISC3ST | Industrial Source Complex 3 – short term |
| I-TEF | International Toxic Equivalency Factors |
| I-TEQ | International Toxic Equivalency |
| IUPAC | International Union of Pure and Applied Chemistry |
| J | Factor used for dispersion coefficient calculation (Equation 19) |
| K | Factor used for dispersion coefficient calculation (Equation 19) |
| °K | Degrees Kelvin |
| kg | Kilogram(s) |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| kg/hr | Kilogram(s) per hour |
| kg/yr | Kilogram(s) per year |
| km | Kilometer(s) |
| kmph | Kilometer(s) per hour |
| km/hr | Kilometer(s) per hour |
| L | Liter(s) |
| L/min | Liter(s) per minute |
| LAR | Linear Angular Rank |
| lbs. | Pounds |
| LD | Lethal Dose |
| LIMS | Laboratory Information Management System |
| LIS | Laboratory Information System |
| Ln | Natural log |
| Lpm | Liters Per Minute |
| LQ | Liquids |
| LR | Linear Regression |
| LRMS | Low Resolution Mass Spectrometry |
| LRT | Long-Range Transport |
| LRTAP | Long-Range Transport of Air Pollutants |
| LSB | Laboratory Services Branch |
| m | Meter(s) |
| $m^2$ | Meter(s) squared |

| | |
|---|---|
| $m^3$ | Cubic meter(s) |
| M | Slope of linear regression plot |
| MAPS | Monitoring Air Pollution Sources |
| MAX. | Maximum |
| med. | Median |
| MET | Meteorology, meteorological |
| ug/L | Microgram(s) per liter (also parts per billion) |
| $ug/m^2$ | Microgram(s) per meter squared |
| $ug/m^3$ | Microgram(s) per cubic meter |
| mg/dscm | Milligram(s) per dry standard cubic meter |
| mg/kg | Milligram(s) per kilogram |
| $mg/m^3$ | Milligram(s) per cubic meter |
| MH | Mixing height |
| mi/hr | Mile(s)/hour |
| min. | Minute(s) |
| MIN. | Minimum |
| mL | Milliliter(s) |
| MNUT | Manganese |
| MOE | Ontario Ministry of the Environment |
| mol | Mole |
| MOL | Ministry of Labor |
| mph | Mile(s) per hour |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| mps | Meter(s) per second |
| m/s | Meter(s) per second |
| MS | Mass Spectrometry/Spectrometer |
| MS/MS | Mass Spectrometry/Mass Spectrometry |
| MSWI | Municipal Solid Waste Incinerator |
| MW | Molecular weight |
| MWP | Modular Waste Processor |
| n | Number of observations |
| $n$ | number of moles |
| N | North |
| n.a. or N/A | Not applicable or not analyzed |
| NaCl | Sodium Chloride (salt) |
| NATO | North Atlantic Treaty Organization |
| ND | Non-detected or not detected |
| ng/acm | Nanogram(s) per actual cubic meter |
| ng/dscm | Nanogram(s) per dry standard cubic meter |
| ng/kg | Nanogram(s) per kilogram |
| $ng/m^3$ | Nanogram(s) per cubic meter |
| ng/s | Nanogram(s) per second |
| NIOSH | National Institute for Occupational Safety and Health |
| NIUT | Nickel |
| no. | Number |

## LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| NOAA | US National Oceanographic and Atmospheric Administration |
| NonaPCB | Nonachlorobiphenyl |
| NOx | Nitrogen Oxides |
| NP | Population |
| n.s. | Not specified |
| NTP | National Toxicology Program |
| NW | Northwest |
| $O_2$ | Oxygen |
| OC | Organochlorines |
| OCDD | Octachlorodibenzo-p-dioxin |
| OCDF | Octachlorodibenzofuran |
| OctaPCB | Octachlorobiphenyl |
| OL | Oils |
| ON | Ontario |
| Ont. | Ontario |
| OR | Occurrence Reports |
| O.Reg. | Ontario Regulation |
| OSHA | Occupational Safety and Health Administration |
| p | Probability |
| P&R | Proctor and Redfern Ltd. (now EarthTech Canada) |
| Pa | Pascals |
| $P_a$ | Partial pressure (also abbreviated as $P_v$) |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| PA | MOE LIS Test Group Code |
| PAH | Polycyclic Aromatic Hydrocarbons |
| PAPCB | MOE LIS Test Group Code |
| PAVOC | MOE LIS Test Group Code |
| Pb | Lead |
| PBT | Persistent bioaccumulative toxin |
| PCB(s) | Polychlorinated Biphenyl(s) |
| PCBDEC | Decachlorobiphenyl |
| PCBDI | Dichlorobiphenyl |
| PCBHEPT | Heptachlorobiphenyl |
| PCBHEX | Hexachlorobiphenyl |
| PCBNON | Nonachlorobiphenyl |
| PCBOCT | Octachlorobiphenyl |
| PCBPNT | Pentachlorobiphenyl |
| PCBTET | Tetrachlorobiphenyl |
| PCBTOT | Total polychlorinated biphenyl |
| PCBTOT_1 | Total polychlorinated biphenyl, <W flagged values = 0 |
| PCBTOT_2 | Total polychlorinated biphenyl, <W and <T flagged values=0 |
| PCBTOT_3 | Total polychlorinated biphenyl, <W and <T values assumed present at half the specified limit value |
| PCBTOTDET | Total polychlorinated biphenyl, detected values (not <W or <T) only |
| PCBTRI | Trichlorobiphenyl |

| | |
|---|---|
| PCC | Primary Combustion Chamber |
| PCDD | Polychlorinated dibenzo-p-dioxins |
| PCDD/DF | Polychlorinated dibenzo-p-dioxins/dibenzofurans |
| PCDF | Polychlorinated dibenzofurans |
| PCGC | Packed Column Gas Chromatography |
| PCP | Pentachlorophenol |
| PeCDD | Pentachlorinated dibenzo-p-dioxin |
| PeCDF | Pentachlorinated dibenzofuran |
| PentaPCB | Pentachlorobiphenyl |
| pg | Picogram(s) |
| $pg/m^3$ | Picogram(s) (1E-12) per cubic meter |
| pH | -log of Hydrogen ion concentration |
| PI or $\pi$ | Mathematical constant |
| PID | Photo Ionization Detector |
| $p^o_L$ | Subcooled liquid vapor pressure |
| PNNAPH | Naphthalene |
| POI | Point of Impingement |
| POP(s) | Persistent Organic Pollutant(s) |
| ppb | Parts per billion (also ug/kg and ug/L) |
| ppm | Parts per million |
| ppt | Parts per trillion (also ng/kg and ng/g) |
| pt | Point |

| | |
|---|---|
| PTB | Persistent Toxins That Bioaccumulate |
| PUF | Polyurethane Foam |
| $P_v$ | Partial Pressure (also abbreviated as $P_a$) |
| $P_{vap}$ | Vapor Pressure (also abbreviated as VP) |
| PVC | Polyvinyl Chlorine |
| PW | Process water |
| $\Phi$ | Phi (Particle associated fraction in Equation (2)) |
| Q | Emission rate in units of mass/time |
| $\mathcal{Q}$ | Emission rate (or flux) (g/m$^2$/s) |
| QA/QC | Quality Assurance/Quality Control |
| QAPP | Quality Assurance Project Plan |
| QC | Quality Control |
| QL | Quantitation Limit |
| QSAR | Quantitative Structure Activity Relationship |
| r | Correlation coefficient |
| $r$ | Hypotenuse in calculating sine or cosine |
| R | Universal Gas Constant |
| R | Radius for unit circle |
| R&D | Results and Discussion Chapter of Thesis |
| Reg. | Regulation |
| REG | Regression |
| rel. | Relative |

## LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| RH | Relative humidity |
| ri | Average theta rank (Equation 15) |
| RM | Receptor models or modeling |
| RSQ | Correlation coefficient squared (also $r^2$) |
| RTP | USEPA Research Triangle Park, North Carolina |
| S | South |
| $\sigma_y$ | Horizontal dispersion coefficient |
| $\sigma_z$ | Vertical dispersion coefficient |
| SAS | Statistical Analysis System$^{tm}$ |
| SAS Proc Reg | Regression Procedure in SAS$^{tm}$ |
| SB | MOE LIS Sample Class Code for PCB in Air Analyses at Ortech |
| SBPCB | MOE LIS Test Group Code for Smithville PCB Analyses at Ortech |
| SC | MOE LIS Sample Class Code for VOC in Air Analyses at Ortech |
| SCC | Secondary (2°) combustion chamber |
| Score | Wind Sector Score |
| Score_rev | Revised (Corrected) Wind Sector Score |
| SE | South East |
| sec | Second(s) |
| Shredr | Shredder source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, no weighting |

| | |
|---|---|
| Shredr1 | Shredder source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, weighting for 10% precision |
| Shredr2 | Incinerator Shredder source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, weighting for 20% precision |
| sin | Sine |
| Site_id | Site Identification |
| Site ID | Site Identification |
| $S_j$ | Concentration contribution of material from source j in Equation (12) |
| $S_{jk}$ | Total contribution of source j to k in Equation (11) |
| SL | Soils |
| SM | Smithville (also abbreviated as 'SV') |
| SMDXN | MOE LIS Tests Group Code for Smithville Dioxin Analysis |
| SMVOC | MOE LIS Tests Group Code for Smithville VOC |
| sq. | Square |
| sqrt | Square root |
| $SO_2$ | Sulfur Dioxide |
| SSI | Sewage Sludge Incinerator |
| Stack | Incinerator stack source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, no weighting |
| Stack1 | Incinerator stack source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, weighting for 10% precision |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| Stack2 | Incinerator stack source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, weighting for 20% precision |
| std. | Standard |
| Std. dev. | Standard Deviation |
| Std. Err. | Standard Error |
| STEV | Short term exposure value |
| Stn. | Station |
| STP | Sewage Treatment Plant |
| STYR | Styrene |
| SV | Smithville ('SM' also used) |
| SVOC | Semi-Volatile Organic Compounds |
| SW | South West |
| SW | Swabs |
| SZ | MOE LIS Test Class Code for Dioxin Analysis |
| t | Table LXXX etc |
| t | Tonnes (metric ton) |
| $t$ | $t$ statistic |
| T | Temperature |
| <T | Approximately equivalent to or less than QL |
| t/hr | Tonnes/hour |
| TAGA | Trace Atmospheric Gas Analysis |
| TAT | Turnaround Time |
| tb or TB | Trip Blank |

## LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| $T_c$ | Parameter in Linear Angular Rank Equation (13) |
| TCDD | Tetrachlorodibenzo-p-dioxins (same as TeCDD) |
| TCDF | Tetrachlorinated Dibenzofurans |
| TCE | Trichloroethylene |
| TCP | Trichlorophenol |
| TeCB | Tetrachlorobenzene |
| TeCDF | Tetrachlorodibenzofurans |
| TeCDD | Tetrachlorodibenzo-p-dioxins |
| TEF | Toxic Equivalency Factor(s) |
| temp. | Temperature |
| tempdiff | Temperature difference |
| TEQ | Toxic Equivalency |
| TetraPCB | Tetrachlorobiphenyl |
| THC | Total Hydrocarbons |
| Thomas | Thomas water treatment building source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, no weighting |
| Thomas1 | Thomas water treatment building source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, weighting for 10% precision |
| Thomas2 | Thomas water treatment building source contribution in ambient air samples determined by CMB modeling, SAS Proc Reg, weighting for 20% precision |
| $\Theta$ | Wind direction in radians (theta) |
| ~ | Approximately (tilda) |
| TP | Total Particulates |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| TrCB | Trichlorobenzene |
| TriPCB | Trichlorobiphenyl |
| TRV | Thermal Relief Vent |
| $T_s$ | Parameter in Linear Angular Rank Equation (13) |
| TSCA | Toxic Substances Control Act |
| TSP | Total Suspended Particulates |
| TSS | Total Suspended Solids |
| TWA | Time Weighted Average |
| TWAEV | Time Weighted Average Exposure Value |
| UIC | University of Illinois, Chicago Campus |
| $U_n$ | Test Statistic, see Equation (14) |
| UN | United Nations |
| UNEP | United Nations Environmental Programme |
| UNIFAC | Universal quasi-chemical functional group activity coefficients |
| US | United States |
| USEPA | United States Environmental Protection Agency |
| v | Wind velocity (vector quantity containing wind speed and direction) |
| V | Volume |
| Var. | Variance |
| VN | MOE LIS Sample Type Code |
| VP | Vapor Pressure |
| V/P | Vapor/Particle Ratio |

| | |
|---|---|
| VOC | Volatile Organic Compounds |
| vs. | Versus |
| VVUT | Vanadium |
| W | West |
| <W | Approximately equal to or less than DL |
| WCR | West Central Region |
| WHO | World Health Organization |
| winddir | Wind direction, Smithville |
| winddir1 | Wind direction, Allanburg Level 1 (in degrees) |
| winddir2 | Wind direction, Allanburg Level 2 (in degrees) |
| windsect | Wind sector |
| windspd | Wind speed , Smithville (in km/hr) |
| windspd1 | Wind speed, Allanburg Level 1 (in km/hr) |
| windspd2 | Wind speed, Allanburg Level 2 (in km/hr) |
| WS | Wind Speed |
| wt. | Weight |
| x | Wind sector score |
| $x$ | Length in Box Model (m or km) |
| $x$ | Distance (m or km) |
| X | Mole Fraction |
| $\chi^2$ | chi squared, see Equation (14) |
| XAD-2 | Amberlite XAD-2$^{tm}$ resin |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| $x_i$ | Tracers |
| $x/r$ | Value of cosine for average angle in radians |
| XRF | X-ray Fluorescence Spectrometry |
| Xvp | Virtual point distance |
| X1BDCM | Bromodichloromethane |
| X1CHLM | Chloromethane |
| X1ACRY | Acrylonitrile |
| X1CTET | Tetrachloromethane |
| X1DBET | 1,2-Dibromoethane |
| X1DCLE | 1,1-Dichloroethene |
| X1DCLM | Dichloromethane |
| X1HCBD | Hexachlorobutadiene |
| X1TCLM | Trichloromethane |
| X1TETR | Tetrachloroethene |
| X1TRIC | Trichloroethene |
| X1VCL | Chloroethane |
| X13VCL | 1,3-Butadiene |
| X111CE | 1,1-Dichloroethane |
| X112CE | 1,2-Dichloroethane |
| X112CP | 1,2-Dichloropropane |
| X1112T | 1,1,2-Trichloroethane |
| X113DP | Cis-1,3-dichloropropene |

# LIST OF ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| X11122 | 1,1,2,2-Tetrachloroethane |
| X1112T | 1,1,2-Trichloroethane |
| X2CREN | Chlorobenzene |
| X2HCB | Hexachlorobenzene |
| X2HCE | Hexachloroethane |
| X2OCST | Octachlorostyrene |
| X2PNCB | Pentachlorobenzene |
| X2T26A | 26A Trichlorotoluene |
| X2T236 | 2,3,6 Trichlorotoluene |
| X2T245 | 2,4,5 Trichlorotoluene |
| X212CB | 1,2-Dichlorobenzene |
| X213CB | 1,3-Dichlorobenzene |
| X214CB | 1,4-Dichlorobenzene |
| X2123 | 1,2,3 Trichlorobenzene |
| X2124 | 1,2,4 Trichlorobenzene |
| X2135 | 1,3,5 Trichlorobenzene |
| X21234 | 1,2,3,4 Tetrachlorobenzene |
| X21235 | 1,2,3,5 Tetrachlorobenzene |
| X21245 | 1,2,4,5 Tetrachlorobenzene |
| $y$ | Width |
| $y$ | PCBTOT concentration (mg/m$^3$) |
| y/$r$ | Value of sine for average angle in radians |

## LIST OF ABBREVIATIONS AND ACRONYMS (continued)

yr or YR                    Year

$z$                         Various mixing heights

# SUMMARY

From 1978 to 1985, Chemical Waste Management Ltd. (CWML) operated a polychlorinated biphenyl (PCB) transfer and storage facility in Smithville (SV or SM), Ontario, Canada (Site). These operations left extensive on- and off-site contamination with PCBs and other chemicals. Mobile high temperature incineration was selected for the remediation of surface soils and other materials that were stored at the Site. The incineration of PCB materials at the Site began in early February 1991 and finished in mid-December, 1992.

An environmental monitoring program was developed and implemented to determine the effect, if any, of the incineration project on the surrounding environment. This program included sampling and analysis of ambient air, soil, water, and other materials before, during, and after incineration. Over 13,000 environmental samples were collected during the course of the project. Source testing showed that the incinerator achieved >99.9999% destruction and removal efficiency (DRE) and met the other regulatory limits. Ambient air monitoring was carried out, on a weekly schedule for inorganics, volatile organic compounds (VOCs), and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/PCDF), and on a daily schedule for PCBs, at four (4) local ambient air monitoring locations, as well as on-site. No excedance of the applicable regulatory standards was observed at any of the four local air monitoring stations.

## SUMMARY (continued)

Nonetheless, on occasion, elevated concentrations of PCBs were observed at the air monitoring locations. The PCB results from the summer of 1991 were more elevated than those in the summer of 1992. It was postulated by the project manager that the PCB levels that were observed were primarily due to fugitive emissions from Site activities or (possibly) longer ranger transport **and not** the incinerator itself. However, no detailed analysis of the air monitoring data was carried out to qualitatively, or quantitatively, evaluate the impact of the Site activities.

In this research, the data obtained for almost 1600 ambient air PCB samples and 200 PCDD/DF samples were analyzed to examine the possible contribution of the Site in general, as well as specific Site activities, to the observed levels. A seasonal effect was observed for the PCB concentrations. While the amount of PCB contaminated soils treated was similar during the two calendar years, the concentration range was much greater in the first year of operation. As a first step, the PCB results were analyzed using Site meteorology (wind direction, wind speed, and air temperature). While the overall data did not indicate a wind direction effect, the data in the warm summer months showed a correlation with winds passing over the CWML SV Site. A positive temperature effect was observed. A smaller, negative effect was observed for wind speed. Results from testing of the incinerator showed that the incinerator emissions were constant over the project, and not temperature related. Modeling using Gaussian air dispersion modeling and receptor modeling were used to

## SUMMARY (continued)

identify contributions from the incinerator and other on-site fugitive emission sources. These modeling results indicate that the incinerator was only responsible for a small fraction (estimated 10% maximum on any day) of the observed PCB concentrations. Similar results were obtained from analyzing the PCDD/DF data. The primary factor found responsible for the elevated PCB concentrations was the existence on-site, and consequent volatilization, of high concentration polychlorinated biphenyl liquids (oils).

The results from this research study have a number of implications for PCB management policies in particular, as well as air monitoring studies in general.

1) The on-going storage of PCB contaminated material can result in air emissions to the environment at environmentally significant concentrations.

2) High concentration PCB liquids are more responsible for elevated PCB concentrations and will result in higher concentrations and/or mass emissions of PCBs to the environment relative to PCB contaminated soils.

3) Once high level liquids are destroyed, local concentrations fell to levels more typical of rural (or background) levels within one season.

4) Wind sector scoring is a practical and easily automated method for looking at possible effects from local sources.

## SUMMARY (continued)

This work has several implications for regulators and environmental policy makers:

A)   The definition of "closed system" needs to be revisited. Unless containers are sealed airtight, there will be some volatilization of PCBs. Depending on the concentration of PCBs present and maximum temperatures, this volatilization can result in elevated ambient air PCB concentrations and/or emissions.

B)   The on-going storage of PCB materials is not a solution to the occurrence of PCBs in the environment. **Destruction** of these materials must be done. Disposal in landfills or by solidification does not remove the materials as potential, future sources of PCB to the environment.

C)   High level (> about 10,0000 ppm) PCB liquids are responsible for a major fraction of the emissions from PCB storage and/or use. For PCB liquids, **destruction** is the only permanent way to remove the PCBs from the environment.

# 1. INTRODUCTION

## 1.1 Persistent Organic Pollutants

Persistent Organic Pollutants (POPs) is a name gaining increasing acceptance for long-lived organic compounds that become concentrated, or bioaccumulate, as they move through the food chain [1]. Other names for POPs include the United States Environmental Protection Agency's (USEPA) "bioaccumulative chemicals of concern" (BCC), "persistent bioaccumulative toxins" (PBT) and the term "persistent toxins that bioaccumulate" (PTB) [1]. A number of studies have shown that POPs can move and be deposited thousands of kilometers from a source, primarily by long range atmospheric transport [2-5].

Concerns about POPs are related to: 1) their long latency period in the environment; 2) the potential for long range, including transboundary, transport; and 3) their observed toxic effects on animal reproduction, and developmental, immunological, carcinogenic [6] and other effects, such as endocrine disruption [7-9]. There is increasing concern about their impact on humans.

Many of the POPs are semi-volatile organic compounds (SVOC). These POPs are volatile enough to evaporate and deposit (or condense) among the air, water and soil compartments in the environment. Wania and Mackay have proposed that a global fractionation process occurs [10]. Temperature can be used as a crude measure of a POPs movement direction. Warmer temperatures favor partitioning of the POPs into the atmosphere. Cooler temperatures favor partitioning of the POPs into the atmospheric particulate, soil and/or water compartment. One aspect of this is the so-called "grasshopper

effect," which results in the movement of POPs to higher latitudes with the changes in temperatures due to seasons. POPs have been observed at elevated concentrations in areas where they have never been used, such as the Arctic and Antarctic [2, 4, 11]. The presence of these compounds is attributed to long-range transport (LRT) of air pollutants (LRTAP). Many POPs have been banned in developed countries, but are still used in developing countries and/or still have significant amounts in environmental compartments [12]. Consequently, environmental concentrations have not diminished as much as would be expected with the reduction in usage.

Recently, concerns about the detrimental impacts of POPs and their potential for transport across international boundaries have led to a proposal for the control of 12 POPs [13, 14]. The 12 POPs proposed for reduction and/or elimination are listed in Table I.

Polychlorinated biphenyls (PCB or PCBs) (Figure 1) and the structurally related polychlorinated dibenzo-p-dioxins (PCDD) (Figure 2) and polychlorinated dibenzofurans (PCDF) (Figure 3) are 3 of the 12 POPs slated for control. The distribution of the PCB has been observed to correlate with latitude and/or temperature in several studies [2, 4, 5, 15]. Polychlorinated biphenyls have been shown to bioconcentrate by factors of up to 70,000 [16, 17]. The work in this thesis focuses on atmospheric transport processes of PCB and PCDD/DF near a local source.

**TABLE I**

LIST OF PERSISTENT ORGANIC POLLUTANTS PROPOSED FOR CONTROLS
UNDER AARHUS PROTOCOL [13]

| Chemical name | CAS No. | Type of Control |
|---|---|---|
| Aldrin | 309-00-2 | Elimination (Annex I) |
| Chlordane | 57-74-9 | Elimination (Annex I) |
| Chlordecone | 143-50-0 | Elimination (Annex I) |
| DDT | 50-29-3 | Elimination (Annex I) &/or Restriction (Annex II) |
| Dieldrin | 60-57-1 | Elimination (Annex I) |
| Endrin | 72-20-8 | Elimination (Annex I) |
| Heptachlor | 76-44-8 | Elimination (Annex I) |
| Hexabromobiphenyl (HBB) | 3655-01-8 | Elimination (Annex I) |
| Hexachlorobenzene (HCB) | 118-74-1 | Reduction in Emissions (Annex III) |
| Hexachlorocyclohexanes (HCH) | 608-73-1 | Restrictions on Use (Annex II) |
| Mirex | 2385-85-5 | Elimination (Annex I) |
| Polycyclic Aromatic Hydrocarbons (PAH) | | Reductions in Emissions (Annex III) |
| PCB | | Elimination (Annex I) &/or Restrictions on Use (Annex II) |
| PCDD | | Reductions in Emissions (Annex III) |
| PCDF | | Reductions in Emissions (Annex III) |
| Toxaphene | 8001-35-2 | Elimination (Annex II) |

**Note:**

CAS = CHEMICAL ABSTRACTS SERVICE

4
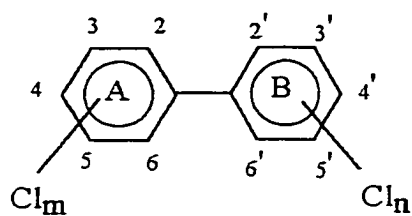


Figure 1.    General structure for polychlorinated biphenyl (PCB) molecule.
(m + n = 1 to 10; 209 possible compounds.)
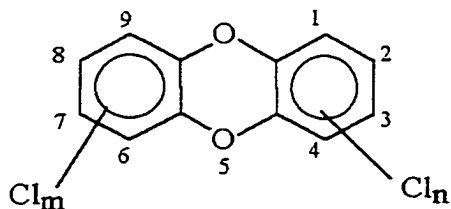


Figure 2.    General structure for polychlorinated dibenzo-p-dioxin (PCDD) molecule.
(m + n = 1 to 8; 75 possible compounds.)
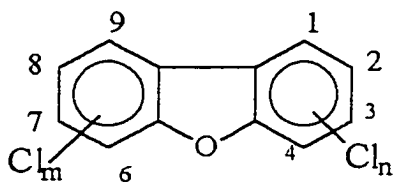


Figure 3.    General structure for polychlorinated dibenzofuran (PCDF) molecule.
(m + n = 1 to 8; 135 possible compounds.)

## 1.2    Polychlorinated Biphenyls

## 1.2.1    General

### 1.2.1.1 Properties of Polychlorinated Biphenyls

Polychlorinated biphenyls are a class of chemicals in which there are 1 to 10 chlorine atoms bonded to a biphenyl molecule (Figure 1). A total of 209 possible structures (or congeners) exist for the mono-deca PCB. The PCBs can be divided by the degree of chlorination into homologs (mono-deca PCB). The full chemical names of the individual PCB congeners can be unwieldy. To simplify the nomenclature of PCB, a convention for naming individual congeners by a number was first proposed by Ballschmiter (BZ no.) [18] and has been accepted with minor modifications by the International Union of Pure and Applied Chemistry (IUPAC no.) [19, 20]. Jonathan Barney of USEPA Region V has published a listing of all 209 PCB congeners and their associated Ballschmiter (BZ) and IUPAC congener number on the internet at: www.epa.gov/toxteam/pcbid/table.htm. Table II presents a number of key physical properties for PCB homologs. The degree of chlorination and position of chlorination control the vapor pressures and boiling points for PCB molecules. In general, the vapor pressures decrease with increasing chlorination. In water, the volatilization of PCBs is controlled by their Henry's Law constant (H). The Henry's Law constant is a measure of the equilibrium distribution coefficient between air and water (or other gas and liquid). Quantitative Structure Activity Relationships (QSAR) have been used to predict the Henry's Law Constant and other properties [21]. The UNIFAC model has been found to predict the Henry's Law constant and other physical properties of PCB [22].

# TABLE II

## PHYSICAL PROPERTIES OF POLYCHLORINATED BIPHENYLS HOMOLOGS[a]

| PCB Homolog Group | %Cl | Mean MW [g] | No. of Isomers | Melting Point (°C) [b] | Boiling Point (°C) [b,c] | Vapor Pressure (Pa) At 25 °C [c-e] | Water Solubility At 25°C (g/m³) [e,f] | Log Octanol-Water Partition Coefficient [c,f] | Approximate Bioconcentration Factor in Fish [c,f] | Approximate Evaporation Rate at 25°C (g/(m² h)) [c,f] |
|---|---|---|---|---|---|---|---|---|---|---|
| Biphenyl | 0 | 154.2 | 1 | 71 | 256 | 4.9 | 9.3 | 4.3 | 1000 | 0.92 |
| Mono PCB | 19 | 188.7 | 3 | 25-77.9 | 285 | 1.1 | 4.0 | 4.7 | 2500 | 0.25 |
| Di PCB | 32 | 223.1 | 12 | 24.4-149 | 312 | 0.24 | 1.6 | 5.1 | 6300 | 0.065 |
| Tri PCB | 41 | 257.6 | 24 | 28-87 | 337 | 0.054 | 0.65 | 5.5 | 1.6E4 | 0.017 |
| Tetra PCB | 49 | 292.0 | 42 | 47-180 | 360 | 0.012 | 0.26 | 5.9 | 4.0E4 | 4.2E-3 |
| Penta PCB | 54 | 326.4 | 46 | 76.5-124 | 381 | 2.6E-3 | 0.099 | 6.3 | 1.0E5 | 1.0E-3 |
| Hexa PCB | 59 | 360.9 | 42 | 77-150 | 400 | 5.8E-4 | 0.038 | 6.7 | 2.5E5 | 2.5E-4 |
| Hepta PCB | 63 | 395.3 | 24 | 122.4-149 | 417 | 1.3E-4 | 0.014 | 7.1 | 6.3E5 | 6.2E-5 |
| Octa PCB | 66 | 429.8 | 12 | 159-162 | 432 | 2.8E-5 | 5.5E-3 | 7.5 | 1.6E6 | 1.5E-5 |
| Nona PCB | 69 | 464.2 | 3 | 182.8-206 | 445 | 6.3E-6 | 2.0E-3 | 7.9 | 4.0E6 | 3.5E-6 |
| Deca PCB | 71 | 498.7 | 1 | 305.9 | 456 | 1.4E-6 | 7.6E-3 | 8.3 | 1.0E7 | 8.5E-7 |

**Notes:**

[a]    Many values are approximations of the range across the isomers

[b]    Average properties of all isomers in group

[c]    Shui and Mackay, 1986

[d]    Shui and Mackay, 1986 [17]

[e]    Mean value for liquid

[f]    Shui and Mackay, 1986 [17]

[g]    Based on natural isotopic abundance of carbon, chlorine and hydrogen

Source:  Adapted from data in Erickson [19]

The information on Henry's Law constants of PCB has been reviewed by Shui and Mackay [17] and others [19]. A more extensive review of the physical properties of PCBs has been provided by Shui and Mackay [17]. Additional information on PCB properties can be found in Hutzinger, et al. [23] and Erickson [19] and Mackay, et. al. [24].

## 1.2.1.2 Polychlorinated Biphenyl Production and Uses

Polychlorinated biphenyls are chemically and physically stable molecules and are good electrical insulating fluids, properties that led to their commercial utility. Polychlorinated biphenyls were commercially produced as complex mixtures, usually as distillation fractions from the chlorination of biphenyl. Polychlorinated biphenyls were commercially produced from 1929 to the mid-1970's in North America [19] and were still being produced in the 1990's in some less developed countries [13]. Total commercial PCB production worldwide has been estimated at 1.1 E6 tonnes, although this estimate has a wide error component [19]. In North America, Monsanto Corporation (St. Louis, MO) was the major producer of a PCB mixture marketed under the trade name Aroclor®. Aroclor® mixtures marketed in North America typically contained 21-68% Cl by weight, with the majority in the 42-60% range. Information on the congener composition of various commercial PCB mixtures is provided in Table III. Homolog composition data for Aroclors is provided in Table IV. Some physico-chemical data for Aroclor mixtures is presented in Table V. The physico-chemical properties of Aroclors have been reviewed by Metcalfe, et al. [25].

# TABLE III

## MAJOR CONGENER COMPOSITION OF COMMERCIAL POLYCHLORINATED BIPHENYL MIXTURES (in wt. %)[a]

| PCB No. | Structure | # of Cl atoms | Type:[b] origin: %Cl | A30 FRG 42 | A40 FRG 48 | A50 FRG 54 | A60 FRG 64 | 1221 U.S. 21 | 1242 U.S. 40-42 | 1248 U.S. | 1254 U.S. 52-54 | 1260 U.S. 60 | D103 CSSR 48 | Kan. Japan ~45 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 1 | | | | | | 32.1 | | | | | | |
| 2 | 3 | 1 | | | | | | 2.7 | | | | | | |
| 3 | 4 | 1 | | | | | | 19.1 | | | | | | |
| 4 | 2,2' | 2 | | | | | | 4.8 | 4 | | | | 2.4 | |
| 5 + 8 | 2,3 + 2,4' | 2 | | 6.1 | | | | 10.2 | 9 | | | | 7.1 | |
| 6 | 2,3 | 2 | | | | | | 3.1 | | | | | | |
| 18 | 2,2',5 | 3 | | 9.9 | 3.8 | | | | 9.4 | | | | 8.5 | 3.5 |
| 15 | 4,4' | 2 | | 9 | | | | 3.6 | | | | | | |
| 17 | 224 | 3 | | | | | | | 2.9 | | | | 5.2 | |
| 16 | 223 | 3 | | | | | | | 3.2 | | | | 5.8 | |
| 32 | 246 | 3 | | | | | | | 2.2 | | | | | |
| 26 | 235 | 3 | | 2.1 | | | | | | | | | | |
| 31 | 245 | 3 | | 6.8 | 2.4 | | | | 4.5 | | | | 9.1 | 5.2 |
| 28 | 244 | 3 | | 9.9 | 4 | | | | 13.3 | | | | 13 | |
| 20 | 233 | 3 | | | | | | | 3.6 | | | | | |
| 21 + 33 | 2,3,4+2',3,4 | 3 | | 4.6 | | | | | 2.8 | | | | 7 | |
| 22 | 2,3,4' | 3 | | | | | | | 2.6 | | | | | |
| 52 | 2,255 | 4 | | 3.1 | 7.3 | 6.8 | 5 | | 4.1 | | | | 4.4 | 2.8 |
| 75 | 2,446 | 4 | | | | | | | 2.2 | | | | | |
| 49 | 2,245 | 4 | | | 4.1 | | | | 3.3 | | | | | |
| 44 | 2,235 | 4 | | 3 | 6.6 | 3.3 | | | | | | | | 2 |
| 42 | 2,234 | 4 | | | | | | | | | 2.2 | | | 2.1 |
| 41 | 2,234 | 4 | | | 3.5 | | | | | | | | | 2 |
| 35 | 334 | 3 | | | | | | | | | | | 3.6 | |
| 39 | 345 | 3 | | | | | | | | | | | 2.3 | |
| 37 | 344 | 3 | | 3.2 | | | | | | | | | 2.5 | |

**TABLE III (Continued)**

MAJOR CONGENER COMPOSITION OF COMMERCIAL POLYCHLORINATED BIPHENYL MIXTURES (in wt. %)[a]

| PCB No. | Structure | # of Cl atoms | Type:[b] origin: %Cl | A30 FRG 42 | A40 FRG 48 | A50 FRG 54 | A60 FRG 64 | 1221 U.S. 21 | 1242 U.S. 40-42 | 1248 U.S. | 1254 U.S. 52-54 | 1260 U.S. 60 | D103 CSSR 48 | Kan. Japan ~45 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 61 | 2,345 | 4 | | 2.2 | | | | | | | | | | |
| 91 | 22,346 | 5 | | | | | | | | | 5 | 3.2 | | |
| 121 | 23,456 | 5 | | | | | | | | | 3.5 | | | |
| 74 | 2,445 | 4 | | | | | | | 2 | | | | | |
| 70 | 2,345 | 4 | | | | | | | | | 4.8 | | | 3.1 |
| 80 | 3,355 | 4 | | 2.5 | | | | | | | | | | |
| 66 | 2,344 | 4 | | 2.3 | 5.7 | | | | | | 2.2 | | | 2.2 |
| 60 | 2,344 | 4 | | | 3.1 | | | | | | | | | |
| 95 | 22,356 | 5 | | | | 2.33 | 3.9 | | | | | | | 3.1 |
| 84 | 22,336 | 5 | | | | 2.7 | | | | | | | | |
| 101 | 22,455 | 5 | | | 2.3 | 6.1 | 4.1 | | | | 7 | 5 | | 3.3 |
| 99 | 22,445 | 5 | | | | 2.5 | | | | | 6.1 | | | |
| 97 | 22,345 | 5 | | | | | | | | | 2.6 | | | |
| 87 | 22,345 | 5 | | | | 3.5 | | | | | 3.8 | | | |
| 90+116 | 2,2',3,4,5'+ 2,3,4,5,6 | 5 | | | | | | | | | | | | |
| 110 | 23,346 | 5 | | | 2.8 | 9.7 | 3.6 | | | | 8.5 | 3.6 | | |
| 151 | 223,556 | 6 | | | | | 4.7 | | | | | | | |
| 149 | 223,456 | 6 | | | | 4.1 | 9.6 | | | | 3.6 | 9.5 | | 3.3 |
| 118 | 23,445 | 5 | | 2.5 | 6.7 | 10.5 | 1 | | | | 8.1 | 2 | | 2.8 |
| 153 | 224,455 | 6 | | | | 3.2 | 8.6 | | | | 3.3 | 8.2 | | 4.6 |
| 132 | 223,346 | 6 | | | | 3.1 | 4.6 | | | | 2 | 2.8 | | |
| 138 | 223,445 | 6 | | | | 6 | 11.3 | | | | 4.2 | 5 | | 4.9 |
| 187 | 2,234,556 | 7 | | | | | 3.8 | | | | | | | |
| 183 | 2,234,456 | 7 | | | | | 3.1 | | | | | 2.6 | | |

6

# TABLE III (Concluded)

MAJOR CONGENER COMPOSITION OF COMMERCIAL POLYCHLORINATED BIPHENYL MIXTURES (in wt. %)[a]

| PCB No. | Structure | # of Cl atoms | Type:[b] origin: %Cl | A30 FRG 42 | A40 FRG 48 | A50 FRG 54 | A60 FRG 64 | 1221 U.S. 21 | 1242 U.S. 40-42 | 1248 U.S. | 1254 U.S. 52-54 | 1260 U.S. 60 | D103 CSSR 48 | Kan. Japan ~45 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 167 | 234,455 | 6 | | | | | 4.9 | | | | | | | |
| 174 | 2,233,456 | 7 | | | | | 3.4 | | | | | | | |
| 185 | 2,234,556 | 7 | | | | | | | | | | 5.6 | | |
| 181 | 2,234,456 | 7 | | | | | | | | | | 2.7 | | |
| 171 | 2,233,446 | 7 | | | | | | | | | | 4.3 | | |
| 180 | 2,234,455 | 7 | | | | | 8.9 | | | | | 7.2 | | 3.9 |
| 170 | 2,233,445 | 7 | | | | | 5.2 | | | | | | | |
| 193 | 2,334,556 | 7 | | | | | | | | | | 2.3 | | |
| 194 | 2,2',3,3',4,4',5,5' | 8 | | | | | | | | | | 2.2 | | |
| Totals | | | | 67.2 | 52.3 | 63.83 | 85.7 | 75.6 | 69.1 | 0 | 66.9 | 66.2 | 70.9 | 48.8 |

**Notes:**

1)  [a] = only percentages >2 given

2)  [b] = Trade name

3)  For all of these congeners, BZ and IUPAC numbers are the same.

Source: Adapted from Erickson [19]

## TABLE IV

### POLYCHLORINATED BIPHENYL HOMOLOG COMPOSITION
### OF SOME AROCLORS

| Homolog Group | 1232 | 1016 | 1242 | 1248 | 1254 | 1260 |
|---|---|---|---|---|---|---|
| 0 | | | | | | |
| 1 | 26 | 2 | 1 | | | |
| 2 | 29 | 19 | 13 | 1 | | |
| 3 | 24 | 57 | 45 | 22 | 1 | |
| 4 | 15 | 22 | 31 | 49 | 15 | 12 |
| 5 | | | 10 | 27 | 53 | 42 |
| 6 | | | | 2 | 26 | 38 |
| 7 | | | | | 4 | 7 |
| 8 | | | | | | 1 |
| 9 | | | | | | |
| 10 | | | | | | |
| Totals | 94 | 100 | 100 | 101 | 99 | 100 |

Source: Adapted from Erickson [19]

## TABLE V

### SOME PHYSICAL/CHEMICAL CHARACTERISTICS OF AROCLORS

| Aroclor | Density (at 20°C) | Pour Point (°C) | Distillation Range (°C) | Vaporization Rate $(g/cm^2/hr)*10^6$ at 25°C | Solubility in Water at 25°C (ug/L) |
|---|---|---|---|---|---|
| 1221 | 1.18 | 1 | 275-320 | 1740 | 15000 |
| 1232 | 1.26 | -35 | 270-325 | 874 | 1450 |
| 1016 | 1.37 | | 323-356 | | 420 |
| 1242 | 1.38 | -19 | 325-366 | 338 | 240 |
| 1248 | 1.44 | -7 | 340-375 | 152 | 52 |
| 1254 | 1.54 | 10 | 365-390 | 53 | 12 |
| 1260 | 1.62 | 31 | 385-420 | 13 | 3 |
| 1262 | 1.64 | 35-38 | 390-425 | 9 | |
| 1268 | 1.81 | | 435-450 | | |
| 1270 | 1.95 | | 450-460 | | |

Source: Adapted from Erickson [19]

Polychlorinated biphenyls have been used in a wide variety of applications. By far, the major use of PCB was as dielectric fluids in transformers and capacitors [19]. Other uses have included carbonless copying paper, printing inks, paints, lubricating and cutting oils, adhesives, sealants, dedusting agents, metal coatings, heat transfer fluids, and hydraulic fluids. Aroclors were often mixed with trichlorobenzenes or other chemicals in transformers; this product class was known as "Askarel."

In addition to their deliberate commercial manufacture, PCBs were unintentionally produced as byproducts in a number of chemical processes with chlorine and hydrocarbons present under certain conditions. They have also been implicated as possible products of water chlorination. Finally, trace levels of PCB (and other chemicals such as PCDD and PCDF) can be formed from pyrolysis of chloralkenes and the combustion of chlorinated hydrocarbons [19].

In Canada (CDN) and the United States (US), concern about the environmental impacts of PCBs (see 1.2.2 below) led to restrictions on their production and use in the early 1970's. Production of PCBs was banned in the US (Toxic Substances Control Act (TSCA)) and Canada in the late 1970's by a series of regulations. However, significant quantities of PCBs continue to be used, primarily in "in-service" electrical equipment.

Additional information on the uses and properties of PCB can be found in books by Erickson [19] and Hutzinger et al. [23].

## 1.2.2 Polychlorinated Biphenyls in the Environment - General

The same chemical and physical stability that made PCBs so useful commercially has also been responsible for the PCB environmental problem. As a result of their stability, PCBs do not degrade readily in environment and can build up in the food chain. Beginning in 1966 with the report of Jensen [26], numerous researchers have shown that PCBs are now ubiquitous environmental pollutants. Higher concentrations are often found in the animals that are near the top of the food chain, such as birds of prey (eagles), seals, bears, and beluga whales [27]. In many instances, elevated concentrations have been observed in animals which are remote from any local sources or in which the concentrations of other environmental compartments are considered to be relatively low [28]. In Northern Quebec, PCB concentrations in human infants are elevated and believed to be causing immune system impairment [29].

While PCB levels in the environment are generally declining, the rate of decline has slowed and there is concern that they may be reaching a new equilibrium [30, 31].

## 1.2.3 Polychlorinated Biphenyl Sources in the Environment

As a result of the wide variety of uses for PCBs the list of environmental sources is quite extensive and includes:

- past open and/or uncontrolled uses

- past disposal practices

- illegal disposal

- accidental releases

- present uses in electrical equipment

- recycling of PCBs from contaminated soil and vegetation

The use of inks and paints containing PCBs has led to widespread, low level environmental contamination [19]. The use of high level PCB fluids in industrial systems led to more localized "hot spots" through spills, leaks, and improper maintenance [32]. Uncontrolled disposal in landfills and illegal dumping also occurred. These past disposal practices make any landfill and hazardous waste site a likely source for PCBs. Elevated levels of PCB have been found near many sites of high-level PCB usage [33]. Over time, the PCBs have undergone environmental transport and dispersal, resulting in widespread background contamination at lower levels.

Of the 5.7E8 – 6.8E8 kg (1.25-1.5E6 lbs) of PCBs that were estimated to have been produced in the US, approximately 1.1E7 kg (1.5-2%) has been estimated to be environmentally available [19, 34].

## 1.2.4 Environmental Fate and Transport of Polychlorinated Biphenyls - General

The environmental transport of PCBs is complex and involves transport by air, water, soil particles, fish, birds, and other routes. The PCBs are deposited from air by rain, snow, dry fallout (of particulates), and vapor phase deposition. These mechanisms result in differing relative concentrations in the various environmental compartments and also may result in altering of the composition of commercial PCB mixtures. For example, the lower PCB homologs have higher vapor pressures, which explains the observation that there is

selective vaporization of the lower chlorinated congeners from Aroclor[tm] and other PCB

mixtures. Polychlorinated biphenyl movement in the environment is summarized in Figure 4

below.
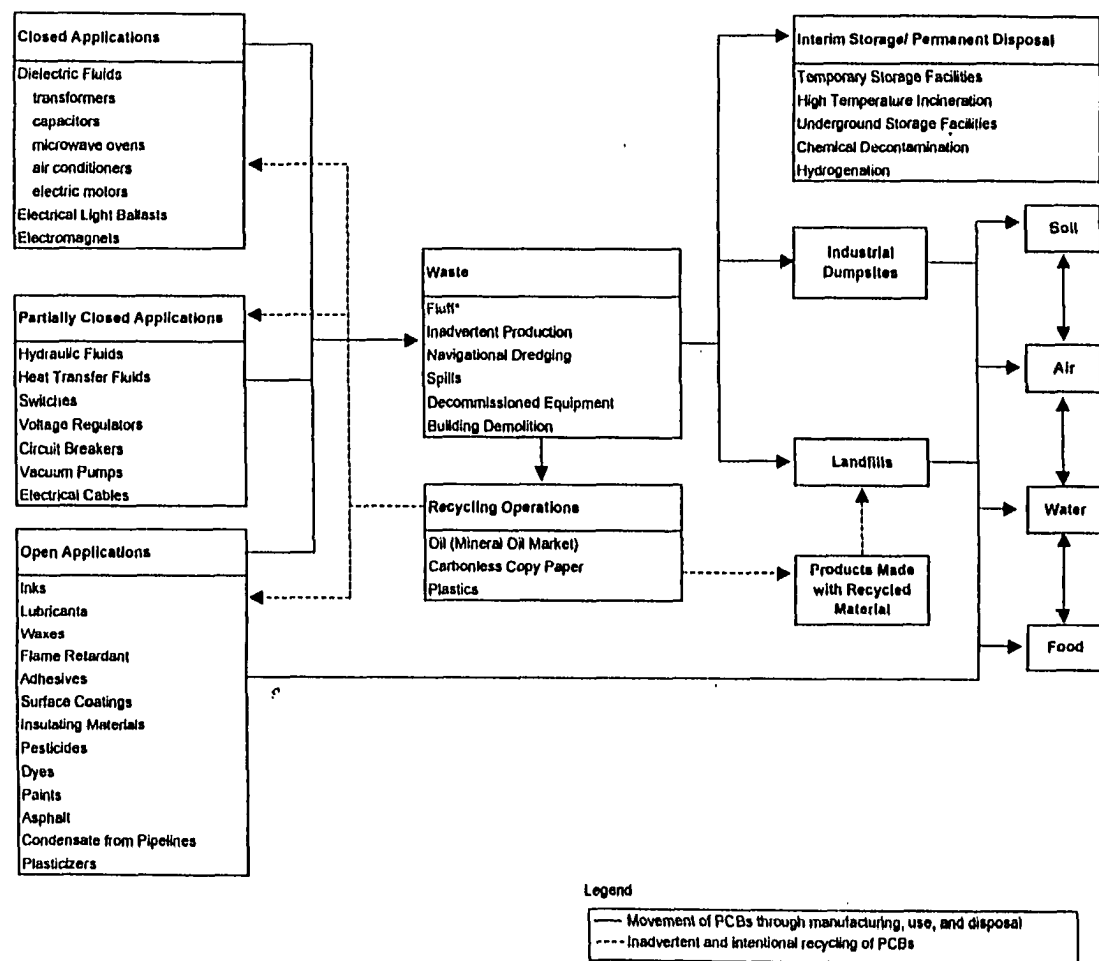
Figure 4.  Polychlorinated biphenyl movement in the environment.  Adapted from [35].

## 1.2.5 Atmospheric Transport and Reactions of Polychlorinated Biphenyls

## 1.2.5.1 Atmospheric Deposition Processes - General

Atmospheric deposition of PCBs and other gaseous or particulate POPs occurs by two major types of processes, wet and dry deposition [36]. Most POPs, including PCBs, have vapor pressures (VP) of roughly between $10^{-4}$ and $10^{-11}$ atmospheres (atm) (1 atm=101325 Pascal (Pa)) at ambient temperatures. These chemicals exist in the atmosphere in the gas phase, as particles or in the particulate phase, or are distributed between the two phases [36]. For PCBs, both phases are important to their atmospheric deposition.

Dry Deposition

Dry deposition can be broadly defined as "the transport of gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation" [37]. Dry deposition processes also include vapor exchange across the air-water interface. The factors that affect dry deposition include the chemical properties of the depositing species, the amount of atmospheric mixing and the nature of the surface on which deposition is occurring. Seinfeld [37] has described the dry deposition process of gases and particles in terms of 3 steps:

1) aerodynamic transport down through the atmospheric surface layer to a very thin layer of stagnant air just adjacent to the surface;

2) molecular (for gases) or Brownian (for particles) transport across this thin stagnant layer of air, called the *quasi-laminar sublayer*, to the surface itself; and

3) uptake at the surface.

Semi-volatile organic compounds appear to be bound to atmospheric particles in two fractions, a non-exchangeable fraction, which is strongly adsorbed and is not in equilibrium with the vapor phase, and an exchangeable fraction, which is in equilibrium with the vapor phase concentration of the SVOC. Semi-volatile organic compound adsorption appears to be controlled by the vapor pressure of the sub-cooled liquid ($p^{\circ}_L$) [38]. Semi-volatile organic compounds in air are typically sampled using an air-sampling device with a filter (usually a glass fiber or Teflon coated glass fiber filter), followed by a solid adsorbent trap (usually polyurethane foam (PUF) or XAD-2 resin). The filter catch is used as an estimate of the particle phase concentration, while the amount in the sorbent is considered gaseous phase. Depending upon how temperature and vapor phase concentrations change during the collection period, this rough classification may underestimate the particulate phase. Degradation of chemicals collected on the filter may also occur. The use of diffusion denuder sampler reduces the errors due to these factors. The adsorption of a chemical to aerosol particles depends upon the vapor pressure of the compound, the amount and type of particulate present, and the ambient temperature [38].

Surface properties greatly influence the rate of dry deposition of gases and particles. Air-plant exchange processes are receiving increasing attention. Plant biomass has been suggested to play a significant role in the environmental partitioning of PCBs and other POPs [4]. Recently, McLachlan and Horstman [39] developed a model to describe the dry deposition of SVOC to the forest canopy. The SVOC found in foliage have been found to result from air-plant partitioning of gas phase SVOC [19]. Studies of the surface or forest canopy dry deposition processes are major areas of current research [37].

Vapor exchange across the air-water layer is an important dry deposition process for some SVOC. This mass transfer process is governed in part by the Henry' Law constant of the chemical. The equilibrium partitioning can be described by Henry's Law Equation (Equation (1)):

$$H = \frac{P_a}{C_w} \quad (1)$$

Where:    H = Henry's Law constant (atm L mol$^{-1}$)

Pa = partial pressure for chemical (i.e., gas phase concentration)(atm)

Cw = aqueous concentration of chemical (mol/L)

At equilibrium, the ratio of the gas phase to aqueous concentrations will be given by the value of H [40]. The exact units of H will depend on the units used for Pa and Cw. In the environment, a system will try to achieve equilibrium. Thus, if the vapor phase concentration of the chemical were lower than would be calculated by Equation (1) (assuming we know H and Cw), the system would tend to vaporize chemical out of the water until equilibrium is achieved.

The importance of dry deposition, relative to wet deposition, depends on a number of factors including:

- Form in which the SVOC is present, i.e., gaseous or particulate;
- Vapor-Particle partitioning processes;
- Solubility of the SVOC in water;

- Amount of wet deposition that occurs; and

- The terrain and type of surface cover.

Although there has been increasing awareness and research on the importance of dry deposition in the fate of airborne pollutants, many uncertainties exist in the methods used to measure and calculate dry deposition [41].

Wet Deposition - General

In wet deposition, such as rain, fog, clouds, or snow, scavenging of vapors and particles is followed by droplet precipitation (rain or snow) or impaction on the earth's surface (e.g., fog droplets) [42]. Wet deposition is one of the most complex atmospheric processes.

Seinfeld [37] has summarized "Wet Deposition" as the following processes:

- Precipitation scavenging, e.g. the removal of species by a raining cloud;

- Cloud interception, e.g., the impaction of cloud droplets on the terrain usually at the top of mountains;

- Fog deposition, e.g., removal of material by settling fog droplets; and

- Snow deposition, e.g., removal of material during a snowstorm.

In each of the above processes, there are three steps necessary for wet deposition of a chemical or species to occur:

1)    The chemical must be brought into the presence of condensed water;

2)    The species must be "scavenged" by the rain, snow, etc.; and

3)    The species needs to be delivered to the earth's surface.

Each of these steps may involve numerous chemical reactions and other processes. Furthermore, most of the chemical reactions and processes that occur are reversible [37].

Wet deposition of inorganics, such as sulfates and nitrates, has received considerable research attention as a result of the concerns about "acid rain" [43] and more recently with the "Great Waters" Report [44] and the concerns about airborne nutrient input into the Chesapeake Bay [44, 45]. However, less is known about wet deposition of organics [46]. Recent work has indicated that, for PCB and PAH at least, submicron particulate scavenging is probably the dominant mechanism of scavenging by rain [47, 48], and that previous work implicating gas exchange as a major process probably overestimated this pathway.

The rates of dry and wet deposition can differ significantly for an area. Additional discussion of wet deposition phenomena can be found in Seinfeld [37] and Finlayson-Pitts [49].

### 1.2.5.2 Atmospheric Deposition of Polychlorinated Biphenyls

Although it is estimated that >99% of PCB mass in the environment is found in soil, volatilization of PCBs from spills, landfills, road oils, hazardous waste sites, etc. results in measurable air concentrations [50]. Atmospheric transport and deposition are the primary methods of global distribution of PCBs [19]. Polychlorinated biphenyls have been observed

in the Antarctic [51] and Canadian Arctic at sites where the only plausible transport mechanism is long-range atmospheric transport [11, 52]. In the US, it has been estimated that 9E8 g (gram) of PCBs cycled through the atmospheric environment in 1985 [53].

In general, air levels of PCBs increase near the source of the PCBs. As a result, urban areas have air concentrations that are generally higher than rural areas, which in turn are higher than remote (or pristine) locations. Cotham and Bidleman [54] sampled ambient air at an urban site (Chicago) and a rural location (Green Bay). An order of magnitude difference was observed for the mean concentrations (1.3 vs. 0.3 ng/m$^3$). Lee [55] has suggested ranges for typical PCB (total) concentrations in remote (<0.5 ng/m$^3$), rural (0.5-1 ng/m$^3$), and urban (>1ng/m$^3$) areas. However, their literature review was limited and did not include data from more recent studies, such as Hoff et al. [56, 57], Cotham and Bidleman [54], and Stern [58], as well as others which suggest that concentrations in remote areas are more likely <0.3 ng/m$^3$ and rural location concentrations are in the range of ~ 0.3-0.8 ng/m$^3$.

Indoor concentrations are often more elevated than the ambient air, a situation that has been found for other air pollutants [59, 60]. Occupational exposures have often been several orders of magnitude larger than ambient air levels (see Table VI).

A summary of the concentrations of PCB that have been reported for ambient air, indoor air, occupational exposures, and stack gas has been provided in Table VI below. It must be cautioned that differences in sampling and analysis (including quantitation) methods,

as well as temperature, geographical location, frequency, and duration of PCB samples, can sometimes make direct intra- and intersite comparison of results difficult and/or misleading.

## Dry Deposition Studies

The majority of studies of PCB in air have involved dry deposition, that is 1) particle and/or 2) gas phase deposition to surfaces, as well as 3) air/water gaseous exchange processes. In air, PCBs will exist between particle and gas phase. The exact distribution will depend primarily upon the congener composition of the source material, the vapor pressure of the PCB congener(s) and temperature. The vapor pressures of PCB congeners present in Aroclors are sufficiently high that the PCBs will be partitioned mainly into the vapor phase [61].

**TABLE VI**

SUMMARY OF POLYCHLORINATED BIPHENYL CONCENTRATIONS
REPORTED IN AIR

| Location | Classification | Concentration (ng/m$^3$) | Reference(s) |
|---|---|---|---|
| Arctic and Antarctic | Remote | 0.002-0.150 | [51] [52] [58] [62] [63] [64] |
| Lake Tahoe, US | Remote | 0.062-0.083 | [65] |
| Bermuda | Remote/Rural | 0.1-1.5 | [66] [67] |
| Germany | Rural | 0.670 | [10] |
| US Rural Sites | Rural | 0.04-0.9 | [68] [54] |
| UK sites | Rural | 0.037-1.155 | [69] [70] [71] |
| Great Lakes, (General and IADN) | Remote, Rural and Urban | 0.09-0.360  0.1-5 | [57] [72] [61] [73] [74] |
| Southern Ontario | Rural | 0.06-0.823 | [10] [56] |
| London and Manchester UK | Urban | 0.150-3.5 | [75] |
| Bloomington, IN | Urban | 0.7-2.5 | [76] |
| Chicago, IL | Urban | 0.3-22.8 | [54] [53] [77] |
| South Chicago, IL | Urban/ Industrial and Local Influenced | 0.079-41.9 | [78] [79] |
| Taiwan, Petroleum Refinery | Urban/ Industrial | 2.62-7.77 | [55] |
| Incinerator Stack Gas | Local Source | 10-58,000 200-1600 15-1200 | [19] [80] [81] |
| US Landfills Air Emissions | Local Source | 2-143000 | [82] [83] |
| Bloomington, IN Superfund Sites | Urban/Local Source Influences | 0.04-4 | [84] |

**TABLE VI (Concluded)**

SUMMARY OF POLYCHLORINATED BIPHENYL CONCENTRATIONS
REPORTED IN AIR

| Location | Classification | Concentration (ng/m³) | Reference(s) |
|---|---|---|---|
| Around PCB Storage Sites, Canada | Local Source | 12-250 70-560 1-4700 | [85] [86] [87] |
| PCB Storage Site | Indoors | 36-100000 | [87] |
| US PCB Spill Site | Indoors | 10-10,800 | [82] |
| PCB Analysis Lab | Indoors, Local Influence | 6-480 | [60] [88] [53] |
| Germany, Schools with PCB Sealants | Indoors, \\ | 500-10000 | [89] [90] |
| US, After Light Ballast Burnout | Indoors, Local Source Influence | 5800 | [82] |
| US Electrical Substations | Indoor Air/Local Source | 1-47 | [82] |
| US Electrical Manufacturing and Repair Plants | Indoors | 1-5800000 | [91] |
| ON, Canada | Ambient Air Standards MOE | 450 (1/2 hr ave.) 150 ( 24 hr) 135 (48 hr) | |
| ON, Canada and US | Workplace Air Standard MOL & OSHA | 50000 (8 hr TWA) | [91] [19] |
| US | Workplace Air Standard NIOSH | 1000 | [19] |

**Notes:**

| | |
|---|---|
| IADN: | Integrated Atmospheric Deposition Network |
| MOE: | Ministry of the Environment |
| MOL: | Ministry of Labor |
| NIOSH: | National Institute for Occupational and Health |
| ON: | Ontario |
| OSHA: | Occupational Safety and Health Administration |
| US: | United States |

However, the PCB congener patterns observed in air samples are typically different from the congener profile in Aroclors due to selective volatilization of the lower chlorinated PCB from sources, as well as selective adsorption of the higher PCBs by organics in soil, mineral oil, etc. Relative amounts of congener and homolog groups can still be used to differentiate between different potential sources, but care must be exercised. One exception is natural gas pipeline samples, where the parent Aroclor pattern is maintained, indicating that PCB aerosol transport was taking place rather than volatilization and condensation [19].

With particles, especially coarse particles (>10 um), represented a significant fraction Holsen, et al. [92] found that dry deposition fluxes of PCBs were up to three times higher in urban compared to non-urban settings. They also found that PCBs associated of total PCB dry deposition, even though PCBs were primarily present in the gas phase. The analysis of PCB dry deposition in La Jolla, CA led McClure [93, 94] to conclude that aerosol transport of SVOC was a mesoscale (100-500 km) as opposed to a hemispheric or global transport phenomenon.

Phase Distribution of PCB Dry Deposition

Many researchers have studied the distribution of PCBs in the gas and particle phase. Typically, operationally defined "particle bound" or "particulate phase" are assigned to the PCBs found on the filter and "gas phase" or "vapor phase" to PCBs found in the sorbent (see section on sampling and analysis, below). The distribution of PCBs between gas and particle phase is dependent on the ambient temperature, the amount and type of particulate matter present, vapor pressure, molecular weight, and relative humidity of air [38, 55, 95-100]. Falconer and Bidleman [95] have used empirical data to predict particle/gas distributions of

PCBs as a function of temperature and ortho-chlorine distribution. Cotham and Bidleman [38] predicted the particle-associated fraction ($\phi$) using the Junge-Pankow Adsorption Model (Equation (2)) [96]:

$$\varphi = c\theta/\left(p_L^o + c\theta\right) \qquad (2)$$

*where :*

$p_L^o$ = *liquid phase saturation vapor pressure of the pure compound (Pa)*
$c$ = *a parameter which depends on the thermodynamics of the adsorption properties*
$\Theta$ = *the particle's surface area concentration ($cm^2$ aerosol/$cm^3$ air)*
$\varphi$ = *the fraction of SVOC compound adsorbed to particles*

The more toxic (see section 1.4 below) mono- and non-ortho-substituted PCBs were found to be associated with particles in the air, thereby increasing the likelihood of their removal by wet or dry deposition.

A number of researchers have examined the distribution of PCBs between the "particulate" and "gas" phase. Ballschmiter [101] found that at $-8^{\circ}C$, approximately 70% of the observed total PCBs, were in the particulate phase. The amount in the particulate phase increased with the degree of chlorination at $10^{\circ}C$; 2-5% of trichlorobiphenyl (PCBTRI) was found in the particulate phase, > 90% of octachlorobiphenyl (PCBOCT) was in the particulate phase. Lee [55] found a mean of 63% PCBs in the gas phase for industrial and urban areas, while rural areas had a mean of 51%. As expected, the gas phase contains mainly lower chlorinated PCB congeners. Possible reasons postulated by Lee for the differences between rural and urban samples were sorption of PCB to particles during transport or reaction of the gas phase PCB. Panshin and Hites found only 5-10% of PCBs in

Bloomington air samples in the particulate phase [76]. In the IADN program, gas phase concentrations of PCBs exhibit a seasonal trend [72], with higher gas phase concentrations and partitioning in the summer months. A simultaneous plot of temperature and gas phase PCB concentrations shows a definite cyclic pattern, with the highest concentrations seen for the warmer months (see Temperature Effect below).

Wania, et al. [102] has noted that cyclic fluctuations of SVOCs, including PCBs, have been observed with both annual and daily periodicity. In general, the driving forces for the periodicity that were identified by them were, emissions and human behavior, degradation processes, phase composition and surface properties, and meteorological and climatic conditions. Temperature was noted to have a marked impact on concentrations.

Effects of Temperature on Atmospheric Concentrations of PCBs

As mentioned above, temperature effects are significant in the volatilization of PCB from soil and in vapor/particle fractionation of PCB. Polychlorinated biphenyls exhibit strong temporal and diurnal trends, primarily as a result of their temperature dependence. Therefore, intercomparison of results between sites is often difficult unless the temperature is taken into account. Hoff, et al. [56] were the first to report a high temporal resolution data set for PCBs in air. They found definite seasonal variability in PCBs and other OC concentrations. The concentrations observed were found to fit best to a Lorentzian model correlating with seasonal temperatures.

Recently, with long-term studies such as IADN [57, 72, 103], the temperature effect has been established and is now well accepted. In general, average air concentrations observed for PCBs are higher for warmer periods.

Hermanson and Hites [84] found higher concentrations of *vapor phase* PCBs in the summer months than winter months in the vicinity of several Superfund sites. There was also a good correlation (correlation coefficient = 0.8-0.9) at three sites for *total* PCB concentration and temperature. They attributed the effect to increased evaporation of the PCBs from local sources during the warm summer months. They also found the logarithm of the vapor/particle ratio (V/P) correlated with the inverse temperature ($r^2$=0.67-0.78) for the three sites. This relationship is expected based on the work of Bidleman [36] and others [95, 104].

Monosmith and Hermanson [74] studied the temporal trends of PCBs at three sites on the central and upper Great Lakes. They found similar correlations (0.75-0.8) to Hermanson and Hites for temperature and total PCB concentrations.

The temperature dependence of atmospheric PCB (and other SVOC) concentrations has been explained [102, 105] in terms of atmosphere-surface equilibrium consistent with the Clausius-Clapeyron Equation (Equation (3)):

$$\ln P_{vap} = \frac{\Delta H_{vap}}{RT} + constant \qquad (3)$$

Where:

$\Delta H_{vap}$ = heat of vaporization (J/mol)

$P_{vap}$ = partial vapor pressure ( Pa)

R = molar gas constant;

$(8.31451 \frac{J}{mol*K}$ or $8.31451 \frac{m^3 *Pa}{mol*K}$

T = temperature (K)

For temperature controlled vaporization, a plot of the natural logarithm of concentration (expressed as partial vapor pressure ($P_a$ in some publications)) as a function of the reciprocal temperature (in K) should yield a straight line with a negative slope, in which the slope is equal to the heat of vaporization divided by the gas constant. The partial vapor pressure is obtained from the air concentration of the compound using the Ideal Gas Law (Equation (4)):

$$P V = nRT \qquad (4)$$

where :

$P = P_{vap}$

$V = volume (m^3)$

R, T = as defined above

Equation (4) can be rearranged to give the moles/volume from the Ideal Gas Law (Equation (5)):

$$\frac{n}{V} = \frac{P_{vap}}{R * T} \qquad (5)$$

Equation (5) can be rearranged to solve for the $P_{vap}$ from the concentration and average temperature for a sampling period as shown in Equation (6):

$$P_{vap} = \left(\frac{n}{V}\right) * R * T \qquad (6)$$

where :

$$\frac{n}{V} = \frac{mass/MW}{V}$$

MW = molecularweight (g/mole)

Equation (3) can be rewritten in the form of Equation (7):

$$Ln(P_{vap}) = -\left[\frac{\Delta H_{vap}}{R}\right]\frac{1}{T} \qquad (7)$$

Therefore (assuming the compound observed is in the gas phase), a linear regression analysis of a plot of the natural logarithm of vapor pressure vs. 1/T (in K) will yield a line with slope M and x intercept b, as shown in Equation (8):

$$M = -\left[\frac{\Delta H_{vap}}{R}\right] \qquad (8)$$

Note that slope is the same whether atm or Pa is used for units of pressure.

Equation (8) can be rearranged to Equation (9) to solve for an observed value of

$\Delta H_{vap}$:

$$\Delta H_{vap}(observed) = \frac{-m}{R} \qquad (9)$$

$$R = 8.31451 \frac{J}{mole * K} \quad \text{to give} \quad \Delta H_{vap} \text{ in } \frac{J}{mole}$$

or

$$R = 0.00831451 \frac{kJ}{mole * K} \text{to} \quad \text{give} \quad \Delta H_{vap} \text{ in } \frac{kJ}{mole}$$

Because the vapor pressure of PCBs generally decreases with the degree of chlorination (see Table II) it would be expected that slope of Equation (3) might vary with homolog groups. This has been observed by Wania, et al. [102]. Hoff, et al. [56] and others [105] have noted that the temperature dependence of the slope for Equation (3) at temperatures <0°C is minimal, leading to the "hockey stick" type of plot. A similar lack of temperature relationship has been noted for sites in the high Arctic or remote from any local sources. Recently, Hoff, et al. [105] has provided a possible explanation for the "hockey stick" effect, based upon the relative importance of long-range transport for a sampling site. Wania, et al. [102] have advanced a similar explanation using air-soil equilibrium processes in concert with soil fugacity concepts. Both explanations lead to a similar conclusion. Mainly, that the stronger the temperature-concentration relationship (i.e., the higher the slope of Equation (3)), the greater the contribution of local or regional transport compared to long-range transport. Observation of a "hockey stick" plot provides a more conclusive indicator of the relative strength of local and LRT contributions if temperature is the principal driver. It is important to understand the difference between a statistically stronger correlation (e.g., a

higher $r^2$ value) as opposed to a stronger temperature effect (e.g., a steeper slope for the temperature-concentration plot).

## PCBs in Air in the Vicinity of Landfills and Hazardous Waste Sites

Dry deposition is the major deposition pathway for PCBs in the vicinity of landfills and hazardous waste sites. Hosein, et al. [85] examined the relationship of "vapor" versus "particulate" phase PCB in the vicinity of a soil cleanup at a General Electric facility in Toronto, Canada. At the worksite itself, air concentrations of 117-123 ng/m$^3$ were observed. The concentrations had fallen to 4-8 ng/m$^3$ 100 m from the source. They found that in most cases the particulate and vapor phase PCBs were within 10-15% of each other. They interpreted their results to mean that most of the PCBs were associated with the particulate phase. This result is different from that observed for many others in the Great Lakes area, where PCBs are primarily in the vapor phase [56, 57, 72, 84]. The reason for the discrepancy is not clear, but some suggested reasons are: 1) the Great Lakes air sampling results are generally 3 orders of magnitude lower than the levels observed by Hosein, and 2) Hosein used Florisil™ cartridges, which will actually collect both particulate and vapor phase PCB, although they did attempt to account for particulate. A definite temperature effect was observed by Hosein, with higher concentrations observed for temperatures > 16°C. This was interpreted as being indicative of increasing volatilization of the PCBs from the soil. Increased PCB concentrations were also observed for wind speeds of < 8 km/h.. Unfortunately, the data was reported as "Aroclors" (which technically is not correct for quantifying air samples unless it exhibits an Aroclor pattern, such as from an oil aerosol). No homolog or congener data, which might have assisted the data interpretation, was provided.

Murphy, et al. [53] sampled municipal landfill gas vents and found detectable concentrations of PCBs (37-390 ng/m$^3$) in the landfill gases. The lower chlorinated PCBs were the main ones observed, indicating most of the PCBs were in the vapor phase. Murphy also sampled exhaust gases from municipal solid waste incinerators, sewage sludge incinerators, and natural gas pipelines, and found detectable quantities of PCBs.

Lewis, et al. [83] also studied PCB emissions from four landfills known to contain large quantities of PCBs. Three of the landfills were uncontrolled and one was a state-of-the-art TSCA regulated PCB landfill. Concentrations ranging from <20 up to 142,000 ng/m$^3$ were measured in the TSCA landfill vents. Fenceline sampling at the TSCA landfill did not detect any PCBs. Air sampling on site at the uncontrolled disposal sites had the highest concentrations observed in this study (up to 193,000 ng/m$^3$). Air concentrations measured downwind at the uncontrolled sites were much higher than for the TSCA landfill (<40-33,800 ng/m$^3$). A definite diurnal concentration dependence was observed, with higher concentrations in the middle of the day. A vertical profile was also observed for PCBs at the uncontrolled sites, with highest concentrations seen at 2 cm above the ground (271,000-1,053,000 ng/m$^3$) and lowest at 180 cm above the ground (1300-21,000 ng/m$^3$). Air concentrations decreased significantly after the sites underwent an emergency cleanup.

Darrow [79] and Scheff and Darrow [78] analyzed the PCB ambient air monitoring data for 3 air monitoring stations located in South Chicago, IL in the vicinity of a number of known and/or suspected PCB sources. They found total PCB concentrations ranged from 0.079-41.9 ng/m$^3$, with an average of 3.32 ng/m$^3$. Results were found to be significantly

correlated for samples downwind from a PCB incinerator, a sewage treatment plant (STP), and water bodies with known elevated PCB concentrations. Polychlorinated biphenyl concentrations showed a strong temperature effect, indicating PCB volatilization was a strong factor. Unfortunately, the analytical method used (conversion of all PCB to decachlorobiphenyl (PCBDEC)) did not provide any homolog or congener data.

Summertime dredging of sediments contaminated with PCBs at the New Bedford Harbor Superfund site resulted in outdoor concentrations of PCBs of up to 53 ng/m$^3$, which levels were elevated compared to sampling carried out before dredging, and 7-8 times higher than the comparison neighborhood (sampled at the same time). However, indoor air concentrations taken at the same time at both locations (near the dredging and in the comparison neighborhood) were higher than the outdoor air concentrations. Sampling during winter periods, when volatilization of PCB was low, did not show a difference between neighborhoods. Other work at the New Bedford Harbor site has shown elevated breast milk levels of PCBs in some women living adjacent to the site [106] and in produce grown near the site [107].

Hermanson and Hites [84] sampled PCB in air in the vicinity of several Superfund sites in the Bloomington, IN area. They found that "vapor phase" PCB concentrations were significantly higher in summer (1.7-3.8 ng/m$^3$) compared to winter (0.27-0.58 ng/m$^3$). "Particulate phase" PCB did not differ significantly, and averaged only 0.04 ng/m$^3$. Although there were differences in the levels seen at the different sampling sites, no clear correlation could be found with distance or direction relative to a Superfund site.

An industrial facility in the US was contaminated with PCBs and PCDD/DF as a result of improper incineration of Askarel at the facility and PCB spills. Widespread surface contamination with PCB, PCDD and PCDF was found in many of the buildings at the facility. Polychlorinated biphenyl concentrations were elevated in the buildings with a range of 310-3200 ng/m$^3$ [108].

Grundy, et al. [33] studied the weathering and dispersal of PCBs from contaminated soil at former radar sites in the Canadian Arctic.

<u>Wet Deposition Studies</u>

Polychlorinated biphenyls are known to be removed from the atmosphere quite effectively by precipitation [47, 48, 109]. In Lake Michigan, wet deposition is responsible for 80% of the PCB atmospheric deposition away from urban areas. [110]. Some measurements in Lake Huron have indicated a prevalence (>75%) of wet depositions [111]. Under urban air conditions, PCB scavenging by particle-based rainout processes can be quite effective. Offenberg and Baker [110] found concentrations of PCB in precipitation samples collected within tens of kilometers of Chicago were 2-400 times greater than background. Air samples collected during the same storm events, but farther away from Chicago, had much lower concentrations, indicating that effective scavenging had taken place. The mechanism was postulated to be particle scavenging due to the enrichment of particle phase (particularly sub-micron particulate bound) PCBs in the precipitation [110]. Poster and Baker [47, 48] found that while the "particle phase" PCB in air samples were found to be <3%, the levels of PCB in the operationally defined "dissolved" phase or precipitation were

much higher than could be accounted for by gaseous exchange with PCB vapor phase, suggesting sub-micron particulates were a factor. Recently, Franz and Eisenreich [46] examined scavenging of PCB and PAH in Minnesota by snow, rain, and combinations of the two. Particle scavenging was found to be the dominant contributor to the total concentrations observed in snow, but was less important in rain. The most likely reason for the difference was postulated to be that additional gas phase scavenging can occur for rain events (as a function of Henry's Law constant etc.). These authors did not address the sub-micron particulate scavenging issue.

## PCBs in the Great Lakes

The Great Lakes have been an area of active research on the fate, transport, and effects of PCBs and other POPs. Atmospheric transport is a major pathway by which PCBs reach the Great Lakes [44]. Up to 96% of PCBs in some of the Great Lakes have been estimated to have come from atmospheric deposition [57]. The 1987 Great Lakes Water Quality Agreement established IADN in order to provide regular updates of the atmospheric deposition of toxic chemicals (including PCBs) to the Great Lakes and allow their comparison to other sources. Five master stations, one on each lake, have been established. These stations are Eagle Harbor (US, Lake Superior), Sleeping Bear Dunes (US, Lake Michigan), Burnt Island (CDN, Lake Huron), Sturgeon Point (US, Lake Erie), and Point Petre (CDN, Lake Ontario). The sampling and analysis methodologies being used have been described [112]. Atmospheric deposition monitoring at theses sites began in 1988-1990, and is ongoing. The results obtained have been reviewed by Hoff, et al. [57] and Hillery [103].

Although the air concentrations of PCB are relatively constant throughout the Great Lakes air shed, the relative contribution of atmospheric deposition differs significantly [57, 110]. It has been estimated that 90%, 78%, 50% of the PCBs in Lakes Superior, Lake Huron, and Lake Michigan respectively are from atmospheric deposition. Whereas for Lake Erie and Lake Ontario, the values are only 13% and 7%, respectively. The reasons for the differences include, hydraulic residence times, surface area to volume ratios, lake surface area to drainage basin area, and relative strength of local emission sources [110].

While most atmospheric depositions studies have focused on deposition into water bodies, the reverse process is also occurring in the Great Lakes via evaporation and aerosolization [19]. The amount of volatilization that will occur is partly dependent on Henry's Law partitioning. Recently, with the reduction in PCB air concentrations in the Great Lakes area, the net flux of PCBs for some of the Lakes has now been found to be out of the Lakes. The air-water exchange is seasonal, with volatilization dominating in the warmer summer months and net deposition occurring in cooler spring and fall months. Overall net volatilization of PCB has been predicted for Lake Superior, Lake Michigan, and Lake Ontario [113]. Scheff and Darrow [78] found a correlation with length of time air parcels spent over contaminated water bodies and air concentrations measured in South Chicago.

Transboundary air pollution transport is a significant issue for PCB and other POP in the Great Lakes since control strategies for POP control may not be effective unless LRT is controlled in both countries.

## Atmospheric Reactions of PCBs

The chemical loss processes for organic compounds present in the atmosphere in the gas phase primarily involve photolysis and chemical reaction with OH and $NO_3$ radicals and with $O_3$ [37, 49, 114, 115]. The OH radical reaction is the most important of the loss processes for most organics [37]. Reaction of OH with PCBs proceeds almost entirely via OH radical reaction to the aromatic ring [114]. Atkinson [114] used computational and experimental techniques to estimate room temperature reaction rate constants for mono- to hexachlorobiphenyl (PCBHEX or HexaPCB). The reactivity of PCBs to OH radical attack decreases with increasing degree of chlorination. Anderson and Hites determined OH reaction rate constants for mono- to pentachlorobiphenyl [116] and calculated reaction rate constants for 14 PCBs at 298K. The OH radical reaction is estimated to be the major permanent loss process for PCBs from the atmosphere [116]. Others have noted that the photolytic destruction of PCBs in the atmosphere appears to be very slow [101]. An atmospheric half-life on the order of one week in direct sunlight has been determined in laboratory studies [117]. The available information on atmospheric residence time and half-life for PCB are summarized in Table VII below. There is a considerable range in the estimates. The reasons for these ranges are not clear but may be due to differences in calculation methods, definitions and/or assumptions. In any event, the atmospheric reactions of PCB have not appeared to be a significant removal process while emission of PCBs is still taking place.

## TABLE VII

### ESTIMATES OF ATMOSPHERIC HALF-LIFE OR RESIDENCE TIMES
### FOR POLYCHLORINATED BIPHENYLS IN AIR

| Location | Description of Chemical | Time | Comment | Reference |
|---|---|---|---|---|
| Air, Remote Atmospheres | Aroclor 1242 | 30 days 190 days | Residence time | [118] |
| Air, USA | PCB | 7 days | Residence Time | [53] |
| Air, Laboratory Experiments and Calculations | Penta-chlorobiphenyl  Other PCB | 60-120 days | Atmospheric lifetime | [114] |
| Air, Laboratory | PCB | ~ 7 days | Laboratory Photolysis experiment | [117] |
| Air, Lake Superior | Various PCB | >10 yrs | No change in 10 years | [119] |
| Air Ulm, Germany | PCB (28, 52, 101, 118, 153,180) | 100 days  7 days | Residence time-gas phase  Residence time-particulate phase | [101] |
| Air, Bloomington, IN | Various PCB | >7 yrs | Half Life No change in 7 yrs | [76] |
| Air, Bermuda | Various PCB | 20-97 days (range) 86 days (average) | Residence Time | [66] |
| Air, Bermuda | Various PCB | >23 yrs | Half-Life No change in 23 yrs | [66] |
| Air Laboratory Experiments and Calculations | Tetra-PCB Penta-PCB Hex-PCB Hept-PCB | 25 days 30-48 54-79 116-147 | Tropospheric Lifetime | [120] |
| Air. Laboratory Experiments | Mono-PCB Di-PCB Tri-PCB Tetra-PCB Penta-PCB | 2-4 days 5-6 9-12 12-14 14-34 | Atmospheric lifetime  Based on reaction with OH radical | [116] |
| Air, near Lake Michigan and Lake Erie | Various PCB | 6 yrs | Half life for PCB | [72] |
| Air, Lake Superior | Various PCB | >7 yrs | No change since monitoring began | [72] |
| Air, Baltic | PCB (28, 52, 77, 101, 105, 118, 126, 138, 153, 169, 180) | 72-15000 (h) | Model Calculations | [121] |

## 1.2.6  Sampling and Analysis of Polychlorinated Biphenyls in Air

The data presented above on the occurrence and fate of PCBs in the atmosphere are based on the assumption that the sampling and analysis methods that have been used are accurate, precise, and comparable. However, a number of different sampling and analysis methods have been used to measure atmospheric deposition of PCB. Consequently, the assumption of accuracy, precision, and comparability of data may not be valid in all cases.

### 1.2.6.1  Sampling Methods

Dry deposition can be subdivided into particulate phase and gas phase deposition. Dry deposition of particulates is generally measured using horizontal wet or dry samplers [41, 92].

Most ambient air sampling methods for dry deposition have utilized a solid sorbent, with or without a filter, to provide: 1) total combined phase PCB concentration, and/or 2) collection of operationally defined "gaseous phase" and "particulate phases" separately. Solid sorbents which have been used include Florisil$^{tm}$, PUF, XAD-2 Resin, and Tenax$^{tm}$.

Today, most researchers utilize High-Volume (Hi-Vol), air samplers such as an Anderson PS-1, in which a glass fiber, quartz fiber, or Teflon coated glass fiber-filter is followed by a cartridge containing a solid sorbent. The main sorbents used have been XAD-2 and Polyurethane Foam (PUF) or PUF/XAD-2/PUF sandwiches. The PCBs collected on the filter are operationally defined to be "particulate" phase and those collected in the sorbent are considered "gaseous" or "vapor" phase. Caution should be used in applying these

designations absolutely. Since PCBs are SVOC, there will be partitioning between the particulate and gaseous phases while the filters are having air run through them. Sampling for long periods of time and/or at elevated temperatures can result in "blow-off" of the PCB from the filter. Therefore, the amount of PCBs collected on the filter should be considered a minimum value for filters. The solid sorbent used to collect the vapor phase PCBs can also undergo breakthrough. This is especially a problem for long sampling periods or for elevated temperatures. Polyurethane foam suffers breakthrough at summer time temperatures more readily than XAD-2. The Ontario Ministry of the Environment (MOE) and Environment Canada (EC) has used XAD-2 or PUF/XAD-2/PUF cartridges to minimize this problem.

Florisil$^{tm}$ is a magnesium silicate salt that has received limited use for ambient air sampling, although it has had widespread use for source sampling [19]. Florisil$^{tm}$ air sampling methods normally use relatively low flow rates (200 mL/min - 0.5m$^3$/hr). The National Institute of Occupational Safety and Health (NIOSH) has used Florisil$^{tm}$ as a solid adsorbent for analyzing PCBs in workplace air. Atlas & Giam [118] used Florisil$^{tm}$ cartridges for measuring low level PCBs in remote and urban environments. The Ontario Ministry of Environment (MOE) has also used Florisil$^{tm}$ sorbents for ambient air sampling in Ontario [122, 123]. This sorbent collects PCB in both the gaseous and particulate phase, providing a "total" PCB result. In several ambient air and source tests studies, spiked Florisil$^{tm}$ cartridges have shown good recoveries. A disadvantage of Florisil$^{tm}$ is its sensitivity to moisture.

Billings and Bidleman [124] have compared PUF, XAD-2, and Tenax™ GC [124] and found that ambient concentrations obtained by all three sorbents were generally within 10-15% of each other. This is well within the range of comparability obtained for co-located samplers using the same sorbents [125].

PCBs can bioconcentrate in plant biota, such as tree leaves, coniferous needles, and bark. Concentrations measured in plants correlate with air measurements. Biota has been suggested for use for indirect long-term air monitoring of PCBs and other organochlorines (OC). Hermanson and Hites [126] and Meredith and Hites [127] measured PCB concentrations of PCBs in tree bark and wood near known PCB contaminated sites and found that the concentrations varied with proximity to the sites. Pine needles have been used as passive samplers for PCBs [128]. McLachlan and co-workers have developed solid phase "fugacity meters" to monitor vapor phase concentrations of PCB and other SVOCs [129, 130].

### 1.2.6.2 Analytical Methods

During the 1960's and 1970's most air samples were analyzed using packed column (PC) gas chromatography (GC) (PCGC) with Electron Capture Detectors (ECD), Hall Electrolytic Conductivity Detection (HECD) or, in limited cases, mass spectrometry (MS) as the detector. Packed column gas chromatography suffered from poor peak resolution and relatively high detection limits due to the poor resolution. The typical detection limits for air during this period was in the 1-100 ng/m$^3$ range.

The development of high resolution capillary GC (HRGC) in the late 1970's resulted in increased accuracy and sensitivity. In the 1980's and early 1990's, HRGC analyses on one or two columns with ECD detection represented the state of the art. Singer, et al. [122] compared results for air samples taken in Ontario using Florisil[tm] tubes and analyzed by PCGC-ECD, single column HRGC-ECD and dual column HRGC-ECD. They found that air concentrations measured in the same sample decreased approximately one order of a magnitude as the degree of sophistication increased. High resolution capillary GC analytical methods have been developed which can individually separate and analyze all 209 PCB congeners; however, most of these methods require analysis by at least two separate columns in order to separate co-eluting congeners.

Analysis by MS provides much more specific structural information than ECD. However, GC-MS analyses during the 1960's-1970's were usually less sensitive than ECD or HECD detection. As a result, GC-MS analyses were not used as often for trace air analyses as ECD. In the mid 1990's, the detection limits (using specialized ionization methods such as Electron Capture Negative Ionization (ECNI) and improved detectors) and costs of MS detectors have decreased substantially, such that detection limits equivalent to that of GC-ECD can now be achieved. As a result, analyses with GC-MS are often as routine as GC-ECD and provide an extra level of assurance of proper identification and quantitation. Detection limits for typical Hi-Vol air samples are now in the 0.5-1 $pg/m^3$ per congener range.

Besides the type of column and detector used, the quantitation method and lab cleanliness can affect the analytical results. During the early period of air sampling, quantitation was often performed against Aroclor standards using the so-called Webb-McCall method[131]. However, this method may introduce errors in quantitation for air samples 1) because it is comparing relative peak areas (or heights) against Aroclor standards in solution, and 2) because of variations in Aroclor batches. Polychlorinated biphenyls in the atmosphere, more often than not, exhibit different homolog/congener profiles than in Aroclor mixtures as a result of preferential adsorption or vaporization, or differences in the PCB source composition. Therefore, quantification of air samples based on Aroclor standards is not recommended. Instead, quantification using individual congeners or homologs is recommended. Standards are now commercially available for all 209 PCB congeners. It must be recognized that ECD response factors (RF) can vary by 100 X or more within a homolog group [19]; therefore, it is important to have proper congener identification and resolution when using GC-ECD. Mass spectral response factors exhibit much lower differences (a maximum of 2X) between congener groups in a homolog group[19].

Currently, most PCB air samples are analyzed and quantitated on an individual congener basis by (single or dual column) HRGC-ECD or HRGC-MS. Some analytical protocols specify 90 or more different congeners [57], while others may only analyze 5 or 6 [64]. No consistent rationale was found for how the PCB analyte lists that were used were developed and why some have more analytes than others. Comparison of total PCB concentrations between studies is, therefore, difficult and prone to error unless one knows

exactly which PCB quantitation method was used, which congeners were analyzed for, and which quantitation standards and methods were used.

Recently, increased attention has been placed on the effects of indoor air contamination in laboratories on reported ambient air concentrations. Alcock, et al. [88] analyzed samples that had been archived since the late 1800's, prior to the production of PCB, and discovered quantifiable amounts of PCB. Upon further investigation, it was found that soil samples left on countertops in their lab adsorbed PCBs as a function of time. Sampling and analysis of air in their lab revealed air concentrations of 5-8 ng/m$^3$. Wallace, et al. [60] reported that indoor air concentrations in laboratories used for PCB analysis were 5-300 times ambient air levels (range of concentrations was 6-480 ng/m$^3$). The problem was discovered when it was observed that cleaned XAD-2 resin was becoming contaminated while in the laboratory. The air concentration of PCB was strongly correlated with the building construction date. The PCB congener patterns observed were identified by the authors as similar to Aroclors 1242 and 1254. The building air PCB concentrations can affect the accuracy and detection limits for air sampling by: 1) contamination of the sample during analysis, or 2) increased air concentrations for sampling performed on building rooftops that vent the building air near the sampler. The authors recommended that laboratories analyzing PCB should routinely sample their air to determine if there might be a problem.

Caution must be used in interpreting the apparent reduction in air concentrations of PCBs over the last 30 years because the reductions may be due, at least in part, to improvements in sampling and analysis methods including:

1) lower detection limits due to the use of HRGC and larger sampling volumes;

2) increased accuracy due to the use of dual column HRGC-ECD and/or GC-MS;

3) increased accuracy due to individual congener analysis and quantitation methods; and

4) decreased detection limits and lower method blanks in newer (post-1978) analytical lab buildings.

Comparison of results from labs using different quantitation methods or standards is difficult because of these issues[19, 132].

## 1.2.7 Methods of Polychlorinated Biphenyl Disposal and Destruction

As mentioned repeatedly, PCBs are stable compounds and do not degrade easily. They may undergo destruction under certain conditions using chemical, thermal and biological processes. This section briefly describes disposal and destruction methods that have been suggested for PCB material in the US. A document compiling the commercially available PCB destruction capacity worldwide has recently been prepared by the United Nations Environmental Programme (UNEP) [133].

## Landfills

In the US, PCB contaminated material, including solidified liquids, containing less than 500 ppm (by weight) PCB may be disposed of in TSCA permitted landfills. PCB transformers may be disposed of in TSCA permitted landfills after draining and flushing [134]. In Canada, solids with <50 ppm may be disposed of in a permitted landfill. It should be emphasized the PCB are still present and may undergo volatilization from the landfill [83]. A recent UNEP document [35] suggests that the rate of emissions from intact material in a landfill should be "low," but no data was provided to back up this statement. However, in the author's opinion, the available data suggest that this is not in fact the case.

## Solidification/Stabilization

Solidification techniques harden or encapsulate to prevent leaching; stabilization techniques involve chemical bonding of additives to prevent leaching. Both ex-situ and in-situ processes have been developed. Most applications have involved solidification or stabilization prior to landfill disposal. Although the potential for PCB leaching or volatilization is reduced, it is not eliminated because the PCB molecule is not destroyed.

## Soil Washing/Solvent Extraction

Soil washing and solvent extraction are similar processes utilizing water or other solvents, additives, and mechanical agitation (soil washing), or a solvent with or without mechanical agitation. Solvent extraction is typically used for surfaces, equipment, and soils. Soil washing, as the name suggests, is principally limited to soils. The PCB-laden residue produced must then undergo further treatment for destruction or disposal. Many of the solvents that are used present their own health, safety, and environmental concerns.

## Chemical Destruction

A variety of chemical destruction methods have been developed. Currently, the TSCA-permitted options include, chemical dehalogenation (using sodium- or potassium-based processes, including hydroxides and various glycol ethers) and an ammonia-based destruction method. In the late 1980's and early 1990's, a large amount of in-service and out of service electrical equipment was decontaminated using chemical dehalogenation processes. Chemical dehalogenation processes have also been applied to soils.

## Incineration

Incineration of PCBs has destroyed a significant amount of PCB contaminated material in the US. In the US, PCB incinerators are strictly regulated under TSCA and must achieve > 99.9999% destruction and removal efficiency (DRE). Destruction and Removal Efficiency is calculated using Equation (10):

$$DRE = \left[ \frac{mass\ in - mass\ out}{mass\ in} \right] * 100 \qquad (10)$$

In order to ensure that the 99.9999% DRE is achieved, incinerators must typically operate at temperatures of > 1200°C, with combustion gas residence time of > 2 seconds and with good mixing. The exhaust gases must also be treated to remove particulates and acid gases. In Canada, regulations for PCB incineration have typically followed US regulations. There are currently two companies with permitted commercial PCB incinerators in the US at several sites, and only one facility in Canada.

Incineration is often a controversial topic. A major focus of environmental groups has been on possible formation of PCDD/DF by-products. However, incineration has also received much more regulatory scrutiny and technical and commercial testing and utilization than any other PCB destruction method. Incineration is considered the "gold standard" for destruction methods [135]. Repeated testing on incinerator stack gases has shown that a properly run incinerator can easily achieve the 99.999% DRE. Conversely, improper incineration of PCB (prior to the present stringent regulations) resulted in significant contamination of a facility with PCB, PCDD and PCDF [108].

Other Thermal Destruction Technologies

Pyrolysis (high temperatures under reducing conditions) has been utilized for treatment of PCB liquids. Vitrification involves treatment at high temperature (>3000°F) to produce a glass as a final product. Neither process has been used significantly on a commercial basis. Destruction of PCB using thermal reduction with hydrogen gas has also been used on a limited commercial scale. The use of hydrogen gas presents its own health and safety concerns. Molten metal baths have also been advocated for PCB destruction. However, the company that was using this technology has declared bankruptcy. Many of the difficulties encountered by these alternative thermal destruction methods have surrounded material feed handling.

Thermal desorption

Thermal desorption volatilizes PCB from soils or other matrices using temperatures sufficient to raise the vapor pressure without changing the chemical structure of the PCB molecule. The PCB off gas must be collected and treated further. Potential formation of PCDD/DF is a problem with this technology.

## Photolysis, Radiolysis, Ultrasonic

Photochemical dechlorination or destruction methods have been developed for PCBs; however, success on a commercial scale has been limited. Radiolysis using $\gamma$ rays can destroy PCB molecules. Ultrasonic degradation is also possible.

## Biological Degradation

PCBs can be degraded under aerobic (oxidizing) or anaerobic (reducing) environments by microbes. However, the significance of this process under real world conditions appears to be limited [136]. It appears that no PCB sites have been cleaned up using this technology.

A more detailed review of PCB destruction technologies can be found in Erickson [19] and two Environment Canada publications, which were co-authored by the author of this thesis [137, 138]. As mentioned above, a report on worldwide PCB destruction capacity was recently published by UNEP [133]. The USEPA's Office of Pollution Prevention and Toxic Substances [34] has a PCB home page (http://www.epa.gov/opptintr/pcb/) with additional information on US permitted disposal technologies.

## 1.3     Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

### 1.3.1     General

Polychlorinated dibenzo-p-dioxins (Figure 2) and PCDF (Figure 3) are two groups of tricyclic, planar heterocyclic aromatic compounds. There are 75 possible PCDD congeners with mono- to octa-chlorination possible. There are 135 possible mono- to octa-chlorinated PCDF congeners. Only 7 PCDD and 10 of the PCDF congeners are substituted in the 2,3,7,8 positions. The 2,3,7,8- compounds are of concern because of the general pattern of toxicity that they share (see Section 1.4 below).

The most well studied of the PCDD and PCDF is the 2, 3, 7, 8-tetrachlorodibenzon-p-dioxin (2,3,7,8-TCDD or TeCDD), which is often called simply (and misleadingly) "dioxin". This molecule is shown in Figure 5.
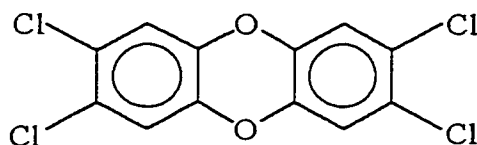


Figure 5.      Structure of 2, 3, 7, 8-tetrachlorodibenzon-p-dioxin (2378-TCDD).

In general, PCDD and PCDF are nonpolar, poorly water soluble, lipophilic chemicals that do not degrade readily [139]. The physical/chemical properties of each congener vary according to the degree and position of chlorine substitution.

In the environment, PCDD and PCDF usually occur as complex mixtures. For risk assessment purposes, analysis results are often reported on a toxic equivalency (TEQ) basis. Under the TEQ methodology, only the 2,3,7,8 substituted isomers are reported using toxic equivalency factors (TEF) relative to 2,3,7,8-TCDD. Additional details on PCDD, PCDF and PCB toxicity and TEQ can be found in Section 1.4.

## 1.3.2 Sources of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

Unlike PCBs, PCDD and PCDF were never intentionally produced, but, rather, were produced as unwanted byproducts in a variety of processes [139-141]. In 1994, the USEPA published a draft reassessment of the sources, environmental behavior, human exposure, and effects of PCDD/DF [142]. Recently, an updated inventory of sources in the US has been produced [141]. Although it has been speculated [143] that PCDD can be formed by natural processes, such as volcanoes and forest fires [144] this has not been demonstrated conclusively [139, 145]. In the last 4 years, ball clay deposits in the southeast US have been identified where elevated PCDD/DF concentrations exist, apparently from natural sources [146, 147]. In any event, anthropogenic emissions have been orders of magnitude larger. This conclusion is based on the observation that, in general, PCDD and PCDF fluxes, as measured by deposition in dated lake sediments, started to increase in the 1930's, continued

to increase through the 1940's and 1950's, reached a sharp peak in the 1960's and early 1970's, and have decreased since that time [139].

The major identified sources of PCDD and PCDF in the environment can be classified as follows: combustion sources, metals smelting, refining and processing, chemical manufacturing, biological and photochemical processes, and reservoir sources. These sources are discussed briefly below.

Combustion sources

Polychlorinated dibenzo-p-dioxins and PCDF are formed in ultra trace amounts in most combustion processes. These processes include waste incineration (Hazardous Waste Incinerators (HWI), Municipal Solid Waste Incinerators (MSWI), Medical/Biomedical Waste Incinerators (BWI), Sewage Sludge Incinerators (SSI), etc.); the burning of various fossil fuels (such as coal, wood petroleum products); other combustion processes (such as cement kilns and mobile sources); and poorly controlled combustion sources (such as building fires, burn pits and backyard burning) [148]. Polychlorinated dibenzo-p-dioxins and PCDF emissions from most waste incineration processes have received considerable regulatory and public interest group attention and have been reduced significantly in recent years. As much as 85% of atmospheric deposition of PCDD/DF in the Great Lakes air shed has been attributed to waste incineration [149].

Improper thermal treatment of PCB materials, such as fires, explosions, electrical arcs, or thermal vaporization in electrical (transformers, capacitors, etc.) and other equipment (e.g., heat transfer oils and hydraulic oils) can be a major pathway to PCDD and PCDF

formation [19, 150]. More often, it is the levels of PCDF that are formed that are of concern in PCB thermal accidents. The mechanism of this reaction has been studied in detail [19].

The PCDF formation reaction involves the intramolecular incorporation of oxygen between the two aromatic rings of a PCB molecule (Figure 6). Up to 7% conversion of PCBs to the much more toxic PCDF has been observed. The PCDD formation reaction is primarily considered to occur via the intermolecular coupling of two chlorophenol molecules (Figure 7). The chlorophenols are often formed from the oxidation of chlorobenzenes present in commercial Askarel mixtures. The PCDD formation reaction is much less efficient (typically 1/1000 or less of PCDF amounts) since it involves intermolecular reactions.

Some authors argue for the so called "de novo" synthesis of PCDD and PCDF in combustion processes [151]. However, most studies have shown that conditions in which precursor concentrations are low will result in very low levels of PCDD and PCDF. When Karasek added isotopically labeled CB (Chlorobenzenes) and CP (Chlorophenol) to fly ash and heated it in air, detectable amounts of isotopically labeled PCDD were formed. However, when isotopically labeled carbon was used to test the de novo synthesis hypothesis, no isotopically labeled PCDD was found [152]. Ethylene can form PCDD and PCDF under certain circumstances; however, this reaction is occurring via CB and CP intermediates [153].

A Friedel-Crafts type chlorination of dibenzo-p-dioxin and dibenzofuran has also been suggested as a possible mechanism of formation for PCDD/DF.
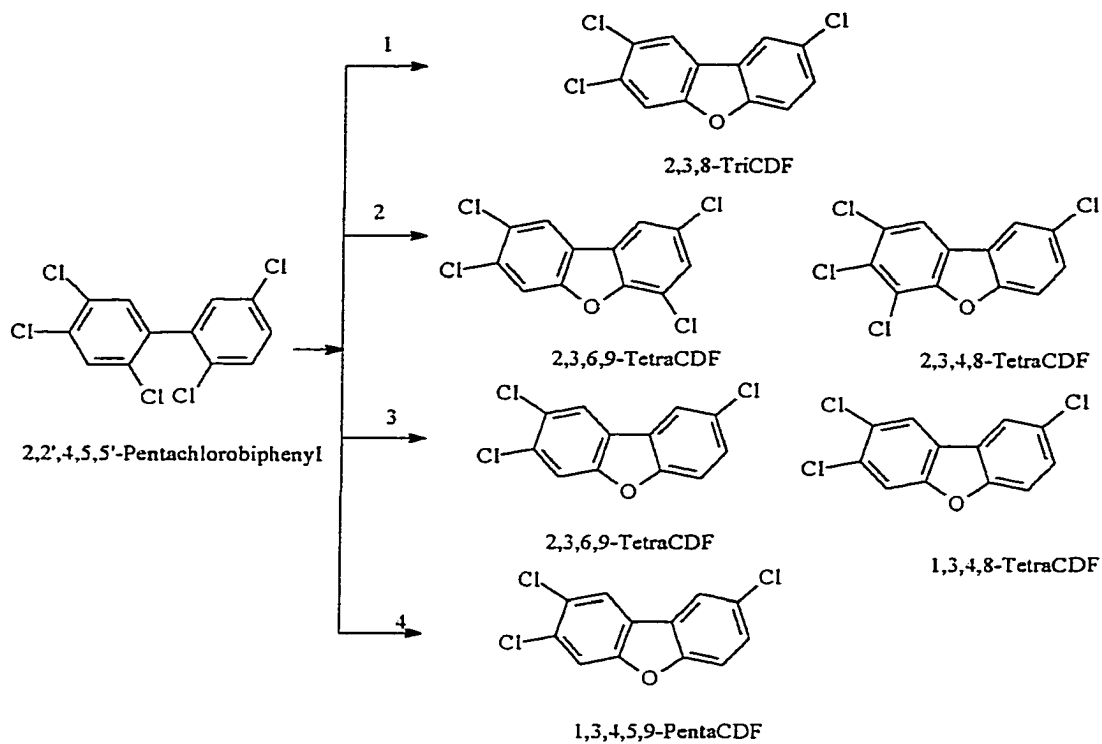
Figure 6.    Formation of polychlorinated dibenzofurans from polychlorinated biphenyls. Adapted from [19].
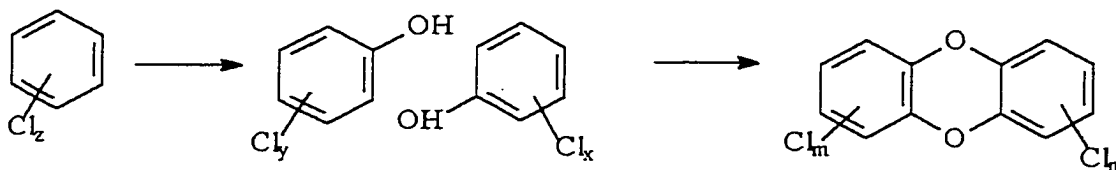


Figure 7.    Generalized    formation    of    polychlorinated    dibenzo-p-dioxins    from chlorobenzenes and chlorophenols.

Metals Smelting. Refining Sources and Processing Sources

PCDD and PCDF can be formed during various types of primary and secondary metals operation including iron ore sintering, steel production, and scrap metal recovery [141, 154].

There has been a huge amount of controversy regarding the importance of chlorine concentrations in feed and PCDD/DF emissions from thermal processes. Numerous studies have been performed on this issue, some of which indicated very little, if any, correlation [155], and others that indicate there is a correlation [156]. Greenpeace (www.greeenpeace.org) has been a very public proponent of chlorine (especially polyvinyl chlorine (PVC)) feed control as a dioxin emission strategy [157]. In many instances, the debate has been more political than technical in nature. In any event, the formation of PCDD/DF in combustion sources is obviously a very complex, multi-factorial process [158, 159].

In theory at least, it appears that any thermal process in which carbon, oxygen, hydrogen and chlorine atoms are present at elevated temperatures can produce trace amounts of PCDD and PCDF. Whether or not actual production of PCDD and PCDF will occur is dependent on a number of factors including, concentration of precursors, temperature, residence time, oxygen content, mixing conditions, amount of particulate, presence of catalytic metals, and surface activity of particulates.

<u>Chemical Manufacturing</u>

Polychlorinated dibenzo-p-dioxins and PCDF have been found as by-products from the manufacture of chlorine bleached wood pulp, chlorinated phenols (such as pentachlorophenol (PCP)), PCB, phenoxy herbicides (e.g., 2,4,5-T), and chlorinated aliphatic compounds (e.g., ethylene dichloride). In the past, this has been a major source of emissions. More recently emissions from these types of processes have been significantly reduced.

<u>Biological and Photochemical Processes</u>

Recent studies have indicated that PCDD and PCDF can be formed under certain environment conditions (e.g., composting) from the actions of microorganisms on chlorinated phenolic compounds. Similarly, PCDD and PCDF have been reported to be formed during photolysis of highly chlorinated phenols.

<u>Reservoir Sources</u>

Reservoirs are materials that contain previously released PCDD and PCDF and have the potential for recirculation of these compounds into the environment. Potential reservoirs for PCDD and PCDF in the environment include soils, sediments, vegetation and PCP-treated wood. Recently, PCDD/DF have been discovered in ball clay deposits [146].

<u>PCDD/DF Profiles</u>

Different PCDD/DF sources may be characterized by different patterns of congeners in their air emissions. These patterns may be used as "fingerprints" of sources. These fingerprints may be seen in environmental samples if degradation and weathering do not lead to changes in the congener patterns. The patterns of PCDD/DF found in air, soil, sediments,

and vegetation may be similar near local source(s). Biota samples tend to be concentrated in 2,3,7,8-substituted compounds and may not reflect the source patterns as closely.

A more detailed review of PCDD/DF sources in the US can be found in a recent report by USEPA [141]. Recent reviews on PCDD/DF in the environment have been written by Baker and Hites [160], Alcock and Jones [139] and Duarte-Davidson, et al. [140].

### 1.3.3 Atmospheric Transport of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

Atmospheric deposition of PCDD/DF by long-range transport has been observed and is a principal pathway for many areas. For example, PCDD/DF has been found in dated sediment cores obtained from a lake on Isle Royale in Lake Superior, a location that can only receive PCDD/DF from the atmosphere [161]. Lohman and Jones have reviewed atmospheric deposition processes for PCDD/DF [162]. Dann [125] has summarized the estimates for source contributions to observed ambient air PCDD/DF concentrations in Canada. This data is provided as Table VIII below.

Concentrations of PCDD/DF observed in air are usually much lower than PCB concentrations, typically by 3 orders of magnitude or more. The ambient air concentrations that have been observed for PCDD/DF are summarized in Table IX. Caution must be used when comparing reported results due to differences in analysis and reporting methodology. However, it is clear that a pattern similar to PCB emerges, that is, Local Source Influenced > Urban> Rural>> Remote sites. The PCDD/DF congener and homolog profiles observed in

sources and ambient environment are often different [163]. Urban air samples more closely resemble source profiles. The main compound seen in ambient air samples is the octachloro-dibenzo-p-dioxin (OCDD). Reasons offered for this difference in congener patterns are preferential degradation of the lower chlorinated homologs and or preferential deposition processes.

Both dry particle deposition and wet deposition are important atmospheric deposition processes [164]. Koestner and Hites found that dry and wet deposition fluxes were similar for Bloomington and Indianapolis, IN [163].

The PCDD/DF can undergo vapor/particle (V/P) partitioning. The two key factors controlling this partitioning are temperature and the compound's vapor pressure [165]. Atmospheric PCDD/DF with six or fewer chlorines exist mainly in the gas phase [166].

Brzuzy and Hites examined the global atmospheric deposition (wet and dry) of PCDD/DF and noted that the deposition's total seems to exceed estimated emissions into the environment [167]. This may be as a result of a) only a limited number of sources being known; or b) total atmospheric deposition is overestimated. Research on this issue is continuing.

**TABLE VIII**

ESTIMATED PERCENTAGE CONTRIBUTION OF SOURCES TO AIR
CONCENTRATIONS OF POLYCHLORINATED DIBENZO-P-
DIOXINS/DIBENZOFURANS TOXIC EQUIVALENCY

| Source Class | Cohen, et al. Great Lakes Region [149]<br><br>1993<br>(% of Total) | Thomas & Spiro, US [168]<br><br>1989<br>(% of Total) | CEPA-FPAC Inventory, Canada [169]<br><br>1990<br>(% of Total) |
|---|---|---|---|
| Medical Waste Incinerators | 53 | 11 | 3.6 |
| Municipal Waste Incinerators | 24 | 48 | 35 |
| Hazardous Waste Incinerators | 6 | 3.2 | <0.1 |
| Apartment Incinerators and Open Garbage Burning | -- | 19 | -- |
| Tepee Burners for Municipal Waste | -- | -- | 20 |
| Secondary Copper Smelters | 5 | -- | -- |
| Wood Combustion | 3.2 | 4.3 | 4.8 |
| Iron Sintering Plants | 2.8 | -- | 12 |
| Coal Combustion | 2.6 | <0.1· | <0.1 |
| Cement Kilns | 2.1 | -- | 6.2 |
| Heavy Duty Diesel Vehicles | 1.5 | <0.1 | 2.3 |
| Sewage Sludge Incinerators | 0.3 | 1.1 | <0.1 |
| Secondary Copper Refiners | 0.1 | 3.2 | -- |
| Gasoline Motor Vehicles | 0.1 | <0.1 | -- |
| Dioxin Contaminated Chemical Application | -- | 2.1 | -- |
| Forest & Agricultural Burning | -- | 4.6 | -- |
| Electric Arc Furnaces | -- | -- | 2.5 |
| Pulp & paper Boilers | -- | -- | 2.8 |
| Industrial Fuel Combustion | ---- | -- | 4.6 |
| Other | -- | 1 | 5.7 |

**Note:**

CEPA-FPAC = Canadian Environmental Protection Act-Federal/Provincial Advisory Panel

Reference: Dann [125]

## TABLE IX

POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN CONCENTRATIONS
OBSERVED IN AMBIENT AIR

| Type of Sample | Location | Concentration | Units | Comment | Reference |
|---|---|---|---|---|---|
| Air, Canada 1987-1997 | Various locations | 38 (mean, rural) 459 (mean, urban) 3.9 (MIN.) 1950 (MAX.) | I-TEQ. $fg/m^3$ | >500 samples from Remote, rural, urban and source impacted areas | [125] |
| Air, Ontario | Dorset | 3.3 (annual average) | I-TEQ $fg/m^3$ | Rural remote | [149], [170] |
| Air, Sweden | Stockholm City center Suburb Rural Coastal, Remote | 1.4 24 13 4.4 2.6 | Total $pg/m^3$ Nordic-TEQ, $fg/m^3$ | | [171] |
| Air, Germany | Hamburg | 3 | $pg/m^3$ Total PCDD/DF | Urban | [172] |
| Air, Hamburg · Germany | Industrial Site Car tunnel | 28 29 | $pg/m^3$ Total PCDD/DF | Local Source influenced | |
| Air, US | Bloomington, IN | 1-4 | $pg/m^3$ Total PCDD/DF | Urban | [165] |
| Air, US | Indianapolis Bloomington Trout Lake | 5.1 1.88 0.42 | $pg/m^3$ Total PCDD/DF | Urban Urban-Rural Rural-Remote | [164] |
| Air, Antarctica | McMurdo Station | 1.1 4.53 0.49 <0.1-0.3 | $pg/m^3$ Total PCDD/DF | Station influenced Station influenced - no incinerator operations Background | [173] |

Atmospheric Reactions of PCDD/PCDF

There is relatively little data on the stability and reactions of PCDD/DF in the atmosphere [174]. What work has been done indicates that these reactions can take place in both the gas and particle phase. Work by Pennise and Kamens [174] has shown that there are many factors that contribute to PCDD/DF reactivity in the atmosphere.

Reaction with the OH radical is expected to be a major reaction pathway for PCDD/DF. Atmospheric residence times of ~8 hours to 3 days have been estimated for the TeCDF and TeCDD compounds [114, 166]. Their conclusion was that the hydroxyl radical reaction could be significant for gas phase PCDD/DF and that other particle phase reactions could also occur (see below).

Pennise and Kamens [174] found that particle phase photolytic degradation was important depending upon the conditions used. They also observed that the lower chlorinated compounds were more susceptible than the higher chlorinated compounds. USEPA [141] has reviewed the literature on PCDD/DF photolysis and noted that this appeared to be an environmentally significant reaction.

Therefore, it appears that the enrichment of environmental samples in the higher chlorinated congeners may be due, at least in part, to both preferential deposition and preferential degradation of the lower chlorinated PCDD/DF.

## 1.3.4 Sampling and Analysis of Polychlorinated Dibenzo-p-dioxins/Polychlorinated Dibenzofurans

Air sampling for PCDD/DF is normally carried out using Hi-Vol air samplers with a filter, followed by a solid sorbent, usually PUF, XAD-2 or a combination of the two. The particle and vapor phases are operationally defined in the same manner as for PCB, that is, the material collected on the filter and sorbent respectively. However, in warmer temperatures, the particle phase may be underestimated due "blow-off" from the filter. Although the air sampling method is very similar to that used for PCBs, much larger volumes and/or sampling times are used due the significantly lower concentrations of PCDD/DF observed in ambient air. The difference in replicates of the Hi-Vol air sampling method used by EC has been shown to be < 20% [125].

The analysis of PCDD/DF at the trace levels typically present in the environment is much more of a challenge than PCB analysis. Numerous procedures have been developed for sampling, sample extraction, and analysis. These different methods have not all been equivalent. In addition, over the last 10 years analysis with high-resolution mass spectrometers (HRMS) has become prevalent, allowing the analysis of femtogram (some researchers suggest we should call it "phantom grams") quantities in environmental samples. Significant interlaboratory variations in quantitation may still occur [139]. Most methods of PCDD/DF analysis have resulted in the reporting of the tetra- through octa-chlorinated PCDD/DF. Jones, et al. [175] recently reported on the analysis of the mono-, di- and tri-chloro PCDD and PCDF. Although these compounds are less toxic than their 2,3,7,8

analogues, they appear to occur at significantly higher concentrations, which might make them useful as tracer or surrogate compounds.

## 1.4 Toxicity of Polychlorinated Biphenyls and Polychlorinated Dibenzo-p-dioxins/Dibenzofurans

The primary reason for concern about PCB and PCDD/DF in the environment is their bioaccumulation, observed toxicity in animal tests, and concern about their possible effects in humans.

### 1.4.1 Polychlorinated Dibenzo-p-dioxin/Dibenzofuran Toxicity

Most of the concerns about health effects of PCDD and PCDF have centered on 2,3,7,8-TCDD (Figure 5). The chemical 2,3,7,8-TCDD has been extensively studied, especially on animals over the last 30-35 years [176]. This chemical is one of the most lethal ever tested on animals, in terms of its lethal dose for 50% ($LD_{50}$), for guinea pigs (emphasis added) according to the National Toxicology Program (NTP) [177]. A variety of toxicological properties have been observed for TCDD in animal testing including lethality, teratogenicity, carcinogenicity [178], and endocrine disruption. A more extensive review can be found in Klassen [179]. However, the data for TCDD carcinogenicity in humans is less clear [180].

Much higher doses of PCDD and PCDF have been received in occupational exposures, compared to environmental exposures. Historically, few if any, acute exposure

symptoms have been noted as markers of exposure. The most widely recognized marker of a high level exposure is the appearance of chloracne, a skin disorder [181, 182].

Recently several epidemiological studies have been published which address some of the weaknesses of previous studies [181, 183-185]. In all of these studies, in contrast to many of the earlier studies, there is exposure information available from the measurement of TCDD in serum. These studies have generally shown a slightly increased incidence of all and/or certain types of cancers consistent with the animal studies.

On the basis of these, and other studies, the International Agency for Research on Cancer (IARC) in February, 1997, classified TCDD as having sufficient evidence to be considered carcinogenic to humans [186]; other PCDD and PCDF are classified as probable human carcinogens.

The exact mechanism of carcinogenicity for TCDD is not fully understood. The primary mode of action for TCDD-induced carcinogenesis is generally thought to be due to its capacity to *promote* tumors rather than *initiate* them (emphasis added) (Hays, 1997). The mechanism by which initiation is thought to occur involved TCDD binding to the arylhydrocarbon hydroxylase (Ah) receptor, which then mediates cell division [179].

## 1.4.2 Toxicity of Polychlorinated Biphenyls

Animal testing of individual and mixtures of PCBs has shown PCBs can cause cancer [187]. However, the degree of toxicity and the nature of effects on humans continue to be

debated. In humans, very little acute toxicity has been observed, except for dermal effects such as chloracne, which is also seen for TCDD. Much of the early work on PCB toxicity for humans is subject to question because of concerns about the type and purity of PCB used. In many of the high level exposures, such as the Yusho and Yucheng episodes, significant amounts of other chemicals, such as the more toxic PCDD and PCDF, were also present [19, 188]. Occupational studies also show increases in cancer mortalities for workers exposed to PCB [187]. Polychlorinated biphenyls are classified by USEPA as a probable human carcinogen. More recently, concerns have focused on their endocrine disrupting potential [7] and other, subtler effects, such as neurological development in children of mothers who eat significant amounts of fish from the Great Lakes [189].

PCBs with mono-ortho or non-ortho chlorine substitution (approximately 14-19 of them) can assume a co-planar shape similar to 2,3,7,8-TCDD. These PCB molecules can elicit TCDD-like responses on *in vitro* Ah receptor systems. There is substantial evidence, but not proof, that PCDDs, PCDFs, and these PCBs are all eliciting their response through the same mechanism, involving the Ah receptor [19].

The other approximately 190 PCB molecules most probably elicit their toxicity in a different manner from the dioxin-like PCB. In general, PCBs appear to be much less toxic than the structurally related PCDD and PCDF. It should be pointed out, however, that PCB concentrations are much higher than PCDD/DF in ambient air. Therefore, the PCB can contribute a significant fraction of the TEQ in a sample.

### 1.4.3   Toxic Equivalency Factors

All of these chemicals (PCB, PCDD, and PCDF) usually occur as complex mixtures in the environment. The concept of Toxic Equivalency (TEQ) has been introduced in an attempt to take into account the different amounts and toxicities of these chemicals. Toxic Equivalency Factors (TEF) are applied to express the chemicals' toxic responses relative to 2,3,7,8-TCDD. Thus, the TEF of 2,3,7,8 is assigned a TEF of 1. The TEFs that are presently used by USEPA for the 2,3,7,8 substituted PCDD and PCDF are shown in Table X. These TEFs, which have been accepted by international convention, are also called International TEF or I-TEF. The biological basis for the TEF values for PCDD/DF has been reviewed by Safe [188].

Subsequent to the development of TEF for PCDD/DF, TEFs have also been developed for PCBs. The TEFs developed for 13 PCBs and used by the World Health Organization (WHO) are shown in Table XI [190]. Alternative TEFs for these, and additional PCBs, have also been proposed [191].

Calculating the TEQ of a mixture involves multiplying the concentration of the individual congener by the individual TEF. The sum of the TEQ of the individual congeners is the TEQ of the mixture. A number of research groups have applied the TEQ to environmental samples. In many cases, it has been found that the PCB fraction contributes much more to the total TEQ than the PCDD and PCDF.

**TABLE X**

TOXIC EQUIVALENCY FACTORS FOR DIOXINS AND FURANS

| IUPAC No. | | Compound | TEF |
|---|---|---|---|
| | | Mono, Di & Tri-CDD | 0 |
| | 1 | 2,3,7,8-TeCDD | 1 |
| | | Other TCDD | 0 |
| | 2 | 1, 2, 3, 7, 8-PeCDD | 0.5 |
| | | Other PeCDD | 0 |
| | 3 | 1,2,3,4,7,8-HxCDD | 0.1 |
| | 4 | 1,2,3,6,7,8-HxCDD | 0.1 |
| | 5 | 1,2,3,7,8,9-HxCDD | 0.1 |
| | | Other HxCDD | 0 |
| | 6 | 1,2,3,4,6,7,8-HPCDD | 0.01 |
| | | Other HPCDD | 0 |
| | 7 | OCDD | 0.001 |
| | | Mono-, Di-, and Tri-CDF | 0 |
| | 8 | 2,3,7,8-TeCDF | 0.1 |
| | | Other TCDF | 0 |
| | 9 | 1,2,3,7,8-PeCDF | 0.05 |
| | 10 | 2,3,4,7,8-PeCDF | 0.5 |
| | | Other PeCDF | |
| | 11 | 1,2,3,4,7,8-HxCDF | 0.1 |
| | 12 | 1,2,3,6,7,8-HxCDF | 0.1 |
| | 13 | 2,3,4;6,7,8-HxCDF | 0.1 |
| | 14 | 1,2,3,7,8,9-HxCF | 0.1 |
| | | Other HxCDF | 0 |
| | 15 | 1,2,3, 4,6,7,8-HPCDF | 0.01 |
| | 16 | 1,2,3,4,7,8,9-HPCDF | 0.01 |
| | | Other HPCDF | 0 |
| | 17 | OCDF | 0.001 |

Reference: USEPA, 1998 [141]

**TABLE XI**

TOXIC EQUIVALENCY FACTORS FOR DIOXIN-LIKE
POLYCHLORINATED BIPHENYLS

| BZ No. | Compound | TEF |
|---|---|---|
| 77 | 3,3',4,4'-tetra | 0.0005 |
| 105 | 2,3,3'4,4'-penta | 0.0001 |
| 114 | 3,3,4,4',5-penta | 0.0005 |
| 118 | 2,3'4,4',5-penta | 0.0001 |
| 123 | 2',3,4,4',5-penta | 0.0001 |
| 126 | 3,3',4,4',5-penta | 0.1 |
| 156 | 2,3,3',4,4'-penta | 0.0005 |
| 157 | 2,3,3',4,4',5-hexa | 0.0005 |
| 167 | 2,3',4,4',5,5'-hexa | 0.00001 |
| 169 | 3,3',4,4',5,5'-hexa | 0.01 |
| 170 | 2,2',3,3',4,4',5-hepta | 0.0001 |
| 180 | 2,2',3,4,4',5,5'-hepta | 0.00001 |
| 189 | 2,3,3',4,4',5,5'-hepta | 0.0001 |

Reference: Ahlborg, et al. [190]

## 1.5 Air Quality Monitoring and Modeling in Vicinity of Suspected Sources

Polychlorinated biphenyls, PCDDs, and PCDFs can be found in the atmosphere from local sources, general urban activities, from LRT and combinations of all these. A number of techniques can be used in attempts to identify the relative contributions of these different source(s) in ambient air samples. The first type involves air monitoring; the second type involves air modeling; and the third type is a combination of the two.

### 1.5.1 General

Ambient air monitoring has been used to identify the impact of local sources [55, 83, 84, 164, 192] and to study long-range transport [56-58, 103]. Besides proper sampling equipment, it is important to collect meteorological information during the sampling period. After sample analysis results are available, they can be combined with the meteorological information to assist in interpretation. One method of analyzing this type of data that has proven effective is to develop pollutant roses to graphically present the effect of wind direction and air pollutant concentration. Mukerjee [192] has used this technique to demonstrate the impact of a biomedical waste incinerator (BWI) on an air sampling location. A clear relationship between types of pollutants, concentrations and wind direction were developed. Wind speed is another meteorological factor to be considered. Wania, et al. [102] found that an inverse relationship existed between PCB concentrations and wind speed [102]. The reason for this was postulated to be that the more stable conditions resulted in lower mixing and increased air pollutant transfer from soil to air.

## 1.5.2　Air Modeling

Ambient air measurements provide a "snapshot" in time of ambient air concentrations. Atmospheric models are used to supplement air-monitoring data, in conjunction with air monitoring data, and sometimes in the absence of air monitoring data. The atmospheric transport models can be separated into two types, physical and mathematical. Physical models normally involve a small-scale representation of an area. For example, an industrial facility and neighborhood scale model are placed in a wind tunnel. Mathematical models essentially involve the use of computers to simulate atmospheric movement or processes. Some examples of mathematical models used include air dispersion models (ADM), receptor models, and trajectory models.

## 1.5.2.1 Air Dispersion Models

Dispersion models may involve simulate changes in the chemical composition of a given air parcel as it is advected in the atmosphere (Lagrangian models), while others may describe concentrations on an array of fixed computational cells (Eulerian models)[37, 42]. A simple Eulerian box model has been used to describe the partitioning of SVOC between the atmosphere and the Earth's surface [193]. Gaussian dispersion models are most often used for local (km scale) modeling [194]. Gaussian dispersion models may use Lagrangian or Eulerian techniques [37]. One of the most commonly used Gaussian dispersion model is USEPA's Industrial Source Complex (ISC) model. Books by Turner [194] and Beychok [195] provide backgrounds on the basics of air dispersion modeling.

### 1.5.2.2 Receptor Models

Receptor modeling is a *statistical mathematical model* [37] as opposed to the air dispersion models, which are based upon a description of *atmospheric physical and chemical processes*. Receptor models are based upon measured mass concentrations of species of interest and the use of appropriate mass balances. While air dispersion models compute the dispersion pattern for the pollutant(s) of interest of a source to a receptor as the product of emission rate multiplied by a dispersion factor, receptor models start with *observed* air concentrations(s) at a receptor site and attempt to apportion the observed concentrations among several source types based upon source composition profiles. Zannetti has shown a mathematical notation for the concentration $c_{ik}$ of the species (compound or element) 'i' in the k-th sample at a monitoring location can be written as Equation (11):

$$c_{i,k} = \sum_{j=1}^{p} a_{ij} D_{jk} E_{jk} \quad i = 1,2,3....n \qquad (11)$$

where:

p sources are assumed to contribute to $c_{ik}$ (concentration of compound or element (i = 1...n) at a specific site, for sample k

$a_{ij}$ is the fractional amount of component i in the emission from the j th source

$D_{jk}$ is the atmospheric dispersion term

$E_{jk}$ is the emission rate

and $D_{jk} E_{jk} = S_{jk}$ the total contribution of the source j to the k - th sample in the receptor

In dispersion models, the terms $a_{ij}$, $D_{jk}$ and $E_{jk}$ are assumed to be known and the $c_{ik}$ term is calculated. For receptor models, the $c_{ik}$ and source $a_{ij}$ are measured and $D_{jk}$ and $E_{jk}$ are computed (as $S_{jk}$).

Receptor models can be classified into 4 categories: [196]:

- Chemical mass balance (CMB);

- Multivariate models (including factor analysis [197]);

- Microscopic models; and

- Source-receptor models.

Only the CMB model will be discussed further here.

The CMB model combines both chemical and physical characteristics of particles or gases measured at sources and receptors. Source apportionment is used to identify relative contributions of different source "fingerprints" to the observed ambient air patterns without reconstructing the dispersion pattern. The CMB models are based upon the solving of the general equation for receptor modeling (Equation 12) for the $S_{j.}$ term:

$$c_i = \sum_{j=1}^{p} a_{ij} S_{j,k} \quad i = 1,2,3....n \quad (12)$$

where:

$c_i$ = concentration of compound or element $(i = 1...n)$ at a specific site

aij = source composition (element or compound i for source j)

$S_j$ = concentration contribution of material from source j

This gives n equations, if p $\leq$n, the $S_j$ term can be determined by solving the series of linear equations. Henry [196] has discussed methods for calculating the $S_j$ term.

Mukerjee [192] used a combination of wind sector analysis, air dispersion modeling, and receptor modeling to study the impact of a BWI at a semi-rural location in NC. They were able to show that the observed air concentrations could be explained to a large degree in

terms of whether or not the BWI was in operation with or without an Air Pollution Control System (APCS) and when it was shut down.


### 1.5.2.3 Trajectory Models

Trajectory models are a reverse application of the models generally used to predict weather patterns. They use stored meteorological data to predict where air masses may have come from during sampling events based primarily on pressure differences, wind speeds, and temperatures. Hoff, et al. [198] was able to explain elevated toxaphene levels measured in Ontario by examining air trajectories. They were able to see that air parcels that had passed over the Midwest during the summer months had much higher concentrations. Their hypothesis was that volatilization of toxaphene from soils was occurring. Oehme used trajectory models to explain elevated levels of certain air pollutants in terms of the arrival of air masses from industrialized areas in continental Europe [64]. Trajectory models have been developed by the US National Oceanographic and Atmospheric Administration (NOAA) (HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT)) [199], EC [200, 201], and others [200, 201]. The HYSPLIT and EC trajectory models are the newest version of a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations. Because of their complexity, trajectory models require tremendous amounts of data and computing power and in the past were often run on supercomputers. With the increase in computing power, they can now be run using desktop computers or remotely using the Internet.

## 1.5.2.4 Fugacity Models

The concept of fugacity was first proposed by Lewis [202] to explain the partitioning of chemicals between compartments based upon their relative tendency (or urge) to flee various situations. The fleeing tendency (or fugacity) of a compound will be related to its chemical potential. In a multi-component system, the fugacities of the different components will drive the chemical movement between components in an attempt to reach the values they would have at equilibrium. The application of the fugacity approach to environmental modeling has been advanced by the work of Mackay [203] and others [40, 129, 204].

The simplest form of fugacity modeling for environmental systems is a Level I model in which equilibrium is assumed between the media compartments. In Level I calculations, the chemical mass in the system is assumed to be conserved. In Level II fugacity modeling, equilibrium is still assumed, but environmental loss and degradation mechanisms are now included in the model. A Level III model simulation describes a situation that is one step more complex and realistic than the Level II model.

*"Unlike the Level II model, equilibrium between media is not assumed and, in general, each medium is at a different fugacity. A mass balance applies not only to the system as a whole, but also to each compartment. Mass balances are calculated for the four bulk media of air (gas + aerosol), water (solution + suspended sediment + biota), soil, (solids + air + water), and sediment (solids + pore water). Equilibrium exists within, but not between media. The model cannot treat ionizing or speciating substances."* (from http://www.trentu.ca/academic/aminss/envmodel/VBL3.html)

The Level III model gives a more realistic description of a chemical's fate including the important degradation and advection losses and the intermedia transport processes. Mackay and Patterson [205] have developed a Level III fugacity model for movement of PCBs in the Lake Ontario region.

# 2. PROJECT BACKGROUND

## 2.1 Phase 1 and 2 Site Activities: Smithville, Canada

The Chemical Waste Management Ltd. (CWML) facility that is the subject of this thesis (not to be confused with Chemical Waste Management Inc., a subsidiary of Waste Management Inc.) was located on a 2 acre (0.8 hectare (ha)) site in Smithville (SM or SV), Ontario (CWML site, SV Site or Site). Smithville is a small rural community approximately sixty miles from Toronto, Ontario, Canada. (Figures 8 and 9). From 1978 to 1982, the Site was operated as a transfer facility for PCB material (primarily electrical) being transported from Canada to the US for disposal. With the closure of the US border to PCB imports (in 1982), the Site's role changed to a storage role because there was no Canadian disposal facility for this material. In 1985, the Site's permit was amended to allow only storage of the current material on-site, and CWML effectively ceased operations at the Site (Figures 10 and 11 depict the CWML site at the time operations ceased). Later in 1985, testing by the MOE revealed on-site, and unexpected off-site, contamination with PCB and other organics. Responding to public concerns, MOE took over management of the Site in the fall of 1985. In late 1985, Proctor and Redfern Ltd. (P&R) was retained by MOE to supervise an emergency cleanup of the Site and develop a long term cleanup plan. In 1985, the CWML site contained a large number of transformers, ballasts capacitors, and miscellaneous equipment, as well as significant quantities of high-level PCB liquids and an estimated 4,000 $m^2$ of contaminated soil. Estimated quantities of materials are shown in Table XII. The cleanup of the Site was performed in three phases: (1) consolidation of materials into secure storage (Phase 1) awaiting final destruction; (2) disposal off-site of materials that were contaminated with low levels of PCBs (Phase 2), and (3) final destruction of the wastes from the Site (Phase 3).
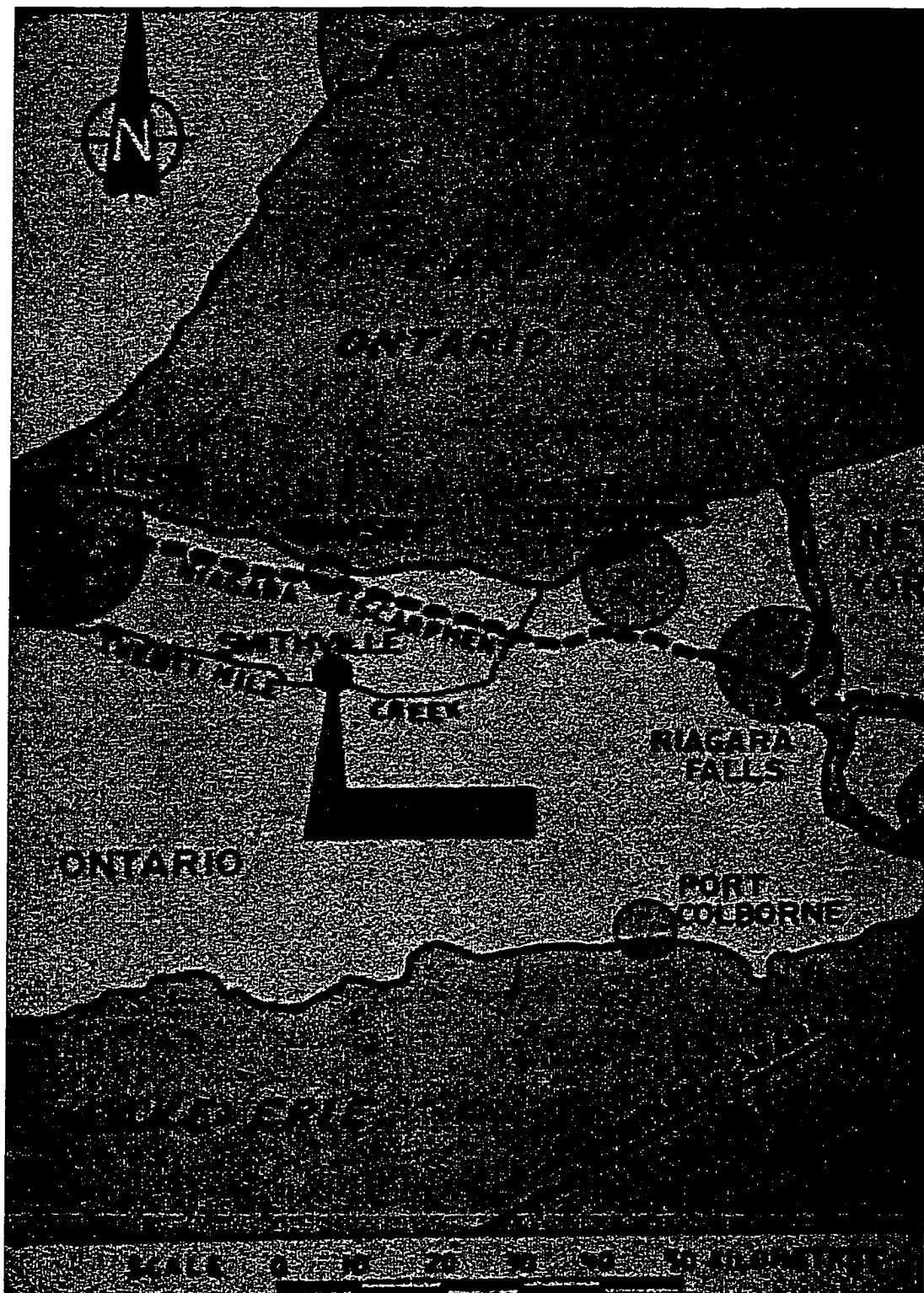
Figure 8.    Smithville general location map.
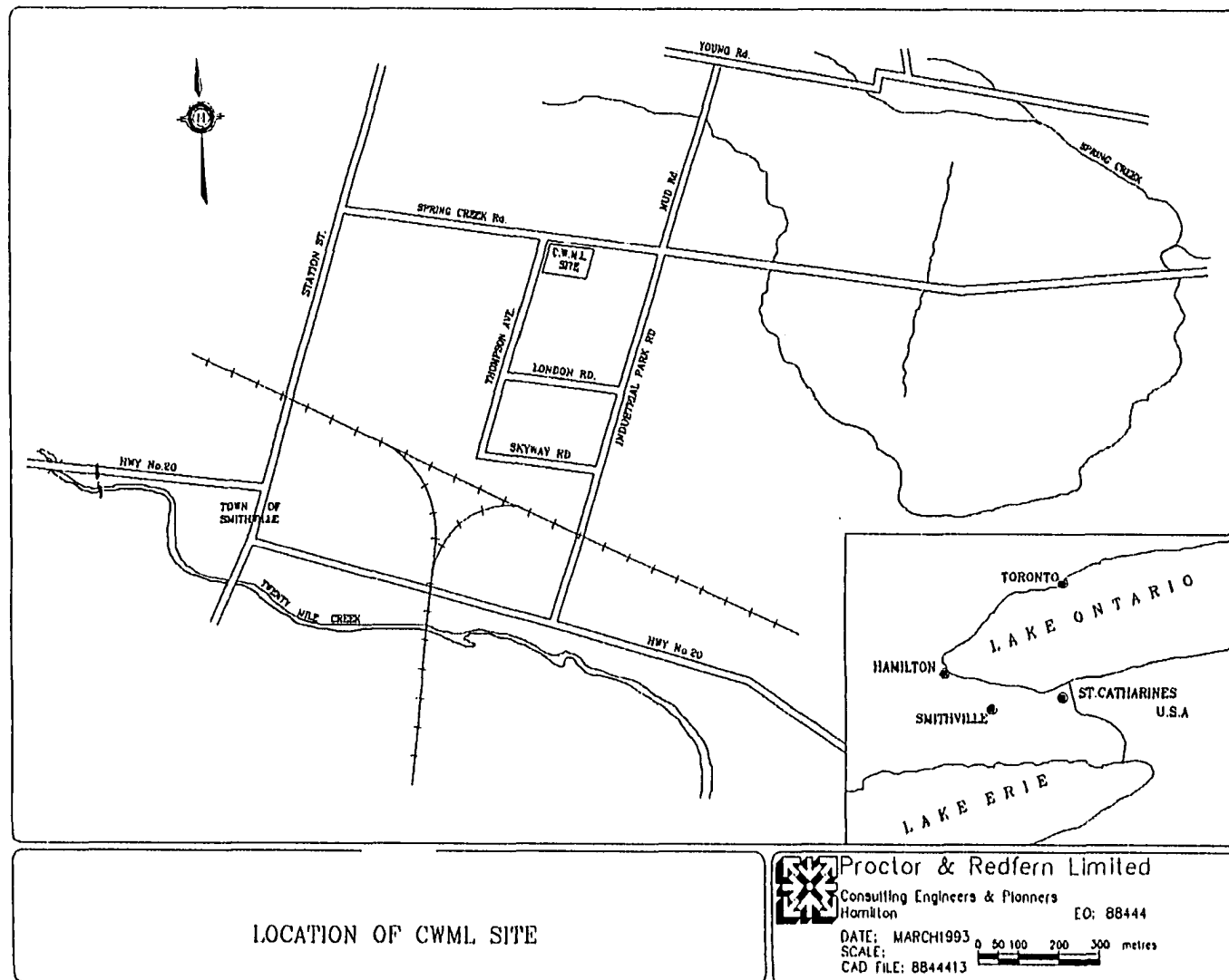
Figure 9.    Local map showing Chemical Waste Management Limited Smithville Site location.
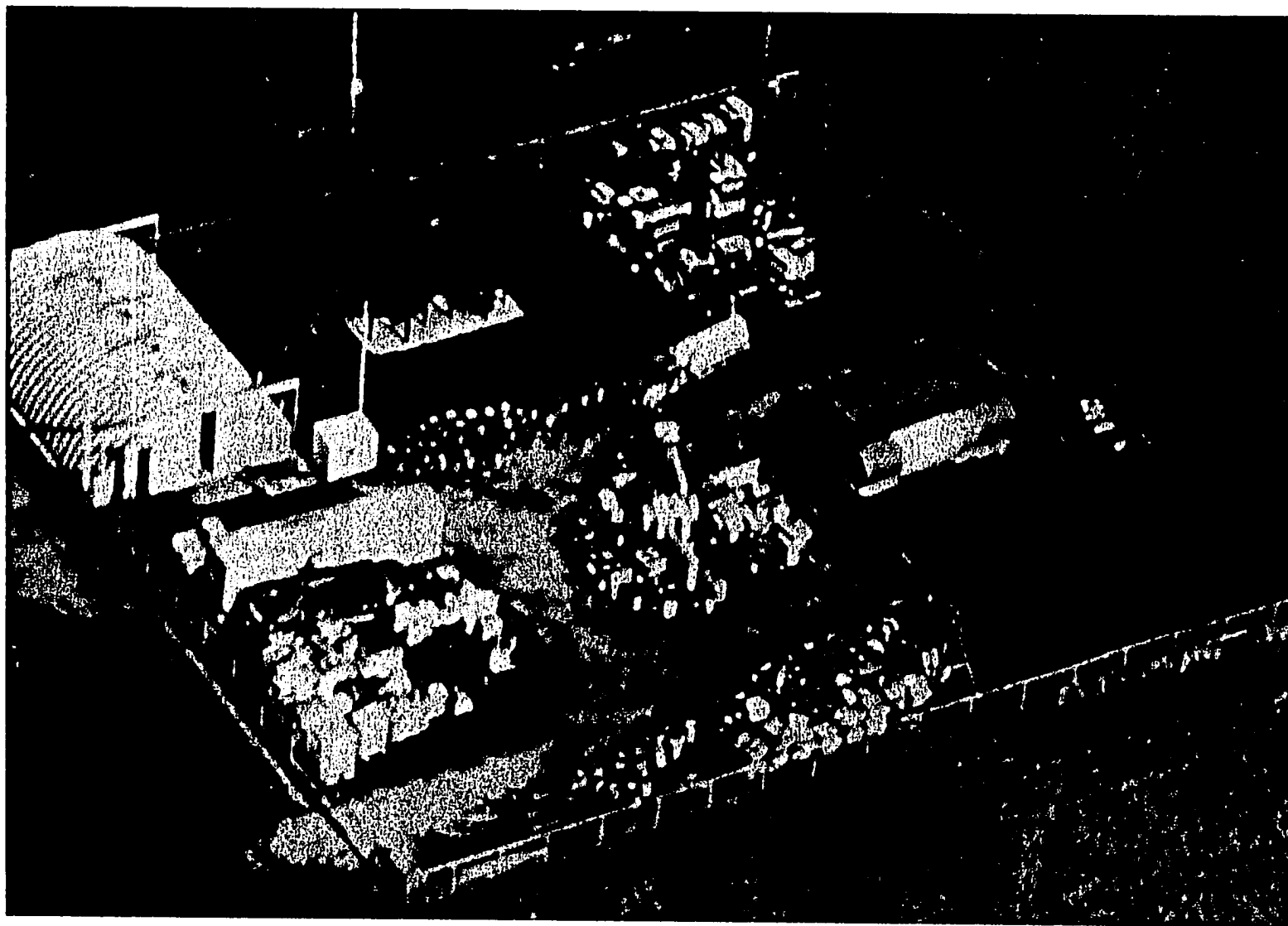
Figure 10.    Photograph of Chemical Waste Management Limited Smithville Site in 1985.

SPRING CREEK ROAD

THOMPSON AVENUE

INDUSTRIAL PARK ROAD

DUCKSET HUT

ORIGINAL COMPOUND

LAGOON

CWML SITE

WOODLOT

LAYOUT OF THE CWML SITE

Proctor & Redfern Limited
Consulting Engineers & Planners
Hamilton                    E.O 88444
DATE: MARCH 1993
SCALE:
CAD FILE: 8844423
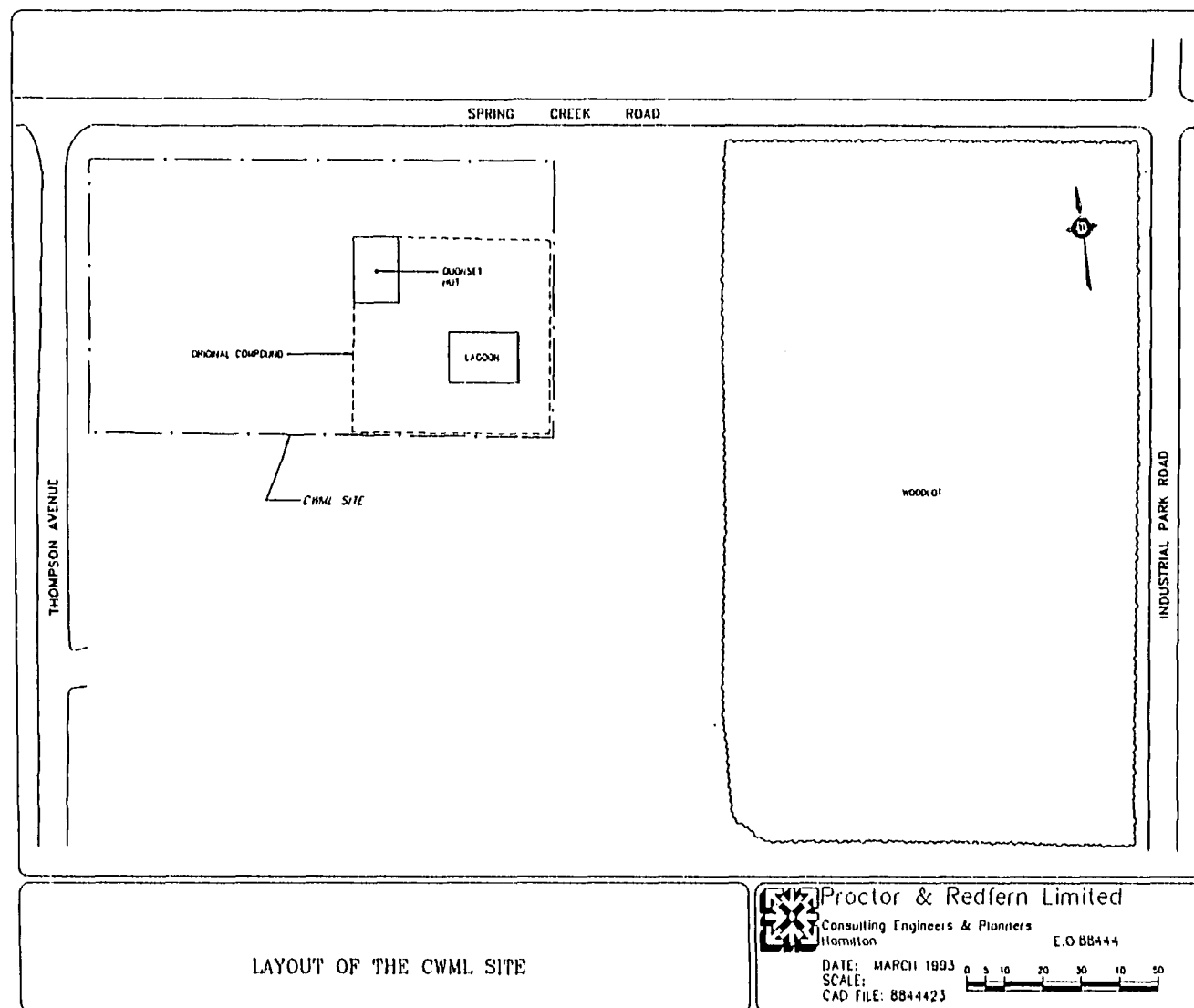
Figure 11.    Layout of Chemical Waste Management Limited Smithville Site - November, 1985.

**TABLE XII**

ESTIMATED QUANTITIES OF MATERIAL
FOR PHASE 3 (INCINERATION) CLEANUP

| Description of Wastes | Original Quantity | Additional Quantity | Total Quantity Treated |
|---|---|---|---|
| Soil | 4,000 m$^3$ | 4,200 m$^3$ | 8200 m$^3$ |
| Liquids (high concentration oils) | 160,000 L | 0 | 160,000 L |
| Drums of Wastes | 1,055 | 194 | 1,149 |
| Vaults | 70 | 0 | 70 |
| Transformers | 82 | 1 | 83 |
| Concrete Rock | 0 | 537 t | 537 t |
| Liquid Laboratory Waste | 0 | 48 L | 48 L |
| Miscellaneous Solid Waste | 0 | 8.7 | 8.7 t |
| Miscellaneous Equipment | 18 | 0 | 18 |

Reference:  Proctor and Redfern Ltd. [91].

The Phase 1 and 2 cleanups for the CWML SV Site have been described previously [206, 207]. During the course of the Phase 1 and 2 cleanup contamination of the aquifer and bedrock under the site with chlorinated solvents and PCBs was discovered and is subject to ongoing ground water treatment and evaluation of remedial options as Phase 4 of the cleanup.

## 2.2    Phase 3 (Incineration) Cleanup

After an extensive review of the available remedial technologies, on-site incineration was chosen as the best option for the work to be carried out for the Phase 3 Cleanup. The ENSCO Environmental Inc. (ENCSCO) MWP-2000 incinerator was selected after submittal of proposals in 1988. After extensive public hearings [208] (as required by Ontario's Regulation 148/86 for mobile PCB destruction technologies), Certificates of Approval (C of A) were issued to ENSCO in August 1990 for the Site [209], the System [210], and Air [211]. ENSCO began mobilization to the Site in October 1990. Site preparation and incineration assembly was completed by the end of January, 1991. The Site plan for the Phase 3 (Incineration) Cleanup project is shown in Figure 12. Emissions from the incinerator were heavily regulated under various regulations, as well as a result of the intense public scrutiny for this first use of mobile incineration for PCB destruction in Ontario. The project environmental standards are summarized in Table XIII and Ministry of Labor (MOL) standards for on-site workers are summarized in Table XIV. Table XV provides a summary of the incinerator operating conditions from the various C of As issued for the Phase 3 Cleanup.

**TABLE XIII**

SUMMARY OF ENVIRONMENTAL STANDARDS FOR PROJECT

| Matrix | Parameter | Limit | Source |
|---|---|---|---|
| Soil | PCB | 1 ppm (total) cleanup or excavation criterion | Contract Specifications |
| Incinerated Soils | PCB | 0.5 ppm (total) | Federal PCB Destruction Reg. |
| | PCDD/DF | 1 ng/kg (TEQ) | Federal PCB Destruction Reg. |
| | Leachate | various | O.Reg. 309 |
| Liquids | PCB | 1ppb (ug/L)(total) | Adopted by Niagara Region |
| | PCDD/DF | 0.25 ng/L (per congener) | O.Reg. 148/86 |
| | Sewer Use Bylaw | various | Niagara Sewer Use By-Law |
| Surfaces | PCB | 1000 ug/m$^2$ (surfaces not to be encapsulated) | C of A (Site), Board Decision |
| | | 10,000 ug/m$^2$ (surfaces to be encapsulated) | C of A (Site), Board Decision |
| Stack Emissions | PCB | 1 mg/kg feed | O.Reg 148/86 |
| | DRE | 99.9999% | O.Reg 148/86 |
| | PCDD/DF | 12 ng/m$^3$ | Project Guideline (Federal PCB Destruction Reg.) |
| | Total Particulates | 50 mg/dscm (MAX.) | C of As (System, Air) |
| | HCl | 40 mg/dscm (ave.) | C of As (System, Air) |
| | Combustion Efficiency | 99% Removal, or 50 mg/dscm | C of As (System, Air) |
| | Total Hydrocarbons | 99.9%, or 50 mg/dscm | C of As (System, Air) |

**TABLE XIII (Concluded)**

SUMMARY OF ENVIRONMENTAL STANDARDS FOR PROJECT

| Matrix | Parameter | Limit | Source |
|---|---|---|---|
| Ambient Air Point of Impingement (POI) | PCB | 450 ng/m³ (1/2 hr ave.)<br>150 ng/m³ (24 hr ave.) | O.Reg. 148/86<br>MOE Guideline |
| | PCDD/DF (I-TEQ) | 20 pg/m³<br>(24 to 72 hr ave.)## | Guideline* |
| | PCDD/DF (totals) | 450 pg/m³ (1/2 hr ave.)**<br>150 pg/m³ (24 hr ave.)<br>130 pg/m³ (48 hr ave.) | O. Reg. 148/86<br>MOE Guideline<br>MOE Guideline |
| | Inorganics | various | C of As (System, Air), Board Decision, O.Reg. 308 |
| | VOC | various | C of As (System, Air), Board Decision, O.Reg. 308 |
| Air From Carbon Filtration Unit (CFU) | PCB at vent | Refer to Table XV | C of A (Air: CFU), O.Reg. 654/86 |
| | PCB at POI | 450 ng/m³ (1/2 hr ave.) | C of A (Air: CFU) |
| | VOC at exhaust (PID) | >50 ppm PCB analysis<br>>100 ppm change Carbon | C of A (Air: CFU)<br>C of A (Air: CFU) |
| | VOC at exhaust (VOC sampler) | various | C of A (Air: CFU), O.Reg. 308 |
| Incinerator Operating Conditions | Various Operating Conditions | Refer to Table XV | C of A (System) |

**Notes:**

| | |
|---|---|
| dscm | dry standard cubic meter normalized to 11% $O_2$ and 25° C |
| ## | Guideline adopted for the PCB Incineration Project at Goose Bay, Labrador, TEQ calculated using TEF values in Federal Mobile PCB Regulation |
| * | MOE Guideline referenced in O. Reg. 148/86 |
| ** | Calculated by $\Sigma PCDD + 1/50(\Sigma PCDF)$ |
| O. Reg. | Ontario Regulation |
| POI | Point of Impingement |
| DRE | Destruction and Removal Efficiency |
| PID | Photoionization Detector |
| AAQC | Ambient Air Quality Criteria |

**TABLE XIV**

ON-SITE WORKER EXPOSURE STANDARDS

| Parameter | TWAEV (mg/m$^3$) | STEV (mg/m$^3$) | CEV (mg/m$^3$) |
|---|---|---|---|
| PCB | 0.05 | | |
| CB | 345 | | |
| 1,2-dichlorobenzene (1,2-DCB) | | | 300 |
| 1,4-dichlorobenzene (1,4-DCB) | 450 | | |
| 1,2,4-trichlorobenzene (1,2,4-TCB) | | | 37 |
| Trichlorethylene (TCE) | 268 | 1075 | |
| Copper dust | 1 | | |

**Notes:**

TWAEV     Time Weighted Exposure Value

STEV     Short Term Exposure Value

CEV     Ceiling Exposure Value

**TABLE XV**

INCINERATOR OPERATING CONDITIONS FOR THE PHASE 3 CLEANUP

| Items | C of A Conditions | | |
|---|---|---|---|
| 1. Operating Conditions for Soil Incineration | - MIN. 1° chamber temperature 788°C<br>- MIN. 2° chamber temperature 1177°C<br>- MIN. gas residence time in $2^2$ chamber 1.8 sec<br>- MIN. $O_2$ in stack gas 3%<br>- MAX. CO in stack gas 50 ppm<br>- Stack gas condensate pH ≥2.7<br>- Ejector scrubber water recirculation flowrate @ 133 L/min.<br>- MIN. kiln negative pressure –0.05" water | | |
| 2. Operating Conditions for Materials Other than Soils | - MIN. 1° chamber temperature 788°C<br>- MIN. $2^2$ chamber temperature 1200° C<br>- MIN. gas residence time in 2° chamber 2 sec<br>- MIN. $O_2$ in stack gas 4%<br>- MAX. CO concentration in stack gas 50 ppm<br>- Stack gas condensate pH> or = 2.7<br>- Ejector scrubber recirculation rate @ 133 L/min.<br>- MIN. kiln negative pressure –0.05" water | | |
| 3. Use of Thermal Relief Vent (TRV) | - Water level in steam drum falls to 0%<br>- Temperature of flue gas at inlet to packed tower exceeds 149°C<br>- Negative pressure in kiln cannot be maintained<br>- Orderly shut down of incinerator | | |
| 4. Automatic Waste Feed Shut-Off (AWFSO) | - When operating conditions in 1 or 2 above are not achieved or maintained<br>- Loss of flame in 2° chamber<br>- Water level in steam drum falls to 25% of full scale<br>- Temperature of flue gas at packed tower entrance exceeds 107°C<br>- Failure of equipment that monitors operating conditions<br>- Solids feed weigh hopper fails and cannot be fixed within 15 minutes<br>- Mass flow meter for liquid fails | | |
| 5. APCS Parameters | - MAX. total particulate emissions of 50 mg/dscm<br>- Average total particulates emission of 40 mg/dscm<br>- MIN. HCl removal efficiency of 99% or MAX. HCl emissions of 50 mg/dscm<br>- MAX. Total Hydrocarbon (THC) content of 50 ppm (methane equivalent) | | |
| 6. Limitations on Wastes | Matrix | MAX. feedrate (kg/h) | %PCB by weight |
| | Soil &Concrete | 8418 | <0.58 |
| | Soil & Concrete | 1818 | >0.58-<1.9 |
| | Transformer cores, capacitors, metals | 341 | 1≤, ≤40 |
| | Other solid materials | 341 | 1≤, ≤40 |
| | Metals or other solids | 909 | ≤1 |
| | Pumpable sludges | 132 | ≤23 |
| | Liquid organic wastes | 959 | ≤42 |
| | Wastewater | 1136 | ≤1 |
| | *- No materials other than clean supplementary fuel could be burned while incinerating soil* | *- MAX. PCB loading 409 kg/h* | *- PCB wastes could be blended* |
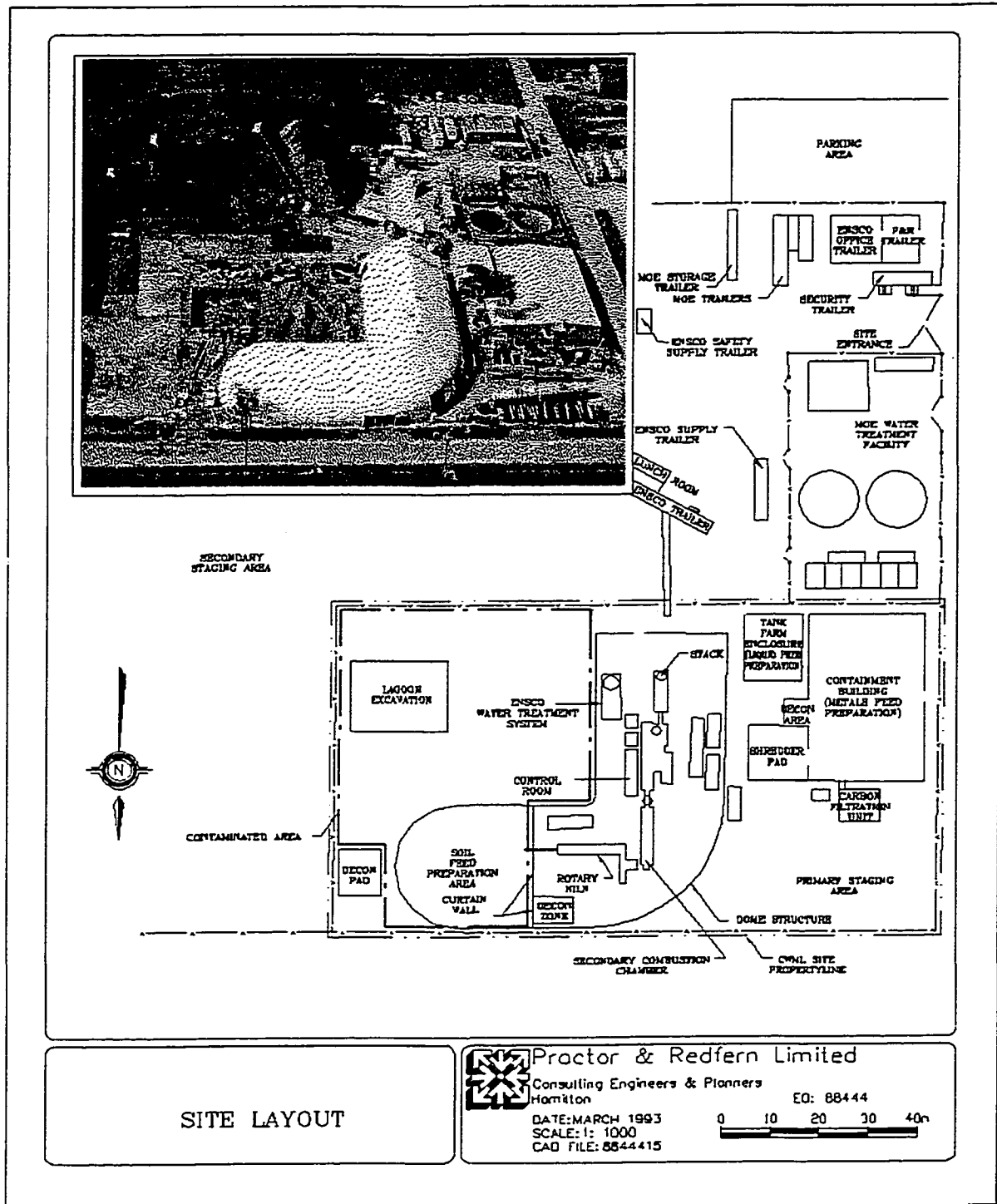
Figure 12.    Site plan for Phase 3 (incineration) cleanup project.

## 2.2.1  Description of ENSCO Modular Waste Processor-2000 Incineration System

The ENSCO MWP-2000 (flow schematic in Figure 13) is a transportable incinerator with a rotary kiln design. Prior to the CWML SV project, the MWP-2000 had been used at several sites to clean up solids and liquids contaminated with PCDD/PCDF, PCB, and other organics.

The MWP-2000 could handle solids (soils, sediments, crushed rock, shredded equipment, such as transformers and capacitors, etc.), sludges, and liquids. Solids were fed into the primary (1°) combustion chamber (PCC), which was a refractory lined rotary kiln, through a conveyor belt and screw auger (soils mostly), or through a drop chute (shredded material). The feed rate of these materials was controlled based on system performance monitoring and the heat content of the feed. The PCC's main purpose was to volatilize organic contaminants into the gaseous state. This was achieved by having a kiln residence time of approximately 30 minutes and a normal operating temperature of >800 °C. Liquids and sludges could also be fed into the kiln through a sludge lance. The off-gases from the PCC were passed through two cyclones to remove particulates before entering the secondary (2°) combustion chamber (SCC).

The off-gases from the PCC and any liquids being treated were exposed to the "three T's" of good combustion (time, temperature, and turbulence) in the SCC. A minimum gas residence time of 1.8-2 seconds, temperature of 1200 °C or greater, and tangential air-flow were maintained in the SCC. Under these conditions, testing has shown that a DRE of >99.9999% can be achieved for organics [212].

The off-gases from the SCC were passed through a waste heat boiler, and then were quickly cooled to <150° C in the quench elbow. At this point, some removal of the HCl was also achieved by using a caustic spray. A temperature lower than 150°C had to be achieved in the quench elbow because the remainder of the APCS is made of fiberglass reinforced plastic (FRP). In cases where cooling water was lost, the system was equipped with a thermal relief vent (TRV) that could open to protect the APCS. In cases where the TRV was opened, an interlock took place, which would result in activation of the automatic waste feed shutoff (AWFSO). The next stage in the APCS was the packed tower. The packed tower resulted in the major removal of acid gases and a further lowering of the gas temperature. Caustic water was sprayed into the top of the tower and trickled down the packing. The packing was designed to maximize the surface contact area so that maximum acid gas removal was achieved.

FEED PREPARATION     INCINERATION     ENERGY RECOVERY     AIR POLLUTION CONTROL SYSTEM (APCS)

PCB WASTE OILS (FROM TANK FORM)

FEED LINE

PREPARED SOLID FEED MATERIALS

ROTARY KILN

TREATED SOLIDS

EMERGENCY THERMAL RELIEF VENT (TRV)

SECONDARY COMBUSTION CHAMBER

GAS FLOW

WASTE HEAT BOILER

BOILER BLOWDOWN

QUENCH

ATOMIZED STEAM

WATER

PACKED TOWER

JET EJECTOR

EJECTOR SCRUBBER

DEMISTER

STACK

EFFLUENT NEUTRALIZATION TANK (ENT)

CAUSTIC & WATER

SCRUBBER JUMP

SETTLING TANK

SCHEMATIC OF INCINERATION FACILITY

Figure 13.     Schematic of ENSCO Environmental Inc. Modular Waste Processor-2000 incinerator.

After passing through the packed tower, the gases entered the steamjet eductor. The steamjet eductor on the ENSCO MWP-2000 system was one of its innovative features; it both removed most particulates, including submicron particulates [213], and acted in place of an induction fan. A major advantage of the use of the steamjet eductor was that in case of a power failure, the unit could still operate (usually 15-20 minutes), maintaining negative pressure in the system until the steam pressure from the waste heat boiler falls below a point where the TRV had to be opened. (In all cases where a power failure occurred, an AWFSO took place.) After passing through the steamjet eductor flight tube, the gases entered a demister to remove water droplets and then exited the stack. The stack gases were continuously monitored by the continuous emissions monitoring (CEM) system for CO, carbon dioxide ($CO_2$) and oxygen ($O_2$). In the event that the CO rose above the preset limit, $O_2$ fell below the regulation limit, or the $CO/CO_2$ ratio (combustion efficiency (CE)) fell below the regulation limit, an AWFSO would take place (see Table XV).

The entire incineration operation process was controlled from the control room that was set up in a trailer located alongside the incinerator (see Figure 12). In the control room, a computerized Data Acquisition System (DAS) monitored and controlled the operations. The computer was programmed to control numerous parameters, such as temperature, feed rate, gas residence time, emissions limits, and other key parameters. The DAS initiated AWFSOs if a parameter exceeded a permissible limit.

Most of the wastes required some preparation prior to incineration. Figure 14 provides schematic summaries of the feed preparation methods for the different types of

wastes: soil, metal, miscellaneous debris, and PCB oils. Fugitive emissions from the feed preparations were one area of concern for this project.

PCB incineration operations at the CWML SV Site began on February 8, 1991 and were completed on December 17, 1992. This was considerably longer than originally planned, primarily due to difficulties in feeding materials, especially soils with high moisture, increased system maintenance requirements, and the larger than originally anticipated amounts of materials that were incinerated (see Table XII).

SOIL
PROCESSOR

ROTARY KILN

SOIL FED
INTO INCINERATOR
BY A CONVEYOR BELT

PCB
CONTAMINATED
SOIL

SOILS WERE WEIGHED

SOIL AND ROCK
SIZED
INTO SMALLER
PIECES

SHREDDER

ROTARY KILN

PCB CONTAMINATED
METAL AND
MISCELLANEOUS
DEBRIS

SHREDDED INTO
SMALLER PIECES

MISCELLANEOUS DEBRIS, SHREDDED METAL,
AND RESIDUAL PCB OILS
AND SLUDGES PACKAGED INTO
5 GALLON PLASTIC BUCKETS
AND SECURED TO PALLETS

BUCKETS HAND
FED INTO
INCINERATOR
DROP BOX

TANK
FARM

DOUBLE PIPED
FEED LINE

SECONDARY
COMBUSTION
CHAMBER

IF PCB CONCENTRATION
EXCEEDED 42% PCB
DILUTED WITH DIESEL FUEL
OR
LOWER PCB CONTAMINATED OILS

PCB CONTAMINATED
OIL STORED IN TANK FARM

TESTED FOR
PCB CONCENTRATION

PCB OIL FED INTO SECONDARY
CHAMBER THROUGH DOUBLE PIPED
FEED LINE

PREPARATION OF FEED MATERIALS

Proctor & Redfern Limited

Consulting Engineers & Planners
Hamilton                          E.O. 88444

DATE: MARCH 1993
SCALE: N.T.S.
CAD FILE: 8844419

Figure 14.    Preparation of feed materials for incineration.

## 2.3    <u>Environmental Monitoring Program for Phase 3</u>

An extensive Environmental Monitoring Program (EMP) was implemented for the Phase 3 Cleanup to monitor any changes in the environment during incineration and to verify the incinerator's compliance with ENSCO's C of As and other regulations or guidelines. The EMP was developed by P&R in association with various branches of MOE and was conducted mainly by P&R and MOE. The EMP had four (4) major elements:

(1)     Process Monitoring: Operating conditions of the incinerator were continuously recorded through ENSCO's DAS computer to monitor compliance with the C of A's.

(2)     Effluent Monitoring: Prior to removal/discharge from the CWML SV Site, all effluent streams (i.e., waste water, incinerated materials, and stack emissions) required analytical testing and approval.

(3)     Decontamination Monitoring: Prior to leaving the CWML SV Site, or contaminated areas within the Site, equipment required surface sampling and analysis for PCBs to ensure that proper decontamination had been performed. Decontamination monitoring was also performed for the on-site buildings once all the PCB wastes had been removed.

(4)     Ambient Environment Monitoring: Ambient air, soil, water, and sediments were analyzed for a variety of parameters (see Table XIII).

The EMP is summarized in Table XVI on the next page. Table XVII summarizes the EMP responsibilities for P&R, MOE and ENSCO.

# TABLE XVI

## SUMMARY OF THE PHASE 3 CLEANUP ENVIRONMENTAL MONITORING PROGRAM

| Sample Type | During Operations | | | | | | | | | | | | | Post Operations | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PCB | CB | PCDD/ PCDF | VOC | INORG | PCB | CB | CP | PCDD/ PCDF | VOC | PAH | INORG | OTHER | PCB | CB | PCDD/ PCDF | VOC | INORG |
| **Process Monitoring** | | | | | | | | | | | | | ♦♦ | | | | | |
| **Effluent Monitoring** | | | | | | | | | | | | | | | | | | |
| Incinerated Materials | | | | | | X | | | X (regularly) | | | | O. Reg. 309 (regularly) | | | | | |
| Feed Sampling | | | | | | X ♦♦♦♦ | | | | | | | | | | | | |
| Brine | | | | | | X | | | | | | | APCS Scan | | | | | |
| Waste Water | | | | | | X | | | X | X | | X | ♦♦♦ | | | | | |
| Stack | | | | | | X | X | X | X | X | X | X | HCl Total Particulates | | | | | |
| **Decontamination** | | | | | | X | | | | | | | | | | | | |
| **Ambient Environmental Monitoring** | | | | | | | | | | | | | | | | | | |
| Ambient Air | X | X | X | X | X ♦ | X | X | | X | X | | X ♦ | | X | X | X | X | X ♦ |
| Ambient Water & Sediment | X | | X | | | | | | | | | | | X | | X | | |
| Ambient Soil | X | | X | | X | | | | | | | | | X | | X | | X |
| Noise | | | | | X other | | | | | | | | X | | | | | |

NOTES:

| | |
|---|---|
| INORG | Inorganics |
| VOC | Volatile Organic Compounds |
| O. REG. 309 | Ontario Regulation 309 Leachate Test for Metals |
| APCS Scan | On-site Air Pollution Control System, can include: pH, conductivity, chloride, and specific gravity |
| ♦ | Inorganics analyzed in the ambient air are the following: cadmium, copper, chromium, iron, manganese, nickel, lead, vanadium, total particulates |
| ♦♦ | Continuous Monitoring of Temperature, CO, $CO_2$, $O_2$, Nitrous Oxides (NOx) |
| ♦♦♦ | Regional Municipality of Niagara Sewer Use By-Law No. 3308-83 |
| ♦♦♦♦ | P&R sampled feed materials once per week during first two weeks of incineration, then as required for Quality Assurance/Quality Control (QA/QC) purposes |

During the incineration of PCB materials, the operating conditions of the incinerator were continuously monitored through ENSCO's DAS. Each week, P&R received computer printouts of the previous week's process parameters. Deviations outside of the C of A operating conditions were identified in printouts and written explanations for the deviations were provided by ENSCO. All reports were then submitted to the MOE. Inspections were made on a regular daily basis into the control room to monitor the equipment and operations.

All discharges from the incineration system and other solids and liquids produced from Site activities were tested prior to release and disposed according to the test results. Release forms were used to document the removal of material from the Site. Incinerated soil treated to below acceptable levels was placed back on-site for eventual reuse as cover material.

Over 13,400 environmental samples were taken during the course of the Phase 3 Cleanup. The break down of samples found in the Smithville Environmental Monitoring database is as follows:

| Sample Type or Description (Description Code) | Quantity |
| --- | --- |
| Ash (AS) or Incinerated solids | 4182 |
| Soils (SL) | 2656 |
| Swabs (SW) | 652 |
| Liquid (LQ) | 1815 |
| Process Water (PW) | 62 |
| Oils (OL) | 15 |
| Quality Control (QC) samples. | 30 |
| Most QC samples were coded for the corresponding environmental sample. | |
| Ambient Air (AA, AR or AM) | 4003 |
| *TOTAL* | *13415* |

It must be noted that not all samples were analyzed and some samples were combined. For example, although more than 4000 air samples were taken, there are actually only about 2800 results.

The laboratories that were used and the matrices that they analyzed are shown in Table XVIII. Additional information on the Environmental Monitoring program can be found in the Environmental Monitoring Manual (EMM) and the Phase 3 Final Report documents that were prepared for the project [91, 214].

# TABLE XVIII

## LABORATORIES FOR PHASE 3 ENVIRONMENTAL MONITORING PROGRAM

| Sample Type | Parameters Analyzed | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | PCB/CB | CP | PCDD/PCDF | VOC | PAH | INORG METALS | O. REG. 309 | SEWER USE/ APSC SCAN |
| Stack Test: | | | | | | | | |
| Series I | EPL performed all analyses | | | | | | -- | -- |
| Series II | EPL performed all analyses | | | | | | -- | -- |
| Series III | Zenon performed all analyses | | | | | | -- | -- |
| Series IV | Zenon performed all analyses | | | | | | -- | -- |
| Series V | MOE performed all analyses | | | | | | -- | -- |
| Series VI | Zenon performed all analyses | | | | | | -- | -- |
| Ambient Air | Ortech MOE LSB (audit) | -- | Zenon MOE LSB (audit) | Ortech MOE LSB (audit) | -- | Bondar-Clegg | -- | -- |
| Waste Water: Decon water Brine | Walkers* Zenon MANN MOE LSB (audit) | -- | Zenon* MANN MOE LSB (audit) | -- | -- | Included in sewer use | -- | Walkers* Zenon MANN MOE LSB (audit) |
| Solids | Zenon* Walkers MANN MOE LSB (audit) | -- | Zenon* MANN MOE LSB (audit) | -- | -- | Zenon* Walkers MANN MOE LSB (audit) | Zenon* Walkers MANN MOE LSB (audit) | |
| Ambient Water (Pre & Post Incineration) | MOE LSB | -- | MOE LSB | -- | -- | -- | -- | -- |
| Ambient Soil (Pre & Post Incineration) | MOE LSB P&R Walkers | -- | MOE LSB | -- | -- | MOE LSB | -- | -- |

NOTES:

| | |
|---|---|
| APCS Scan | Denotes Cl, pH, specific gravity |
| (audit) | Denotes audit analysis |
| O. Reg. 309 | Regulation 309 Leachate Test for Metals |
| Solids | Includes incinerated materials, solids, swabs |
| * | Denotes primary Lab |
| -- | Analysis not required |

Laboratories performing analyses:

| | |
|---|---|
| Bondar-Clegg | Bondar-Clegg & Co. Ltd |
| EPL | Environmental Protection Laboratories |
| MANN | MANN Testing Laboratories Ltd. |
| MOE LSB | MOE Laboratory Services Branch |
| Ortech | ORTECH International |
| P&R | Proctor & Redfern Limited |
| Walker | Walker Laboratories |
| Zenon | Zenon Environmental Inc. |

### 2.3.1 Stack Testing

Ontario Regulation 148/86 (O.Reg. 148/86) specifies that the operator of a mobile PCB thermal process (such as incineration) must conduct stack (source) testing initially (beginning within the first 24 hours of operations) and at least once more during the course of the incineration project. Initial stack testing was required to be carried out for each of the different types of feed materials. The stack tests were designed to verify that the incinerator is operating within the regulatory and C of A requirements.

For the Phase 3 Cleanup, there were two operating modes: (1) soil incineration, and (2) liquids and metals. Therefore, two series of compliance tests were required initially, as well as one verification test at a later date. Each series normally consisted of three runs at near maximum operating conditions for each type of feed material. An extensive list of organic and inorganic contaminants was analyzed from the stack gas, including SVOC (PCB, CB, CP, PCDD/DF, PAH), VOC, total particulates, HCl, and heavy metals. In total, over 150 individual parameters were monitored during a stack test.

A complete list of the source test parameters can be found in the Quality Assurance Project Plan (QAPP) [215] and the Stack Testing reports prepared for the project [216-220]. All stack tests were required to meet the requirements of the QAPP in order to ensure that the results were legally and technically defensible.

One of the major parameters tested was the DRE. In Canada and the US, a DRE of >99.9999% is required of PCB incinerators. The DRE is determined by sampling the feed

material, recording the mass of material fed, and the stack gas (volume flowrate and PCBs) during the stack test. Analyses are then performed to determine the amount of PCB fed into the incinerator and the amount emitted in the stack gas. The DRE is calculated from Equation (10):

$$DRE = \left( \frac{Mass\ in - Mass\ out}{Mass\ in} \right) * 100 \qquad (10)$$

Where:      Mass in = amount of PCB fed into the incinerator (total mass or mass/time)

Mass out = amount of PCB in the stack gas (total mass or mass/time)

Three series of stack tests were initially planned. Series I and II were carried out for the initial compliance testing for soil and liquids/metals. Series III was to be carried out as the additional verification test at a later point in the project. However, as testing proceeded, it became necessary to conduct several additional test series in order to test improvements to the APCS and to rerun some earlier tests which did not comply the QAPP.

Series I

The Series I tests were carried out from February 16-20, 1991 using soil feed. This period was characterized by a winter thaw along with rain, resulting in elevated soil moisture levels. For soils, the moisture content is one of the most important factors affecting the feed rate. Wet soil is both hard to feed and requires more heat energy to raise its temperature. During the Series I tests, the only difficulty encountered was materials handling due to the

extreme wetness of the clay soil at the Site. All results showed excellent compliance with applicable regulations (Table XIX).

## Series II

The Series II tests were carried out from February 22-26, 1991. During the Series II tests, good DRE and HCl removal were observed (Table XIX). During the second and third runs, elevated particulate loadings were observed. As a result, ENSCO was prohibited from further liquid/metals incineration until additional stack testing was performed, and was required to modify the APCS operation and to retest for particulate emissions during another liquid/metals burn.

The ENSCO CEM system was audited during the Series I and II tests using IMET's CEM systems.

## Series III

After some minor APCS modifications, the MWP-2000 was retested during incineration of liquids/metals for particulate emissions only (Series III). The Series III testing took place on May 1 and 2, 1991. The particulate loadings again exceeded the C of A limits. Analysis of these particulates showed over 50% of the mass loading above the 50 mg/m$^3$ project standard to be due to sodium chloride (NaCl). It is believed that the elevated particulate loadings were due to the concentration of NaCl (formed from the quenching and neutralizing of HCl) becoming entrained from the APCS. This problem had been found previously with the ENSCO system [221]. ENSCO was required to perform additional

APCS modifications to reduce salt carryover and verify that the modifications achieved the reductions with an additional stack test (Series IV).

Series IV

Series IV testing was carried out on July 2 and 3, 1991 with liquid/metals feed. Only particulate emissions were tested. Results from this testing showed that, with the APCS modifications, the incinerator was able to achieve the particulate emissions standards in the C of As. ENSCO was permitted to incinerate liquids/metals without restriction from this point on.

Series V

An additional verification test, referred to as Series V, was conducted from July 10-14, 1991 during normal operations with soil feed. The Series V tests were similar to Series I tests. The MOE Air Resource Branch (ARB) Monitoring Air Pollution Sources (MAPS) system was used during this testing to audit the ENSCO CEM. The results for the Series V tests showed that all regulatory requirements were met.

Series VI

Due to some uncertainties with the VOC and total particulate (TP) results generated in Series I tests, an additional test was required to be performed during soil incineration. The Series VI test was carried out on December 17, 1991.

The Stack Tests results obtained for all six series of tests for Phase 3 are summarized in Table XIX.

# TABLE XIX

## SUMMARY OF STACK TEST RESULTS

| Test Number | | PCB Concentration | | Waste Feedrate | | Parameters | | | Total | Particulates** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Solids | Oil (%) | Solids (kg/hr) | Oil (kg/hr) | PCB DRE (%) | PCDD/PCDF (I-TEQ) (ng/dscm) | HCl (mg/dscm) | Test (mg/dscm) | Series Average (mg/dscm) |
| Regulatory Limits | Soil & Concrete | <0.58% | | 4818 | | | | | | |
| | Soil & Concrete | >0.58 - <1.9% | | 1818 | | | | | | |
| | Metals | >1 - <40% | | 341 | | | | | | |
| | Other solid materials | >1 - <40% | | 341 | | 99.9999 | 12 | 50 | 50 | 40 |
| | Metals or other solid materials | < 1% | | 909 | | | | | | |
| | Pumpable sludges | | < 23% | | 132 | | | | | |
| | Liquid organic wastes | | < 42% | | 959 | | | | | |
| | Waste water | | < 1% | | 1136 | | | | | |
| Series I 15(Soil) | Test 1 - Feb 16/91 | 80.4 ppm | 40.3 | 1770.8 | 63.8 | 99.999981 | 0.316 | 0.182 | 12.3 | 6.9 (includes Series VI, Test 1 result) |
| | Test 2 - Feb 19/91 | 19.9 ppm | 37.9 | 3763 | 58.5 | 99.99998 | 0.121 | 0.083 | NA** | |
| | Test 3 - Feb 20/91 | 32.0 ppm | 37.9 | 3408.3 | 48.1 | 99.999973 | 0.138 | 0.101 | 1.9 | |
| Series II (Liquids/ Metals) | Test 1 - Feb 22/91 | NA | NA | NA | NA | NA | NA | 0.337 | 33.3 | 47.6 |
| | Test 2 - Feb 24/91 | 38.1% | 37.9 | 208.7 | 311.2 | 99.999997 | 0.455 | 0.255 | 45.6 | |
| | Test 3 - Feb 25/91 | 26.5% | 37.9 | 219.5 | 408.2 | 99.999998 | 0.696 | 0.073 | 64 | |
| | Test 4 - Feb 26/91 | 28.6% | 37.9 | 199.6 | 466.3 | 99.999997 | 1.651 | NA | NA | |
| Series III (Liquid/ Metals) | Test 1 - May 1/91 | NA | NA | NA | NA | NA | NA | NA | 43.9 | 62.0 |
| | Test 2 - May 1/91 | NA | NA | NA | NA | NA | NA | NA | 48.6 | |
| | Test 3 - May 2/91 | NA | NA | NA | NA | NA | NA | NA | 93.5 | |
| Series IV (Liquid/ Metals) | Test 1 - Jul 2/91 | NA | NA | NA | NA | NA | NA | NA | 26.1 | 21.4 |
| | Test 2 - Jul 3/91 | NA | NA | NA | NA | NA | NA | NA | 20.8 | |
| | Test 3 - Jul 3/91 | NA | NA | NA | NA | NA | NA | NA | 17.3 | |
| Series V (Liquid/ Metals) | Test 1 - Jul 10/91 | 22.0% | 35.0 | 264.6 | 525.2 | 99.999998 | 0.536 | 0.103 | 23.0 | 27.9 |
| | Test 2 - Jul 12/91 | 22.0% | 18.0 | 275.4 | 555.1 | 99.999998 | 0.167 | 0.056 | 16.6 | |
| | Test 3 - Jul 13/91 | 21.9% | 18.0 | 256.7 | 547.9 | 99.999997 | 0.271 | 0.018 | 44.1 | |
| Series VI (Soil) | Test 1 - Dec 17/91 | NA | NA | NA | NA | NA | NA | 2.94 | 6.52 | 6.9 (includes results from Series I) |

## 2.3.2 Ambient Air Monitoring

### 2.3.2.1 General

Ambient air monitoring was carried out before, during and after the incineration operations at the CWML SV Site. Air monitoring was carried out at on- and off-site locations. The purposes of the air monitoring were to ensure compliance with applicable regulations and guidelines and to quantify the impacts, if any, of the incineration operations on the surrounding environment.

### 2.3.2.2 Off-site Air Monitoring

The ambient air monitoring program included off-site sampling at four (4) fixed air monitoring stations, regarded as sensitive receptor areas. These locations included the closest residence (Witmer, Site ID= 23009) and a primary school (School, Site ID= 23013) located relatively close to the Site. The four fixed air monitoring stations, their designations, and approximate locations relative to the CWML SV Site are summarized in Table XX below.

## TABLE XX

### OFF-SITE FIXED AIR MONITORING STATION LOCATIONS AND DESCRIPTIONS

| Name of Off-Site Air Monitoring Station | MOE Station ID (Site ID) | Approximate Direction from CWML SV Site | Distance |
|---|---|---|---|
| Mud Rd. (or Young St.) | 23007 | North (N) | approximately 900 m |
| Witmer | 23009 | East (E) | approximately 350 m |
| Winery | 23011 | Southeast (SE), | approximately 300 m |
| School | 23013 | Southwest (SW) | approximately 600 m |
| Meteorological Station | 23005 | Northwest (NW) | approximately 1 km |

In addition to these off-site air monitoring stations, a meteorology station was set up approximately 1 km NW of the CWML SV Site. The MOE station ID for the meteorological (MET) station was 23005. The locations of the four off-site air monitoring sites are shown in Figure 15. At each of these fixed stations, four samplers were set up to sample for the following parameters: PCB/CB, PCDD/DF, VOC, and Inorganics. In addition, duplicate samplers for PCB/CB, PCDD/DF, VOC, and Inorganics were utilized for QA/QC purposes. These duplicate samplers were rotated through each of the four monitoring station locations on a regular schedule.
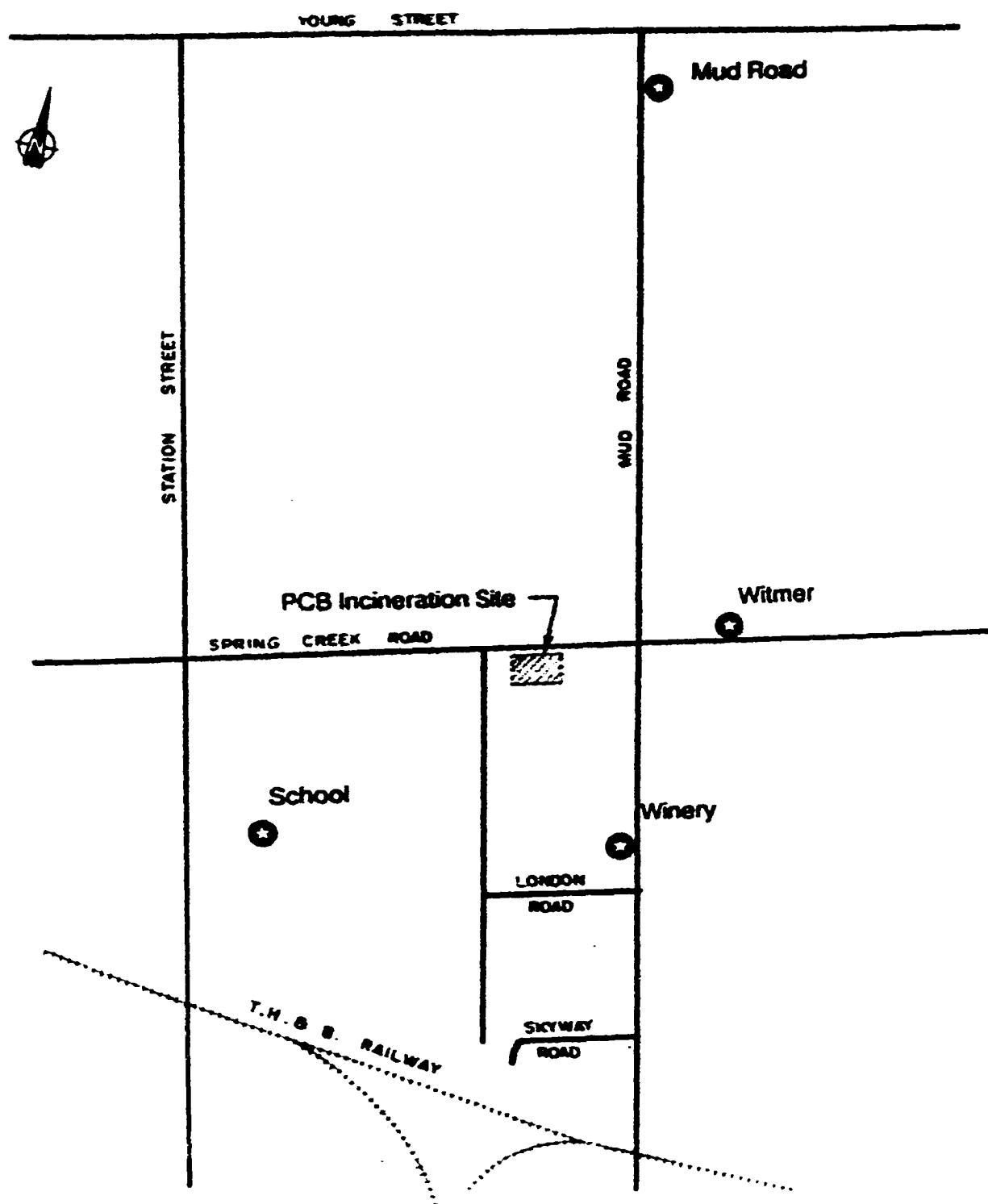
Figure 15.    Off-site air monitoring station locations.

## 2.3.2.3 On-Site Air Monitoring

The ambient air on the CWML site near areas of potential or suspected fugitive emissions sources was also monitored occasionally during the project. The samplers were installed at various locations on the Site (see Figure 16) for specific purposes as described in Table XXI below.

**TABLE XXI**

ON-SITE AIR MONITORING LOCATIONS AND PURPOSES

| Sampler Location | Purpose |
|---|---|
| Location 1 | Inside Dome to monitor PCB (and sometimes PCDD/DF) concentrations in the air potentially caused by fugitive releases from the incinerator. |
| Location 2 | South of the Shredder Pad to monitor PCB concentrations in the air from activities associated with the shredder pad, containment building, and tank farm |
| Location 3 | SE corner of the Site to monitor possible fugitive emissions from excavation and other activities in the contaminated area |
| Location 4 | Inlet and exhaust of the containment building's CFU to determine the effectiveness of the CFU and to verify the CFU's compliance with its C of A [222] |
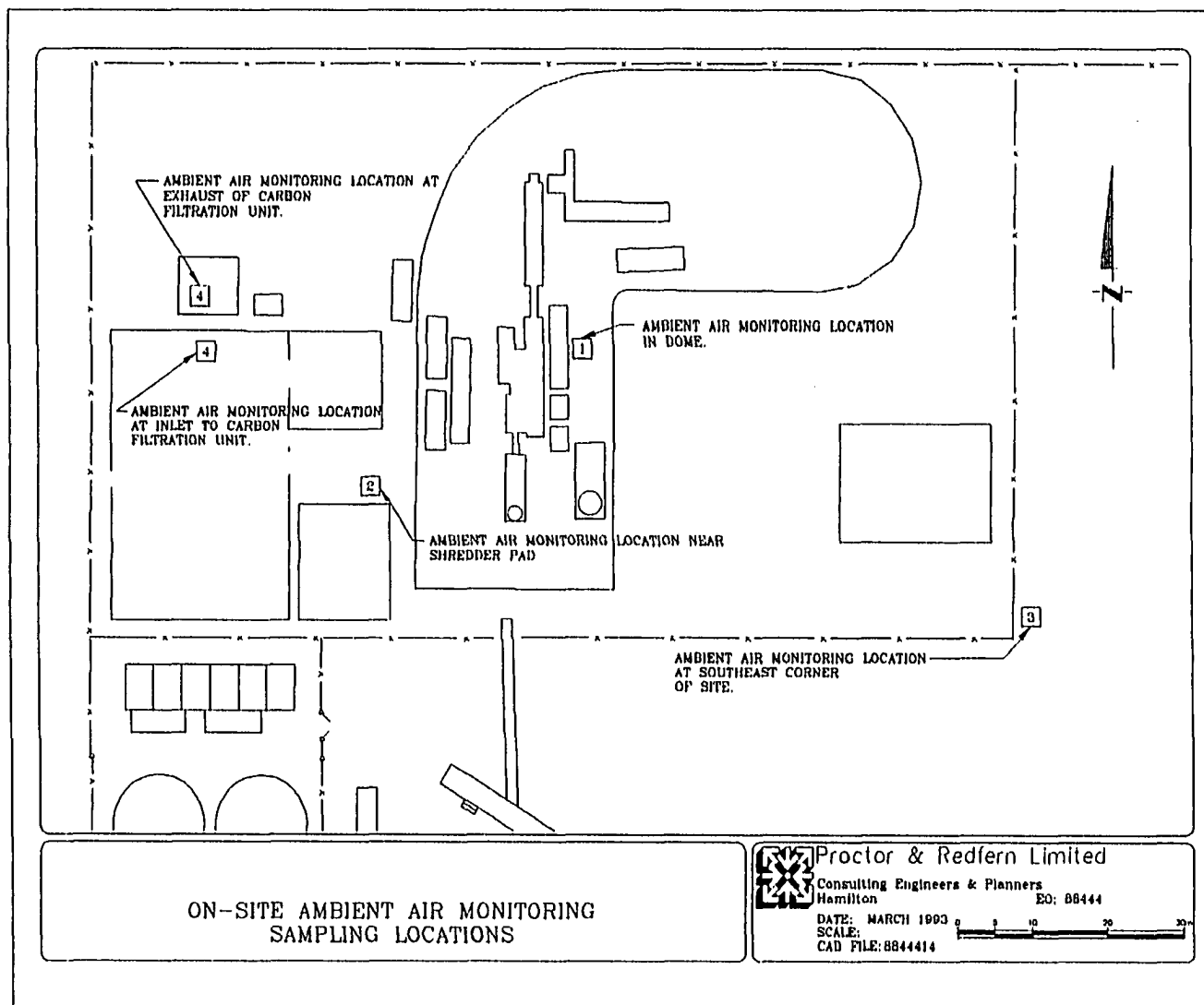
Figure 16.   On-site air monitoring locations.

## 2.3.2.4 Mobile Air Monitoring

In addition to the regular monitoring at the fixed monitoring sites, part of the MOE undertakings to the Environmental Assessment (EA) Board (EAB) was to carry out monitoring during the Phase 3 Cleanup with the ARB's mobile Trace Atmospheric Gas Analysis (TAGA) 6000 unit at various locations surrounding the Site.

The TAGA 6000 is an extremely sophisticated piece of Canadian designed and manufactured equipment (cost of over $1 million) that is equipped with a tandem mass spectrometer (MS/MS) capable of identifying and quantifying a broad range of trace organic compounds in air [86, 223, 224]. The unit's speed of analysis and mobility allow it to track plumes and sample at a number of different locations in a short period of time. Air monitoring was carried out on several occasions before, during and after the incinerator operations, using the TAGA unit (see Section 3.3.4 below).

## 2.3.2.5 Air Sampling and Analysis Methods

The air sampling and analysis methods used for samples taken at the on- and off-site monitoring locations are summarized in Table XXII. The MOE Laboratory Information System (LIS) Test Groups and individual Analyte Codes covered by each of the sampling methods are summarized in Table XXIII. The PCB air results are reported as homolog groups (di-deca). However, it should be noted that the PCB analysis was actually carried out for 78 individual PCB congeners for air samples from the four fixed off-site sampling stations. The PCB congeners that were analyzed in these air samples are shown in Table XXIV.

A view of one of the off-site air monitoring sites (Winery Station) is shown in Figure 17. The PCB air sampling system is shown in Figures 18 and 19. A schematic of the TAGA 6000 is shown in Figure 20. The air samplers used for on- and off-site PCDD/DF sampling are shown in Figure 21. An advantage of the PUF/XAD-2/PUF sorbent system used in the EC design was that PCB, CB and CP could also be determined in the same sample used for PCDD/DF.

**TABLE XXII**

SUMMARY OF AMBIENT AIR MONITORING SAMPLING AND ANALYSIS METHODS

| Sample Type/Parameters | Sampling Method | Analytical Method | Test Group | Locations |
|---|---|---|---|---|
| PCB/CB | Florisil™ Tubes Nutech Medium Volume Sample Pump | GC-ECD, GC-ECD (Dual Column) main method, or GC-MS (semi-quantitative) | SBPCB (Ortech) or PAPCB (MOE) | On- and Off-site |
| PCB (TAGA 6000) | ASTA (SE54 coated wire) | MS/MS with Collisionally Activated Dissociation (CAD) | DiPCB TriPCB TetraPCB PentaPCB | Off-site and perimeter |
| PCB/CB/PCDD/DF | Teflon Coated Glass Fiber Filter (GFF), PUF/XAD-2 sorbent, Hi Vol sampling pumps with bellows gas meter | HRGC-Low Resolution MS (LRMS) | PCB homologs PCDD/DF homologs and 2,3,7,8 Congeners | On-site |
| PCDD/DF | Teflon Coated GFF, PUF sorbent, Hi Vol sampling pumps with liquid gas meter | HRGC-LRMS | SMDXN (Zenon and MOE) PCDD/DF homologs and 2,3,7,8 Congeners | Off-site |
| VOC | Sorbent Tubes with low volume pump | GC-MS | SMVOC (Ortech) or PAVOC (MOE) | Off-site |
| Inorganics | GFF, Hi-Vol | Gravimetric and X-ray Fluorescence Spectrometry (XRF) or A | HV-4 | Off-site |
| Meteorology | Anemometer, wind vane and thermocouple | | Wind Speed Wind Direction Temperature | 1) Site ID23005-Township Public Works Yard 2) Allanburg |

## TABLE XXIII

### AIR MONITORING TEST GROUPS AND ANALYTE CODES

| Air Monitoring Parameters | Analysis Lab | MOE LIS Sample Class | MOE LIS Sample Type | MOE LIS Test Group Code | MOE LIS Analyte Code | Analyte Description |
|---|---|---|---|---|---|---|
| PCB/CB | Ortech | SB | CN | SBPCB | PCBDI | Dichlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBTRI | Trichlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBTET | Tetrachlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBPNT | Pentachlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBHEX | Hexachlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBHPT | Heptachlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBOCT | Octachlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBNON | Nonachlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBDEC | Decachlorobiphenyl |
| PCB/CB | Ortech | SB | CN | SBPCB | PCBTOT | Total PCB congeners |
| PCB/CB | Ortech | SB | CN | SBPCB | X2HCE | Hexachloroethane |
| PCB/CB | Ortech | SB | CN | SBPCB | X2135 | 1,3,5-Trichlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2124 | 1,2,4-Trichlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X1HCBD | Hexachlorobutadiene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2123 | 1,2,3-Trichlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2T245 | 2,4,5-Trichlorotoluene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2T236 | 2,3,6-Trichlorotoluene |
| PCB/CB | Ortech | SB | CN | SBPCB | X21235 | 1,2,3,5-Tetrachlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X21245 | 1,2,4,5-Tetrachlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2T26A | 2,6,$\alpha$-Trichlorotoluene |
| PCB/CB | Ortech | SB | CN | SBPCB | X21234 | 1,2,3,4-Tetrachlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2PNCB | Pentachlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2HCB | Hexachlorobenzene |
| PCB/CB | Ortech | SB | CN | SBPCB | X2OCST | Octachlorostyrene |

TABLE XXIII (Continued)

## AIR MONITORING TEST GROUP AND ANALYTE CODES

| Air Monitoring Parameters | Lab For Analysis | MOE LIS Sample Class | MOE LIS Sample Type | MOE LIS Test Group Code | MOE LIS Analyte Code | Analyte Description |
|---|---|---|---|---|---|---|
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBDI | Dichlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBTRI | Trichlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBTET | Tetrachlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBPNT | Pentachlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBHEX | Hexachlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBHPT | Heptachlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBOCT | Octachlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBNON | Nonachlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBDEC | Decachlorobiphenyl |
| PCB/CB | MOE LSB | PA | FC | PAPCB | PCBTOT | Total PCB congeners |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2HCE | Hexachloroethane |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2135 | 1,3,5-Trichlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2124 | 1,2,4-Trichlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X1HCBD | Hexachlorobutadiene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2123 | 1,2,3-Trichlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2T245 | 2,4,5-Trichlorotoluene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2T236 | 2,3,6-Trichlorotoluene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X21235 | 1,2,3,5-Tetrachlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X21245 | 1,2,4,5-Tetrachlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2T26A | 2,6,$\alpha$-Trichlorotoluene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X21234 | 1,2,3,4-Tetrachlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2PNCB | Pentachlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2HCB | Hexachlorobenzene |
| PCB/CB | MOE LSB | PA | FC | PAPCB | X2OCST | Octachlorostyrene |

**TABLE XXIII (Continued)**

AIR MONITORING TEST GROUP AND ANALYTE CODES

| Air Monitoring Parameters | Lab For Analysis | MOE LIS Sample Class | MOE LIS Sample Type | MOE LIS Test Group Code | MOE LIS Analyte Code | Analyte Description |
|---|---|---|---|---|---|---|
| VOC | Ortech | SC | CN | SMVOC | X1CHLM | Chloromethane |
| VOC | Ortech | SC | CN | SMVOC | X1VCL | Chloroethane |
| VOC | Ortech | SC | CN | SMVOC | X13VCL | 1,3-Butadiene |
| VOC | Ortech | SC | CN | SMVOC | X1ACRY | Acrylonitrile |
| VOC | Ortech | SC | CN | SMVOC | B2ISPR | 2-Methyl-1,3-Butadiene |
| VOC | Ortech | SC | CN | SMVOC | X1DCLE | 1,1-Dichloroethene |
| VOC | Ortech | SC | CN | SMVOC | X1DCLM | Dichloromethane |
| VOC | Ortech | SC | CN | SMVOC | X111CE | 1,1-Dichloroethane |
| VOC | Ortech | SC | CN | SMVOC | X1TCLM | Trichloromethane |
| VOC | Ortech | SC | CN | SMVOC | B1HEXA | Hexane |
| VOC | Ortech | SC | CN | SMVOC | X112CE | 1,2-Dichloroethane |
| VOC | Ortech | SC | CN | SMVOC | X111CE | 1,1,1-Trichloroethane |
| VOC | Ortech | SC | CN | SMVOC | B2BENZ | Benzene |
| VOC | Ortech | SC | CN | SMVOC | X1CTET | Tetrachloromethane |
| VOC | Ortech | SC | CN | SMVOC | BKHEX | Cyclohexane |
| VOC | Ortech | SC | CN | SMVOC | X112CP | 1,2-Dichloropropane |
| VOC | Ortech | SC | CN | SMVOC | X1TRIC | Trichloroethene |
| VOC | Ortech | SC | CN | SMVOC | X1BDCM | Bromodichloromethane |
| VOC | Ortech | SC | CN | SMVOC | X113DP | Cis-1,3-Dichloropropene |
| VOC | Ortech | SC | CN | SMVOC | X1112T | 1,1,2-Trichloroethane |
| VOC | Ortech | SC | CN | SMVOC | B2TOLU | Toluene |
| VOC | Ortech | SC | CN | SMVOC | X1DBET | 1,2-Dibromoethane |
| VOC | Ortech | SC | CN | SMVOC | X1TETR | Tetrachloroethene |
| VOC | Ortech | SC | CN | SMVOC | X2CREN | Chlorobenzene |
| VOC | Ortech | SC | CN | SMVOC | B2EBNZ | Ethylbenzene |
| VOC | Ortech | SC | CN | SMVOC | B2MXYL | m+p-Xylene |
| VOC | Ortech | SC | CN | SMVOC | STYR | Styrene |
| VOC | Ortech | SC | CN | SMVOC | X11122 | 1,1,2,2-Tetrachloroethane |

# TABLE XXIII (Continued)

## AIR MONITORING TEST GROUP AND ANALYTE CODES

| Air Monitoring Parameters | Lab For Analysis | MOE LIS Sample Class | MOE LIS Sample Type | MOE LIS Test Group Code | MOE LIS Analyte Code | Analyte Description |
|---|---|---|---|---|---|---|
| VOC | Ortech | SC | CN | SMVOC | B2OXYL | o-Xylene |
| VOC | Ortech | SC | CN | SMVOC | B23TMB | 1,3,5-Trimethylbenzene |
| VOC | Ortech | SC | CN | SMVOC | B12TMB | 1,2,4-Trimethylbenzene |
| VOC | Ortech | SC | CN | SMVOC | X213CB | 1,3-Dichlorobenzene |
| VOC | Ortech | SC | CN | SMVOC | X212CB | 1,2-Dichlorobenzene |
| VOC | Ortech | SC | CN | SMVOC | X214CB | 1,4-Dichlorobenzene |
| VOC | Ortech | SC | CN | SMVOC | PNNAPH | Napthalene |
| VOC | MOE LSB | PA | CN | PAVOC | X1CHLM | Chloromethane |
| VOC | MOE LSB | PA | CN | PAVOC | X1VCL | Chloroethane |
| VOC | MOE LSB | PA | CN | PAVOC | X13VCL | 1,3-Butadiene |
| VOC | MOE LSB | PA | CN | PAVOC | X1ACRY | Acrylonitrile |
| VOC | MOE LSB | PA | CN | PAVOC | B2ISPR | 2-Methyl-1,3-Butadiene |
| VOC | MOE LSB | PA | CN | PAVOC | X1DCLE | 1,1-Dichloroethene |
| VOC | MOE LSB | PA | CN | PAVOC | X1DCLM | Dichloromethane |
| VOC | MOE LSB | PA | CN | PAVOC | X111CE | 1,1-Dichloroethane |
| VOC | MOE LSB | PA | CN | PAVOC | X1TCLM | Trichloromethane |
| VOC | MOE LSB | PA | CN | PAVOC | B1HEXA | Hexane |
| VOC | MOE LSB | PA | CN | PAVOC | X112CE | 1,2-Dichloroethane |
| VOC | MOE LSB | PA | CN | PAVOC | DOWN | 1,1,1-Trichloroethane |
| VOC | MOE LSB | PA | CN | PAVOC | B2BENZ | Benzene |
| VOC | MOE LSB | PA | CN | PAVOC | X1CTET | Tetrachloromethane |
| VOC | MOE LSB | PA | CN | PAVOC | BKHEX | Cyclohexane |
| VOC | MOE LSB | PA | CN | PAVOC | X112CP | 1,2-Dichloropropane |
| VOC | M OE LSB | PA | CN | PAVOC | X1TRIC | Trichloroethene |
| VOC | MOE LSB | PA | CN | PAVOC | X1BDCM | Bromodichloromethane |
| VOC | MOE LSB | PA | CN | PAVOC | X113DP | Cis-1,3-Dichloropropene |
| VOC | MOE LSB | PA | CN | PAVOC | X1112T | 1,1,2-Trichloroethane |
| VOC | MOE LSB | PA | CN | PAVOC | B2TOLU | Toluene |
| VOC | MOE LSB | PA | CN | PAVOC | X1DBET | 1,2-Dibromoethane |

**TABLE XXIII (Concluded)**

**AIR MONITORING TEST GROUP AND ANALYTE CODES**

| Air Monitoring Parameters | Lab For Analysis | MOE LIS Sample Class | MOE LIS Sample Type | MOE LIS Test Group Code | MOE LIS Analyte Code | Analyte Description |
|---|---|---|---|---|---|---|
| VOC | MOE LSB | PA | CN | PAVOC | X1TETR | Tetrachloroethene |
| VOC | MOE LSB | PA | CN | PAVOC | X2CREN | Chlorobenzene |
| VOC | MOE LSB | PA | CN | PAVOC | B2EBNZ | Ethylbenzene |
| VOC | MOE LSB | PA | CN | PAVOC | B2MXYL | m+p-Xylene |
| VOC | MOE LSB | PA | CN | PAVOC | STYR | Styrene |
| VOC | MOE LSB | PA | CN | PAVOC | X11122 | 1,1,2,2-Tetrachloroethane |
| VOC | MOE LSB | PA | CN | PAVOC | B2OXYL | o-Xylene |
| VOC | MOE LSB | PA | CN | PAVOC | B23TMB | 1,3,5-Trimethylbenzene |
| VOC | MOE LSB | PA | CN | PAVOC | B12TMB | 1,2,4-Trimethylbenzene |
| VOC | MOE LSB | PA | CN | PAVOC | X213CB | 1,3-Dichlorobenzene |
| VOC | MOE LSB | PA | CN | PAVOC | X212CB | 1,2-Dichlorobenzene |
| VOC | MOE LSB | PA | CN | PAVOC | X214CB | 1,4-Dichlorobenzene |
| VOC | MOE LSB | PA | CN | PAVOC | PNNAPH | Napthalene |
| PCDD/DF | Zenon | SZ | CN | SMDXN | | 2,3,7,8 Substituted PCDD/DF and Homolog Groups |
| PCDD/DF | MOE LSB | SZ | VN | SMDXN | | 2,3,7,8 Substituted PCDD/DF and Homolog Groups |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | CDUT | Cadmium |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | CUUT | Copper |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | CRUT | Chromium |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | FEUT | Iron |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | PBUT | Lead |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | NIUT | Nickel |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | MNUT | Manganese |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | VVUT | Vanadium |
| Inorganics | Bondar-Clegg | SA | HG | HV4 | TSP | Total Suspended Particulates |

## TABLE XXIV

### POLYCHLORINATED BIPHENYL CONGENER LIST FOR POLYCHLORINATED BIPHENYL/ CHLOROBENZENE AIR SAMPLE ANALYSIS [225]

| PCB Homolog Group | PCB Congener BZ no. | PCB Isomer | PCB Homolog Group | PCB Congener BZ no. | PCB Isomer | PCB Homolog Group | PCB Congener BZ no. | PCB Isomer |
|---|---|---|---|---|---|---|---|---|
| Di-PCB | 4 | 2,2' | Penta-PCB | 103 | 2,2',4,5',6 | Hepta-PCB | 182 | |
| | 8 | 2,4' | | 101 | 2,2',4,5,5' | | 187 | |
| | 10 | 2,6 | | 84 | 2,2',3,3',6 | | 183 | |
| Tri-PCB | 18 | 2,2',5 | | 97 | 2,2',3,4',5' | | 185 | |
| | 29 | 2,4,5 | | 87 | 2,2',3,4,5' | | 180 | |
| | 31 | 2,4',5 | | 85 | 2,2',3,4,4' | | 177 | |
| | 28 | 2,4,4' | | 118 | 2,3',4,4',5 | | 171 | |
| | 33 | 2',3,4 | | 82 | 2,2',3,3',4 | | 193 | |
| | 21 | 2,3,4 | | 106 | 2,3,3',4,5 | | 173 | |
| Tetra-PCB | 50 | 2,2',4,6 | | 114 | | | 191 | |
| | 53 | 2,2',5,6' | Hexa-PCB | 151 | | | 190 | |
| | 52 | 2,2',5,5' | | 136 | | | 170 | |
| | 75 | 2,4,4',6 | | 144 | | Octa-PCB | 197 | |
| | 49 | 2,2',4,5' | | 134 | | | 198 | |
| | 47 | 2,2',4,4' | | 131 | | | 201 | |
| | 43 | 2,2',3,5 | | 155 | | | 196 | |
| | 44 | 2,2',3,5' | | 141 | | | 195 | |
| | 42 | 2,2',3,4' | | 137 | | | 194 | |
| | 61 | 2,3,4,5 | | 138 | | | 205 | |
| | 40 | 2,2',3,3' | | 158 | | | 199 | |
| | 70 | 2,3',4',5 | | 129 | | | 203 | |
| | 76 | 2',3,4,5 | | 167 | | Nona-PCB | 207 | |
| | 66 | 2,3',4,4' | | 128 | | | 206 | |
| | 56 | 2,3,3',4 | | 156 | | Deca-PCB | 209 | |
| | 60 | 2,3,4,4' | | 157 | | | | |
| | 77 | 3,3',4,4 | | | | | | |

Figure 17.    Photograph of the Winery air monitoring station.   (Note that plume from incinerator can be seen in background.)
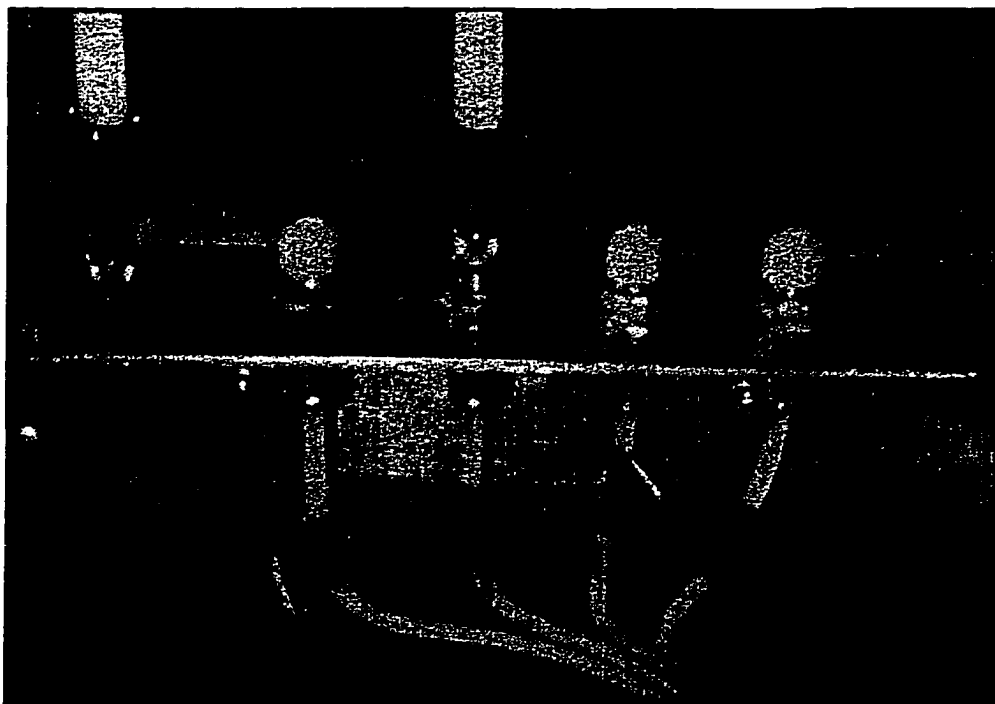
Figure 18.    Polychlorinated biphenyl air sampling system sorbent tube and holder.  (Note field blank in left-most position.)
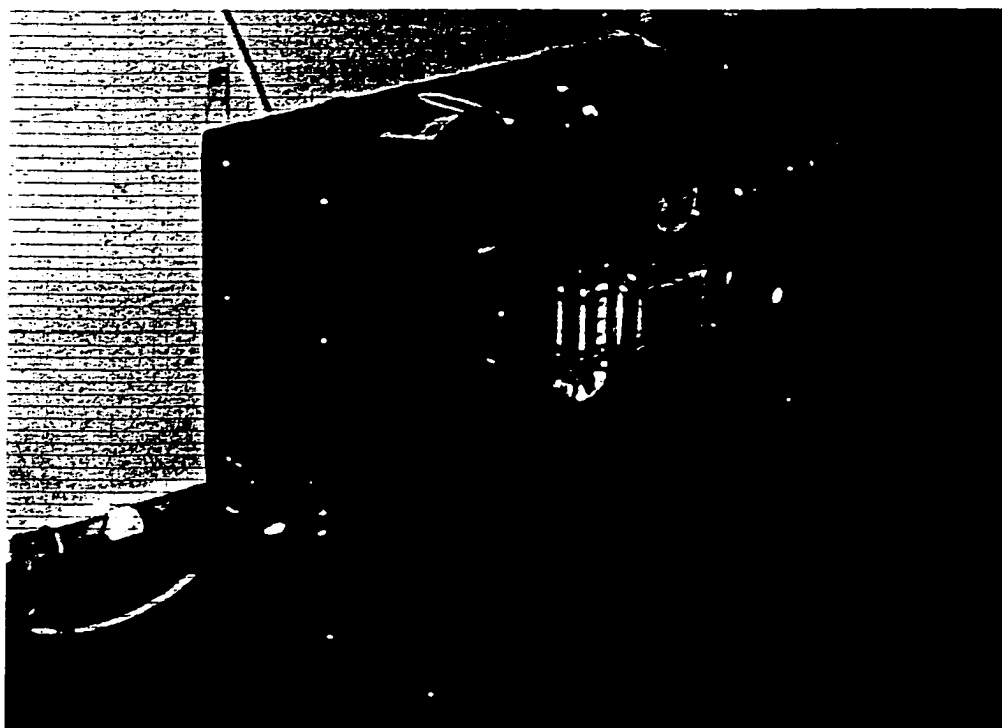


Figure 19.    Air sampling pump for polychlorinated biphenyl air sampling system.
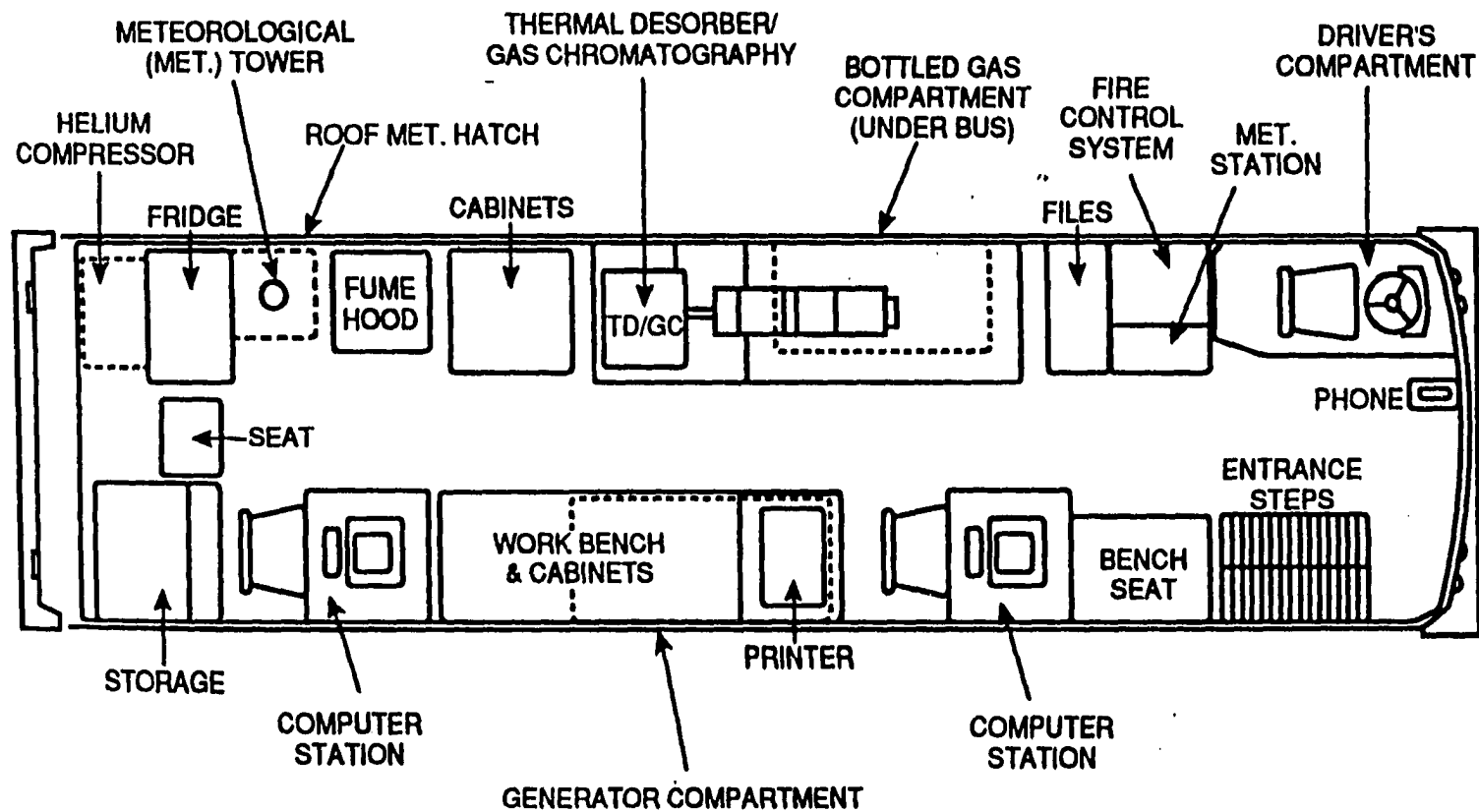
Figure 20.    Schematic of Trace Atmospheric Gas Analysis 6000 mobile polychlorinated biphenyl air monitoring unit.

(A) DIAPHRAGM METER OPTION                    (A) ROTARY VANE METER OPTION
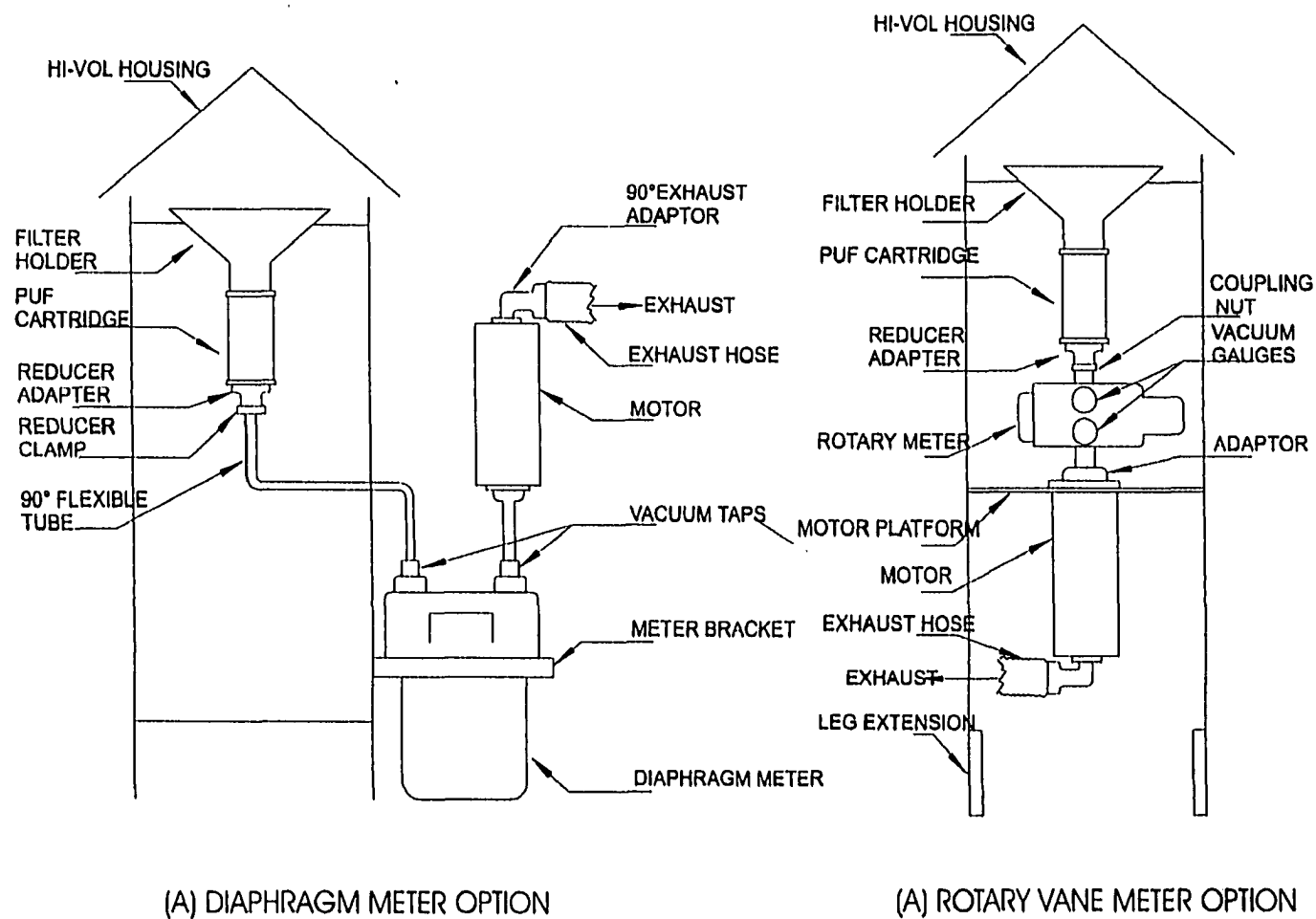
Figure 21.    Air samplers used for on-site polychlorinated biphenyl and polychlorinated dibenzo-p-dioxin/dibenzofuran sampling (left, EC design) and off-site polychlorinated dibenzo-p-dioxin/dibenzofuran sampling (right, MOE design [226]) (diagram from EC [125]).

## 2.3.2.6 Air Sampling Schedule

The ambient air sampling program was originally scheduled as a seven day cycle. This schedule is shown in Table XXV. This sampling schedule was used for pre-incinerator operations (December 19, 1990 - February 13, 1991), during incineration (February 14, 1991 - December 23, 1992) and post-incineration operations (December 18, 1992-January, 14, 1993). This sampling schedule resulted in a large amount of air quality data being produced during the first 11-12 months of operations. Once this ambient air data was analyzed, a level of comfort developed, and the MOE, with the agreement of the CWML Liaison Committee and the township, modified the program. The modified schedule is shown in Table XXVI. In general, this modified sampling schedule was followed from December 24, 1991 to December 17, 1992. The modifications of the air monitoring program primarily resulted in fewer sample analyses, from the use of longer sampling times and/or selection of the samples that were mainly downwind. In addition, it should be noted that samples were not analyzed for periods during which the incinerator did not burn PCB material.

Sampling using the MOE-TAGA was performed in the vicinity of the Site for the Phase 3 Cleanup during the following time periods:

- One week prior to incineration, background sampling (June, 1990);

- One week during incineration operations start-up and the soil stack tests (February 16, 19 and 20, 1991);

- One week during operations start-up for the liquid/metals burn (February 24-26, 1991);

- One week during normal operations (April 15, 16, 17 and 19, 1991);

- One week after the Phase 3 Cleanup was completed, background sampling (April 19-23, 1991).

During the Phase 3 Cleanup a meteorological station was established in the West Lincoln Township Public Works yard located approximately 1 km NW of the CWML SV Site. This meteorological station monitored for wind speed and wind direction, at two different heights (10 and 30 m) (Table XXVII). Temperature was also supposed to be measured at this station. This station logged the data every 15 seconds and downloaded the results via telemetry to the MOE West Central Region (WCR) in Hamilton for further data processing.

## TABLE XXV

### AIR MONITORING SCHEDULE PRE, DURING INITIAL INCINERATOR OPERATIONS
### (FEBRUARY TO NOVEMBER, 1991), AND POST OPERATIONS

| DAY 1 | DAY 2 | DAY 3 | DAY 4 | DAY 5 | DAY 6 | DAY 7 |
|---|---|---|---|---|---|---|
| **PCB/CB**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 travel blank | **PCB/CB**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 travel blank<br>(1st 3 wks only) | **PCB/CB**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 travel blank<br>(1st 3 wks only) | **PCB/CB**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 travel blank<br>(1st 3 wks only) | **PCB/CB**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 MOE spike<br>1 travel blank<br>(1st 3 wks only)<br><br>MOE LSB:<br>1 duplicate<br>1 field blank<br>1 travel blank | **PCB/CB**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 travel blank<br>(1st 3 wks only) | **PCB/CB**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 travel blank<br>(1st 3 wks only) |
| | **PCDD/PCDF**<br>Zenon:<br>1 x 4 sites<br>1 travel/field blank<br>1 MOE spike/2 wks<br><br>MOE LSB:<br>1 duplicate /2 wks | | | **VOC**<br>Ortech:<br>1 x 4 sites<br>1 field blank<br>1 travel blank<br><br>1 MOE spike<br><br>MOE LSB:<br>1 duplicate<br>1 field blank<br>1 travel blank | | **INORGANICS**<br>Bondar-Clegg:<br>1 x 4 sites<br>1 duplicate |

**Notes:**

For Post Operation sampling, only downwind PCDD/PCDF samples analyzed.

Ortech , Zenon, etc. = denotes the laboratory which analyzed the samples

## TABLE XXVI

### MODIFIED AIR MONITORING SCHEDULE NOVEMBER, 1991 TO DECEMBER, 1992

| Day No. | | PCB Sampling | Other Air Sampling | |
|---|---|---|---|---|
| 1 | install | Ortech (4 sites) Sampling Time = 72 hrs | PCDD/ PCCDF: | Zenon (4 sites. tb. spike/2 weeks) |
| 2 | remove | | | MOE LSB (duplicate/2 weeks) |
| | install | | | Sampling Time - 48 hrs |
| 3 | remove | | | Only down wind samples will be analyzed as directed by WCR |
| | install | Ortech (4 sites, fb, tb, spike) MOE LSB (dup, fb, tb)* Sampling Time = 72 hrs | Inorganics: | Bondar-Clegg (4 sites, duplicate) |
| 4 | remove | | | Sampling Time - 24 hrs |
| | install | | | |
| 5 | remove | | | |
| | install | | | |
| 6 | remove | | | |
| | install | Ortech (4 sites) Sampling Time = 72 hrs | VOC: | Ortech (4 sites, tb, fb, spike) |
| 7 | remove | | | MOE LSB (duplicate. tb)** Sampling Time - 24 hrs |
| | install | | | |
| 8 | remove | | | |
| | install | | PCDD/ PCDF: | Zenon (4 sites, tb, spike/2 weeks) |
| 9 | remove | | | MOE LSB (duplicate/2 weeks) |
| | install | Ortech (4 sites) Sampling Time = 72 hrs | | Sampling Time - 48 hrs |
| 10 | remove | | | Only down wind samples will be analyzed as directed by WCR |
| | install | | Inorganics: | Bondar-Clegg (4 sites, duplicate) |
| 11 | remove | Ortech (4 sites) Sampling Time = 72 hrs | | Sampling Time - 24 hrs |
| | install | | | |
| 12 | remove | | | |
| | install | | | |
| 13 | remove | | | |
| | install | | VOC: | Ortech (4 sites, tb, fb, spike) |
| 14 | remove | Ortech (4 sites) Sampling Time = 72 hrs | | MOE LSB (duplicate, tb) Sampling Time - 24 hrs |
| | install | | | |
| 15 | remove install | | | |
| 16 | remove | | | |
| | install | Ortech (4 sites) Sampling Time = 72 hrs | PCDD/ PCDF: | Zenon (4 sites, tb, spike/2 weeks) |
| 17 | remove | | | MOE LSB (duplicate/2 weeks) |
| | install | | | Sampling Time - 48 hrs |
| 18 | remove | | | Only down wind samples will be analyzed as directed by WCR |
| | install | | Inorganics: | Bondar-Clegg (4 sites, duplicate) |
| 19 | remove | | | Sampling Time - 24 hrs |
| | install | Ortech (4 sites) Sampling Time = 72 hrs | VOC: | Ortech (4 sites, tb, fb, spike) |
| 20 | remove | | | MOE LSB (duplicate, tb) Sampling Time - 24 hrs |
| | install | | | |
| 21 | remove install | | | |
| 22 | remove | | | |

## Notes:

4 sites:  the four air monitoring sites

** = From August 1992 duplicate VOCs were run once every 2 weeks

"Ortech (4 sites)" = denotes that the contract laboratory, Ortech, analyzed the samples which were collected at the four monitoring locations

**TABLE XXVII**

METEOROLOGICAL PARAMETERS MONITORED IN PHASE 3

| Parameter ID | Description | Units |
|---|---|---|
| 063 | WIND SPEED 1 (Level 1, BELOW 75') | km/h |
| 065 | WIND SPEED 2 (Level 2 75 – 250') | km/h |
| 073 | WIND DIRECTION 1 (Level 1) | degrees |
| 075 | WIND DIRECTION 2 (Level 2) | degrees |
| 084 | AMBIENT TEMPERATURE | 0.1 (°C) |
| 085 | VERT. TEMP. DIFFERENCE (Level 2 - Level 1) | 0.1 (°C) |

## 2.4    Research Objectives

The research objectives that were initially proposed for this work [227] are reprinted below.

### 2.4.1    Comparison to Other Ambient Air Studies

1)    How do the concentrations and homolog group/congener profiles of PCB and PCDD/DF in the ambient air compare with other (similar) studies?

### 2.4.2    Local Source(s)

2)    Is there a difference between sampling sites that are primarily upwind and those that are primarily downwind?   Can emissions from the Site be seen based upon wind sector analysis of the monitoring Site data?   Do PCB and PCDD/DF concentrations follow similar patterns (i.e., are the highest PCB and PCDD/DF sampling sites downwind of the CWML SV Site)?

3)  How does the PCB homolog pattern observed in the ambient air samples compare to those measured from i) the incinerator stack and ii) on-site (fugitive) emissions?

4)  Can changes in PCB and PCDD/DF concentrations in the ambient air be correlated with any on-site activities, such as incinerator operating conditions (including TRV opening, AWFSO operation, etc.), shredder operations, and soil excavations, etc.?

5)  Is there an effect seen on PCB and/or PCDD/DF concentrations and profiles from physical parameters, such as temperature, wind speed, and relative humidity?

6)  Can transport from urban areas such as Hamilton, Toronto, Buffalo or other areas be seen in the PCB and PCDD/DF data?  Can a relative contribution of local and longer range transport be assigned based upon the ambient air results?

## 2.4.3  Modeling of Data

7)  How well does ADM match the actual ambient air data (fixed and mobile air monitoring data)?  How much difference is there between the modeled results

using site-specific meteorological data and those predicted by modeling prior to the incineration project.

8) Does modeling of the site emissions using both ADM and Receptor Models (RM) provide a better fit to the data?

### 2.4.4 Possible Future Work

9) If a limited number of conditions suggest a significant long-range transport component contribution to the observed concentrations of PCB and /or PCDD/DF, can these conditions be examined using trajectory air models?

As will be seen in Sections 3 and 4 (below), some of these objectives were dropped or modified and additional objectives were identified as the work for this thesis progressed.

## 3. DATA DESCRIPTION AND BASIC STATISTICS

Results for approximately 1600 PCB/CB and 200 PCDD/DF off-site ambient air samples will be used as data in this research. This section contains a brief description of the ambient air data that was produced from the environmental monitoring for the Phase 3 Cleanup as well as some simple descriptive statistics.

The environmental monitoring results reported for VOC, Inorganics, and PCB/CB samples for the Phase 3 Cleanup were downloaded from the MOE LIS and provided in an electronic database in dbase IV$^{tm}$ format by P&R. Data for PCB/CB and PCDD/DF, which was obtained using the modified Hi-Vol samplers, was provided in printed format only. Additional information on each sample was contained on a Sample Information Sheet that was completed for all environmental samples taken after January 1, 1991.

### 3.1 Volatile Organic Compounds Air Sampling Results

The results for 343 VOC air samples taken during the Smithville Phase 3 Cleanup are summarized by sampling location and sampling period in Table XXVIII. The VOC air sampling results for these samples summarized in Table XXIX. In all cases, VOC concentrations observed were far below the applicable standard. No additional data analysis was performed of the VOC results for this research.

133

**TABLE XXVIII**

SMITHVILLE VOLATILE ORGANIC COMPOUND
AIR SAMPLING PROGRAM SUMMARY

| Site | Pre-Incineration | Incineration Operations | Post-Incineration | Totals |
|------|------------------|-------------------------|-------------------|--------|
| 23007 | 1 | 79 | 3 | 83 |
| 23009 | 1 | 80 | 5 | 86 |
| 23011 | 1 | 79 | 3 | 83 |
| 23013 | 1 | 81 | 5 | 87 |
| 23015 (On-Site) | 0 | 4 | 0 | 4 |
| All Sites | 4 | 319 | 16 | 343 |

**Notes:**

1)     Sample numbers based on Benzene results reported

2)     Numbers reported exclude spikes (58), blanks (200), and duplicates (90)

## TABLE XXIX

### SUMMARY OF VOLATILE ORGANIC COMPOUND AIR MONITORING RESULTS

| Analyte Chemical Name | Board Decision Criteria | 24 HR AAQC | Mud Road 23007 | | Witmer 23009 | | Winery 23011 | | School 23013 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | MAX. | Ave. | MAX. | Ave. | MAX. | Ave. | MAX. | Ave. |
| chloromethane* | | 7000 | 33.2 | 9.02 | 81 | 11.02 | 58.9 | 8.87 | 38.3 | 7.97 |
| chloroethane | | 1 | 0.2 | | 0.7 | | 0.2 | 0.4 | | |
| 1,3-butadiene | | | 2.1 | 0.15 | 3.2 | 0.25 | 1.9 | 0.16 | 2.9 | 0.19 |
| acrylonitrile | | 100 | 0.5 | | 0.2 | | 0.6 | | 0.7 | |
| 2-methyl-1,3-butadiene | | | 0.9 | | 1.8 | 0.22 | 1 | 0.17 | 0.6 | 0.12 |
| 1,1-dichloroethene* | 35 | 35 | 1 | 0.22 | 1.2 | 0.18 | 2.1 | 0.22 | 0.8 | 0.19 |
| dichloromethane* | | 1765 | 4.8 | 0.99 | 8.8 | 0.98 | 6.2 | 0.93 | 3.8 | 1.1 |
| 1,1-dichloroethane | | | 0.1 | | 0.9 | | 0.2 | | 0.3 | |
| trichloromethane | | 500 | 1 | | 0.2 | | 0.9 | | 0.8 | |
| hexane* | | 12000 | 28.7 | 4.68 | 34.8 | 4.52 | 21.6 | 3.81 | 35 | 5.37 |
| 1,2-dichloroethane | 1200 | 400 | 0.2 | | 1.5 | | 0.3 | | 0.1 | |
| 1,1,1-trichloroethane | 350000 | 115000 | 4.1 | 1.35 | 3.3 | 1.16 | 3.3 | 1.24 | 5.6 | 0.98 |
| benzene | 10000 | | 2.5 | 1 | 2.9 | 1.04 | 2.7 | 0.96 | 2.5 | 0.88 |
| tetrachloromethane | | 600 | 1.9 | 0.59 | 1.6 | 0.54 | 1.6 | 0.52 | 1.5 | 0.45 |
| cyclohexane | | 100000 | 2.1 | 0.27 | 1.4 | 0.29 | 3.6 | 0.29 | 1.7 | 0.29 |
| 1,2-dichloropropane | | 2400 | 0.1 | | 0.1 | | 0.1 | | 0.1 | |
| trichloroethene | 85000 | 28000 | 0 | | | | | | | |
| bromodichloromethane | | | 0.3 | | 0.4 | 0.4 | 0.4 | | 1.5 | |
| cis-1,3-dichloropropene | | | 1.3 | | 2.6 | | 3.4 | | 2.1 | |
| 1,1,2-trichloroethane | | | 0.2 | | 0.8 | | 0.1 | | 0.3 | |
| toluene | 2000 | 2000 | 3.3 | 1.3 | 7.8 | 1.59 | 5.7 | 1.42 | 4.9 | 0.15 |
| 1,2-dibromoethane | | | 0.1 | | 0.2 | | 0.1 | | 0.1 | |
| tetrachloroethene | | 4000 | 0.8 | 0.24 | 1 | 0.23 | 1.4 | 0.23 | 1.1 | 0.28 |
| chlorobenzene | | | 0.1 | | 0.1 | | 0.1 | | 0.1 | |
| ethylbenzene | 4000 | 4000 | 0.8 | 0.23 | 1.9 | 0.3 | 0.8 | 0.25 | 1.1 | 0.27 |
| m+p-xylene | 2300 (total) | 2300 | 2.1 | 0.64 | 4.4 | 0.82 | 2.6 | 0.71 | 3.2 | 0.76 |
| styrene | 400 | 400 | 0.2 | | 0.3 | | 0.3 | | 0.4 | |
| 1,1,2,2-tetrachloroethane | | | 0.1 | | 0.1 | | 0.1 | | 0.1 | |
| o-xylene | 2300 (total) | | 0.7 | 0.23 | 1.8 | 0.29 | 0.9 | 0.26 | 5.3 | 0.27 |
| 1,3,5-trimethylbenzene | | | 0.6 | | 1.3 | 0.16 | 0.7 | 0.12 | 0.9 | 0.12 |
| 1,2,4-trimethylbenzene | 500 | 1000 | 0.8 | 0.2 | 3.2 | 0.37 | 1.6 | 0.24 | 0.9 | 0.3 |
| 1,3-dichlorobenzene | | | 0.1 | | 0.1 | | 0.5 | | 0.5 | |
| 1,2-dichlorobenzene | | 30500 | 0.1 | | 0.1 | | 0.1 | | 0.1 | |
| 1,4-dichlorobenzene | | | 0.1 | | 0.1 | | 0.1 | | 0.3 | |
| naphthalene | 36 | 22.5 | 1.5 | | 0.9 | 0.14 | 5.5 | 0.17 | 0.4 | |

**Notes:**

All concentrations in ug/m$^3$

\* These compounds are common laboratory contaminants and were frequently detected in lab blanks.

Ave. = arithmetic average concentrations only calculated for compounds with > 20% of results detected.

Non-detected (ND) results were included in arithmetic mean calculations at 1/2 the detection limit (DL).

Non-detection limit = 0.1 ug/m$^3$ for all compounds.

## 3.2    Inorganic Air Sampling Results

A total of 299 air samples for Inorganics that are not spikes, duplicates, or blanks are reported in the environmental monitoring database.

The Inorganic air samples taken during the Smithville Phase 3 Cleanup are summarized by sampling location and sampling period in Table XXX. Table XXXI summarizes the maximum and mean concentrations observed for the 9 inorganic analytes in the Inorganic samples [91]. Only four TSP results and one copper result exceeded the regulatory criteria of 120 ug/m$^3$ and 4 ug/m$^3$ respectively. However, these high results were attributed primarily to local effects such the dirt roads and plowing of fields rather than CWML site activities. These conclusions are based on wind directions (i.e., sites were not downwind of the CWML site for much of the sampling period) and the fact that PCB concentrations at the sites during same periods were all very low. No additional data analysis was performed of the Inorganics results for this research.

## TABLE XXX

SMITHVILLE INORGANIC AIR SAMPLING PROGRAM SUMMARY

| Site | Pre-Incineration | Incineration Operations | Post Incineration | Totals |
|---|---|---|---|---|
| 23007 | 2 | 72 | 2 | 76 |
| 23009 | 2 | 68 | 2 | 72 |
| 23011 | 3 | 70 | 2 | 75 |
| 23013 | 2 | 72 | 2 | 76 |
| All Sites | 9 | 282 | 8 | 299 |

**Notes:**
Summary based on results reported for TSP
Numbers reported exclude spikes (0), blanks (4), and duplicates (69).

**TABLE XXXI**

SUMMARY OF INORGANIC AIR MONITORING RESULTS

| Site Name: | | Mud Road | | Witmer | | Winery | | School | |
|---|---|---|---|---|---|---|---|---|---|
| **Site ID:** | **24 hr.** | **23007** | | **23009** | | **23011** | | **23013** | |
| **Analyte Name** | **Standard** | **MAX.** | **Mean** | **MAX.** | **Mean** | **MAX.** | **Mean** | **MAX.** | **Mean** |
| TSP | 120 | 109 | 25.71 | 128 | 26.57 | 215 | 21.7 | 87 | 20.51 |
| Copper | 50 | 0.04 | 0.01 | 0.12 | 0.02 | 0.07 | 0.01 | 0.17 | 0.01 |
| Nickel | 2 | 0.01 | 0.01 | 0.02 | 0.01 | 0.04 | 0.01 | 0.07 | 0.01 |
| Lead | 5 | 0.05 | 0.01 | 0.09 | 0.01 | 0.06 | 0.01 | 0.08 | 0.01 |
| Iron | 4 | 0.9 | 0.24 | 1.1 | 0.22 | 5.8 | 0.24 | 1.2 | 0.2 |
| Manganese | 2.5 | 0.06 | 0.01 | 0.06 | 0.01 | 0.13 | 0.01 | 0.05 | 0.01 |
| Cadmium | 2 | 0.01 | 0.001 | 0.01 | 0.001 | 0.02 | 0.001 | 0.01 | 0.001 |
| Chromium | 1.5 | 0.14 | 0.01 | 0.03 | 0.01 | 0.04 | 0.01 | 0.23 | 0.01 |
| Vanadium | 2 | 0.03 | 0.01 | 0.02 | 0.01 | 0.04 | 0.01 | 0.01 | 0.11 |

**Notes:**

All units are $ug/m^3$

All samples collected over a 24 hour time period

MAX. = Maximum concentration

Mean = geometric mean concentration

DL = 0.01 $ug/m^3$ for most metals

**3.3**     **Air Sampling Results for Polychlorinated Biphenyls and Chlorobenzenes**

**3.3.1**     **Historical Polychlorinated Biphenyl Air Monitoring Results**

Ambient air monitoring for PCBs had been carried out in the vicinity of the CWML SV

Site, on an intermittent basis, from November, 1985 to January, 1990.   The PCB (total)

(PCBTOT) data was obtained from West Central Region (WCR) of MOE.   A comparison of

these PCBTOT results the concentrations in Table VI indicated that many of the levels that

were observed during the 1985-90 period were much higher than "typical" urban or rural

concentrations (see Section 1.2.5.2 above).   They are, however, in the same range as has been

observed in the vicinity of some Superfund sites, spill areas, or other locally influenced sites.   It

was also noted that the higher PCB concentrations were typically observed in the warmest

weather.   However, since no information was provided on the on-site activities, no firm

conclusions can be made with regards to temperature effects versus (vs.) other effects.   One

would expect a stronger temperature effect (i.e., higher concentration for higher temperatures)

for the lower chlorinated homologs due to their higher vapor pressure ($P_{vap}$).   Unfortunately,

the historical PCB data that was available contained only PCBTOT concentrations, even

though analysis had been carried out for about 70 PCB congeners.

**3.3.2**     **Pre-Phase   3   Background   Polychlorinated   Biphenyl/Chlorobenzene   Air**
           **Monitoring Results**

In June, 1990, MOE WCR carried out ambient air sampling for PCB/CB at the four off-

site fixed ambient air monitoring stations to establish existing "background" concentrations of

the PCB/CB analytes, before the Site preparations began for the ENSCO incinerator.   The

results for these samples are shown in Table XXXII (below). Unfortunately, meteorological data from the Site was not available for this time period.

In general, the concentrations of PCB/CB analytes observed diminished with distance from the Site. The concentrations of PCBTOT observed at the off-site sampling locations are lower than those measured at the CWML site fenceline during the same periods, which in turn are lower than concentrations inside the containment building (which were in the tens of thousands of $ng/m^3$). Several of the fenceline samples were higher than the MOE 24 hr. guideline of 150 $ng/m^3$. This indicates that the Site itself was an ongoing source of PCB/CB **prior** to any of the incineration activities. The main sources of PCBs were believed to be one or more of the following: residual oils in transformers (although most transformers were supposed to be drained), contaminated electrical equipment, such as transformer cores and carcasses, high level PCB oils in the tank farm, PCB contaminated soils, and activities associated with the groundwater treatment system. It should be noted that there was very little disruptive activity going on at the Site during the period of these samples. The results observed are, therefore, considered to be indicative of temperature dependent volatilization of PCB.

# TABLE XXXII

## POLYCHLORINATED BIPHENYL/CHLOROBENZENE AIR SAMPLING RESULTS AT CHEMICAL WASTE MANAGEMENT LIMITED SMITHVILLE SITE, JUNE, 1990

| Sample Location Description | E350 | N1400 | S500 | SW300 | Building Duplicates | | Fence Duplicates | | Building Duplicates | | Fence line Duplicates | | SW600 Duplicates | | E350 Duplicates | | SE400 Duplicates | | NE400 Duplicates | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Date (dd/mm) from 1990 | 19/06 | 19/06 | 19/06 | 19/06 | 20/06 | 20/06 | 20/06 | 20/06 | 21/06 | 21/06 | 21/06 | 21/06 | 26/06 | 26/06 | 26/06 | 26/06 | 28/06 | 28/06 | 28/06 | 28/06 |
| hexachloroethane | | | | | | | | | | | | | | | | | | | | |
| 1,3,5-trichlorobenzene | | | | | 3.7<T | | 1.3<T | 1.3<T | 13.7 | | 1.7<T | | | | | | 1.4<T | | | |
| 1,2,4-trichlorobenzene | | | | | 535.0 | 825.5 | 4.4<T | 3.8<T | 1838.0 | 2095.9 | 16.8 | 17.3 | | | 2.4<T | 1.5<T | 3.4<T | | | 1.5<T |
| hexachlorobutadiene | | | | | | | | | | | | | | | | | | | | |
| 1,2,3-trichlorobenzene | | 1.2<T | | | 942.9 | 1462.6 | 7.2 | 9.0 | 2564.1 | 2949.6 | 31.9 | 29.1 | | 2.0<T | 4.0<T | 3.0<T | 4.1<T | | 1.7<T | 2.2<T |
| 2,4,5-trichlorotoluene | | | | | 4.7<T | | | | 4.9<T | 20.0 | | | | | | | | | | |
| 2,3,6-trichlorotoluene | | | | | | 6.5 | | | 5.3 | 13.4 | | | | | | | | | | |
| 1,2,3,5-tetrachlorobenzene | | | | | 87.7 | 126.5 | 1.4<T | | 139.7 | | 1.5<T | 1.5<T | 1.1<T | | | | | | 1.2<T | 1.0<T |
| 1,2,4,5-tetrachlorobenzene | | | | | 458.6 | 685.0 | 3.6<T | 4.0<T | 733.2 | 1043.3 | 3.5<T | 3.4<T | | | 4.3<T | | 2.3<T | 1.1<T | 1.0<T | 1.6<T |
| 2,6-trichlorotoluene | | | | | | | | | | | | | | | | | | | | |
| 1,2,3,4-tetrachlorobenzene | | 3.0<T | | | 4637.7 | 6468.3 | 22.8 | 25.3 | 6638.6 | 8089.4 | 22.7 | 20.2 | 23.1 | 2.9<T | 22.5 | 4.3<T | | 6.1 | 2.3<T | 9.0 |
| pentachlorobenzene | | | | | 2214.2 | 2359.2 | 7.0 | 8.5 | 2800.0 | 2643.1 | 8.4 | 8.0 | 3.7<T | | 4.1<T | 1.0<T | | 1.2<T | | 1.8<T |
| hexachlorobenzene | | | | | 22.5 | 25.8 | | | 29.7 | 27.4 | | | | | | | | | | |
| octachlorostyrene | | | | | 4.2<T | 5.4 | | | 4.6<T | 6.6 | | | | | | | | | | |
| PCB (total) | 6.3 | 20.2 | 11.0 | 2.3 | 21316.9 | 24814.5 | 163.9 | 208.6 | 28646.0 | 25560.2 | 208.7 | 182.2 | 50.8 | 14.4 | 28.5 | 17.4 | 13.0 | 11.7 | 8.1 | 41.8 |

## Notes:

All results in ng/m$^3$

No meteorological data was available with these sampling results. It is not known if meteorological data was being monitored.

### 3.3.3 Polychlorinated Biphenyl/Chlorobenzene Air Monitoring Results for Phase 3 Cleanup

Data for a total of 1625 ambient air samples for PCB/CB were reported in the electronic database in dbase IV™ format. This database contained only the results from PCB/CB sampling using Florasil™ sorbent tubes and analyzed by either Ortech or MOE laboratories for the 24 PCB/CB analytes using GC-ECD (see Section 2.3.2.5 above and Environmental Monitoring Manual (EMM) [214]. The electronic database contains results produced from air samples taken prior to incineration operations, during incineration operations, and after incineration operations both on-site and off-site. The exact breakdown of ambient air PCB/CB samples in the database is provided in Table XXXIII.

**TABLE XXXIII**

SMITHVILLE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AIR SAMPLING PROGRAM SUMMARY

| Site | Pre-Incineration | Incineration Operations | Post Incineration | Totals |
|---|---|---|---|---|
| 23007 | 8 | 373 | 15 | 396 |
| 23009 | 11 | 365 | 15 | 391 |
| 23011 | 12 | 370 | 15 | 397 |
| 23013 | 10 | 375 | 15 | 400 |
| Off Site Totals | 41 | 1483 | 60 | 1584 |
| 23015 (On-Site) | 2 | 39 | 0 | 41 |
| All Sites | 43 | 1522 | 60 | 1625 |

**Notes:**

1) Numbers based on queries for PCBTOT

2) Does not include spikes, blanks, duplicates or samples taken using EC Hi-Vol samplers and analyzed by Zenon Environmental Laboratories

It should be noted that P&R took additional on-site air samples for PCB/CB (as well as other SVOCs, such as PAH and PCDD/DF) during the project using the EC Hi-Vol samplers (see Section 2.3.2.5) with Teflon coated glass fiber filters and PUF/XAD-2/PUF canisters. These samples were analyzed by Zenon, using GC-LRMS and were reported in printed format only. Numerous air samples were taken over the course of the project with these samplers. However, since the data were not available electronically and it was considered to be too labor intensive to re-enter the data into an electronic format, the data produced from these samples were not used for this research.

The electronic database was divided into two datasets consisting of the 1584 off-site and 41 on-site air monitoring samples. The datasets were then statistically analyzed using SAS$^{tm}$ (SAS Institute, Cary, NC, Version 6.12) Systat$^{tm}$ (SPSS Software Products) or Excel$^{tm}$ (Microsoft, Redmond, WA) data analysis software. The descriptive statistics for the combined (i.e., 23007, 23009, 23011, and 23013 stations) off-site ambient air monitoring results for the 24 PCB/CB analytes are shown in Table XXXIV. The descriptive statistics for the 41 on-site ambient air samples in the database are shown in Table XXXV. Typically, descriptive statistics include parameters such as arithmetic mean, standard deviation, minimum, and maximum, etc. Additional statistical analyses were performed to determine the type of distribution (normal, log-normal, etc.) using indicators such as the geometric mean, median, kurtosis, and skewness [228].

A review of Tables XXXIV and XXXV show that the PCBTOT analyte has the largest maximum value and range for any of the analytes in the ambient air PCB/CB samples taken

during the Phase 3 Cleanup. The data are log-normally distributed (as shown by skewness and kurtosis). The PCBTOT concentrations are plotted as a function of date for: 1) all off-site monitoring locations for the project in Figure 22; and 2) the four off-site air monitoring stations separately in Figure 23 (below).

**TABLE XXXIV**

BASIC STATISTICS FOR OFF-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AMBIENT AIR MONITORING RESULTS

| | PCBDI | PCBTRI | PCBTET | PCBPNT | PCBHEX | PCBHEPT | PCBOCT | PCBNON |
|---|---|---|---|---|---|---|---|---|
| n | 1584 | 1584 | 1584 | 1584 | 1584 | 1584 | 1584 | 1584 |
| Minimum | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Maximum | 28.8 | 32.2 | 41.1 | 16.9 | 6.5 | 5.0 | 1.2 | 0.4 |
| Range | 28.2 | 32.2 | 41.1 | 16.9 | 6.5 | 5.0 | 1.2 | 0.4 |
| Median | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Mean | 0.4 | 0.5 | 0.5 | 0.5 | 0.2 | 0.2 | 0.2 | 0.2 |
| 95% CI Upper | 0.44 | 0.6 | 0.54 | 0.51 | 0.23 | 0.21 | 0.2 | 0.2 |
| 95% CI Lower | 0.33 | 0.45 | 0.4 | 0.41 | 0.2 | 0.2 | 0.2 | 0.2 |
| Std. Error | 0.027 | 0.038 | 0.035 | 0.027 | 0.005 | 0.004 | 0.001 | 0.0 |
| Std. Dev | 1.06 | 1.52 | 1.38 | 1.07 | 0.21 | 0.17 | 0.026 | 0.009 |
| Variance | 1.11 | 2.32 | 1.9 | 1.15 | 0.045 | 0.028 | 0.001 | 0.0 |
| CV | 2.75 | 2.9 | 2.92 | 2.34 | 0.98 | 0.8 | 0.13 | 0.04 |
| Skewness (G1) | 16 | 10 | 19 | 9 | 23 | 24 | 35 | -8 |
| Kurtosis (G2) | 371 | 154 | 499 | 94 | 594 | 610 | 1360 | 525 |

**TABLE XXXIV (Continued)**

BASIC STATISTICS FOR OFF-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AMBIENT AIR MONITORING RESULTS

| | PCBDEC | PCBTOT | X2HCE | X2135 | X2124 | X1HCBD | X2123 | X2T245 |
|---|---|---|---|---|---|---|---|---|
| n | 1584 | 1584 | 1580 | 1581 | 1581 | 1581 | 1581 | 1580 |
| Minimum | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Maximum | 0.2 | 83.2 | 1.0 | 7.1 | 57.0 | 3.1 | 25.2 | 1.0 |
| Range | 0.2 | 83.2 | 1.0 | 7.1 | 57.0 | 3.1 | 25.2 | 1.0 |
| Median | 0.2 | 0.2 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Mean | 0.2 | 1.3 | 1 | 1.1 | 2.2 | 1.0 | 1.3 | 1.0 |
| 95% CI Upper | 0.2 | 1.51 | 1.0 | 1.08 | 2.45 | 1.0 | 1.34 | 1.0 |
| 95% CI Lower | 0.2 | 1.13 | 1.0 | 1.04 | 2.01 | 1.0 | 1.2 | 1.0 |
| Std. Error | 0.0 | 0.095 | 0.001 | 0.011 | 0.11 | 0.002 | 0.036 | 0.001 |
| Std. Dev. | 0.007 | 3.79 | 0.036 | 0.45 | 4.44 | 0.064 | 1.43 | 0.036 |
| Variance | 0.0 | 14.37 | 0.001 | 0.200 | 19.7 | 0.004 | 2.04 | 0.001 |
| CV | 0.036 | 2.87 | 0.036 | 0.42 | 1.99 | 0.064 | 1.13 | 0.036 |
| Skewness (G1) | -28 | 11 | -28 | 9 | 7 | 18 | 9 | -28 |
| Kurtosis (G2) | 788 | 178 | 787 | 94 | 55 | 825 | 112 | 787 |

**TABLE XXXIV (Concluded)**

BASIC STATISTICS FOR OFF-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AMBIENT AIR MONITORING RESULTS

| | X2T236 | X21235 | X21245 | X2T26A | X21234 | X2PNCB | X2HCB | X2OCST |
|---|---|---|---|---|---|---|---|---|
| n | 1581 | 1581 | 1581 | 1581 | 1581 | 1581 | 1581 | 1581 |
| Minimum | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Maximum | 1.0 | 1.0 | 12.7 | 1.0 | 55.9 | 6.4 | 1.0 | 1.0 |
| Range | 1.0 | 1.0 | 12.7 | 1.0 | 55.9 | 6.4 | 1.0 | 1.0 |
| Median | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Mean | 1.0 | 1.0 | 1.0 | 1.0 | 1.3 | 1.0 | 1.0 | 1.0 |
| 95% CI Upper | 1.0 | 1.0 | 1.06 | 1.0 | 1.43 | 1.01 | 1.0 | 1.0 |
| 95% CI Lower | 0.997 | 0.997 | 1.02 | 0.997 | 1.25 | 0.998 | 0.997 | 0.997 |
| Std. Error | 0.001 | 0.001 | 0.009 | 0.001 | 0.047 | 0.004 | 0.001 | 0.001 |
| Std. Dev. | 0.036 | 0.036 | 0.36 | 0.036 | 1.88 | 0.15 | 0.036 | 0.036 |
| Variance | 0.001 | 0.001 | 0.13 | 0.001 | 3.54 | 0.022 | 0.001 | 0.001 |
| CV | 0.036 | 0.036 | 0.35 | 0.036 | 1.4 | 0.15 | 0.036 | 0.036 |
| Skewness (G1) | -28 | -28 | 23 | -28 | 18 | 31 | -28 | -28 |
| Kurtosis (G2) | 788 | 788 | 686 | 788 | 460 | 1135 | 788 | 788 |

**Notes:**

n = number of data (population)

CI = Confidence Interval

Std. Error = Standard Error

Std. Dev.= Standard Deviation

CV = Coefficient of Variance

Minimum, Maximum, Range, Sum, Median, Mean are all in ng/m$^3$

**TABLE XXXV**

**BASIC STATISTICS FOR ON-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AMBIENT AIR MONITORING RESULTS**

|  | PCBDI | PCBTRI | PCBTET | PCBPNT | PCBHEX | PCBHEPT | PCBOCT | PCBNON |
|---|---|---|---|---|---|---|---|---|
| n | 41 | 41 | 41 | 41 | 41 | 41 | 41 | 41 |
| Minimum | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Maximum | 2505 | 7371.0 | 4839.0 | 2830.0 | 1154.0 | 660.4 | 108.0 | 9.5 |
| Median | 87.4 | 90.8 | 79.1 | 49.4 | 26.1 | 12.0 | 1.5 | 0.2 |
| Mean | 290.3 | 380.9 | 328.2 | 206.5 | 116.5 | 68.5 | 14.5 | 1.3 |
| 95% CI Upper | 459.1 | 750.1 | 590.1 | 370 | 190 | 113.1 | 23.4 | 2.02 |
| 95% CI Lower | 121.6 | 11.7 | 66.2 | 43 | 44 | 24 | 5.6 | 0.61 |
| Std. Error | 83.5 | 182.7 | 129.6 | 80.9 | 36.1 | 22.1 | 4.4 | 0.35 |
| Std. Dev. | 534.7 | 1169.7 | 830 | 518.0 | 231.4 | 141.6 | 28.2 | 2.2 |
| Variance | 285945 | 1368101.9 | 688891.6 | 268363.8 | 53522.7 | 20047.0 | 794.5 | 4.97 |
| CV | 1.8 | 3.1 | 2.5 | 2.5 | 2.0 | 2.1 | 2.0 | 1.7 |
| Skewness (G1) | 3 | 6 | 5 | 4 | 3 | 3 | 3 | 2 |
| Kurtosis (G2) | 9 | 34 | 23 | 17 | 10 | 10 | 6 | 4 |

# TABLE XXXV (Continued)

BASIC STATISTICS FOR ON-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AMBIENT AIR MONITORING RESULTS

|  | PCBDEC | PCBTOT | X2HCE | X2135 | X2124 | X1HCBD | X2123 | X2T245 |
|---|---|---|---|---|---|---|---|---|
| n | 41 | 41 | 41 | 41 | 41 | 41 | 41 | 41 |
| Minimum | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Maximum | 1.2 | 18960.4 | 1.0 | 119.7 | 7207.0 | 1.0 | 3419.0 | 101.5 |
| Median | 0.2 | 396.0 | 1.0 | 1.0 | 138.0 | 1.0 | 49.4 | 1.0 |
| Mean | 0.3 | 1325.0 | 1.0 | 5.9 | 683.8 | 1.0 | 416.8 | 4.1 |
| 95% CI Upper | 0.36 | 2338.56 | 1.0 | 11.8 | 1129.5 | 1.0 | 671.2 | 9.1 |
| 95% CI Lower | 0.202 | 311.4 | 1.0 | 0.008 | 238.2 | 1.0 | 162.4 | -0.85 |
| Std. Error | 0.04 | 501.5 | 0.0 | 2.9 | 220.5 | 0.0 | 125.9 | 2.5 |
| Std. Dev. | 0.26 | 3211.3 | 0.0 | 18.7 | 1411.8 | 0.0 | 805.9 | 15.7 |
| Variance | 0.066 | 1.031E+07 | 0.0 | 348.2 | 19931133 | 0.0 | 649490 | 246.7 |
| CV | 0.91 | 2.42 | 0.0 | 3.2 | 2.1 | 0.0 | 1.9 | 3.8 |
| Skewness (G1) | 3 | 5 | . | 6 | 3 | . | 3 | 6 |
| Kurtosis (G2) | 7 | 24 | . | 37 | 11 | . | 6 | 40 |

## TABLE XXXV (Concluded)

### BASIC STATISTICS FOR ON-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
### AMBIENT AIR MONITORING RESULTS

|  | X2T236 | X21235 | X21245 | X2T26A | X21234 | X2PNCB | X2HCB | X2OCST |
|---|---|---|---|---|---|---|---|---|
| n | 41 | 41 | 41 | 41 | 41 | 41 | 41 | 41 |
| Minimum | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Maximum | 83.5 | 284.1 | 1788.0 | 46.1 | 6423.0 | 3798.0 | 106.2 | 25.8 |
| Median | 1.0 | 1.0 | 17.1 | 1.0 | 88.5 | 27.0 | 1.0 | 1.0 |
| Mean | 3.4 | 8.4 | 117.7 | 2.1 | 493.9 | 213.3 | 8.3 | 2.2 |
| 95% CI Upper | 7.5 | 22.3 | 211.7 | 4.3 | 837.1 | 408.9 | 14.4 | 3.6 |
| 95% CI Lower | -0.68 | -5.6 | 23.8 | 0.12 | 150.6 | 17.7 | 2.2 | 0.8 |
| Std. Error | 2.02 | 6.9 | 46.5 | 1.1 | 169.8 | 96.8 | 3.01 | 0.68 |
| Std. Dev. | 13.0 | 44.2 | 297.6 | 7.04 | 1087.4 | 619.8 | 19.3 | 4.4 |
| Variance | 168.2 | 1950.5 | 88581 | 49.6 | 1182414 | 384094 | 372.3 | 19.1 |
| CV | 3.8 | 5.3 | 2.5 | 3.4 | 2.2 | 2.9 | 2.3 | 2.0 |
| Skewness (G1) | 6 | 6 | 5 | 6 | 5 | 5 | 4 | 5 |
| Kurtosis (G2) | 39 | 41 | 26 | 41 | 23 | 30 | 17 | 22 |

**Notes:**

n = number of data (population)

CI = Confidence Interval

Std. Error = Standard Error

Std. Dev.= Standard Deviation

CV = Coefficient of Variance

Minimum, Maximum, Range, Sum, Median, Mean are all in $ng/m^3$
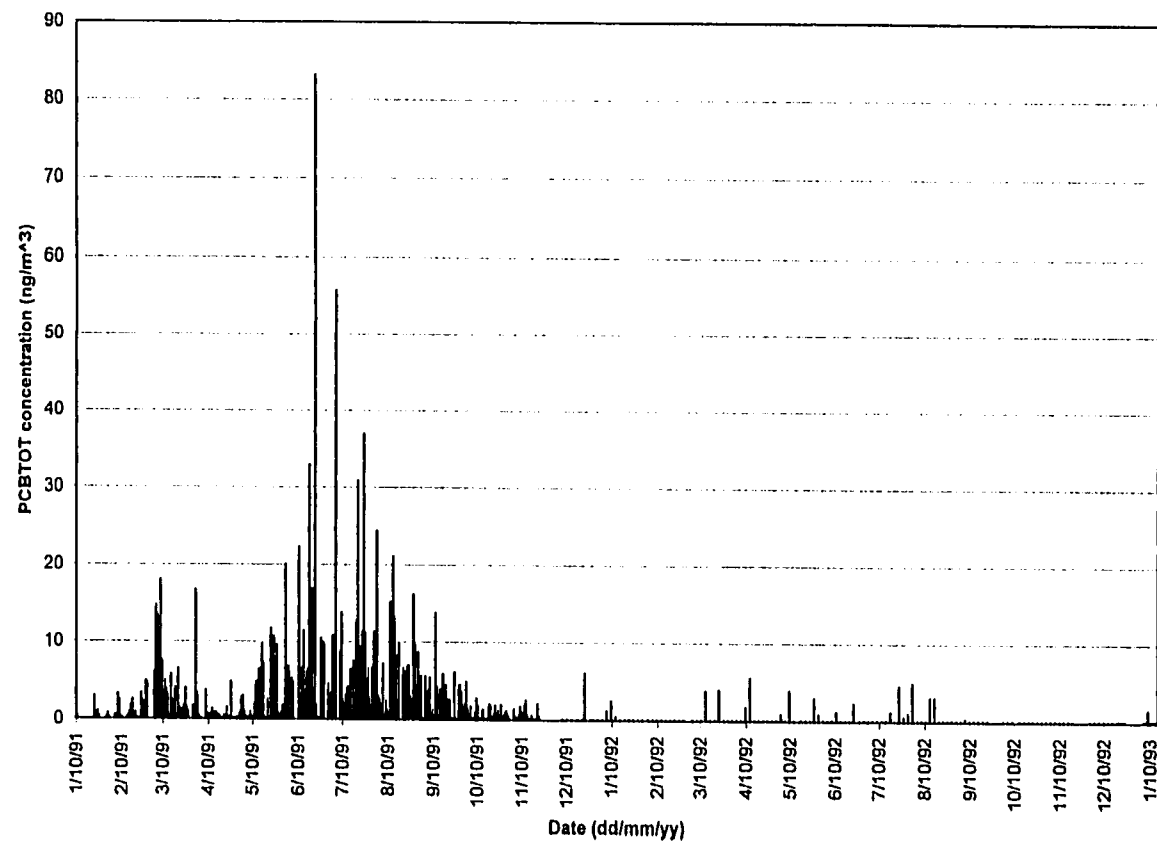
Figure 22.    Polychlorinated biphenyl concentrations for off-site ambient air samples.
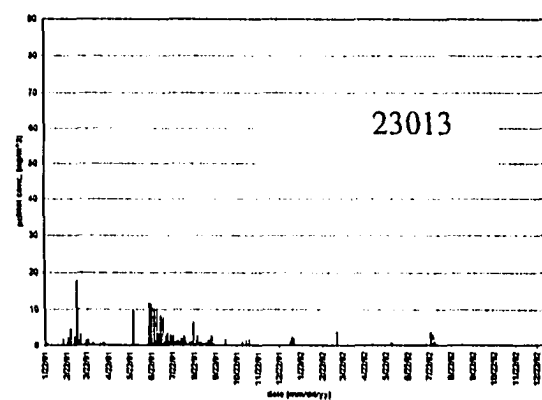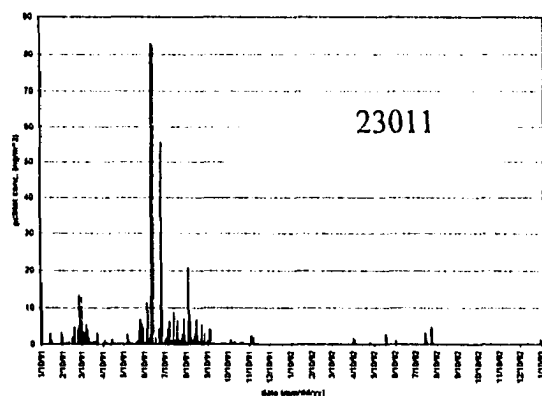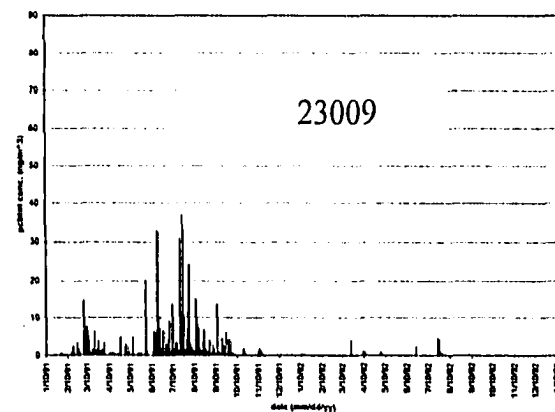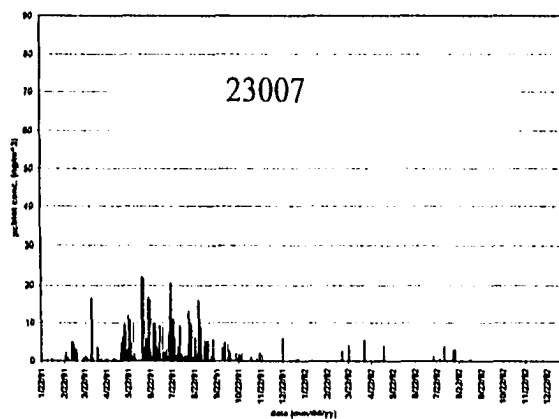
Figure 23. Ambient air total polychlorinated biphenyl concentrations by air monitoring station locations.

The descriptive statistics for PCBTOT from the off-site air monitoring samples are summarized below in Table XXXVI. Note that the air monitoring site 23013 data appears to have different properties than data from the other three air monitoring sites.

## TABLE XXXVI

### BASIC STATISTICS FOR TOTAL POLYCHLORINATED BIPHENYL BY AIR MONITORING STATION

|          | All Sites | 23007 | 23009 | 23011 | 23013 |
|----------|-----------|-------|-------|-------|-------|
| n        | 1584      | 396   | 391   | 397   | 400   |
| MIN.     | 0.2       | 0.2   | 0.2   | 0.2   | 0.2   |
| MAX.     | 83.2      | 22.3  | 37.0  | 83.2  | 18.0  |
| Mean     | 1.3       | 1.6   | 1.6   | 1.4   | 0.7   |
| Median   | 0.2       | 0.2   | 0.2   | 0.2   | 0.2   |
| Std Dev. | 4.4       | 3.1   | 4.0   | 5.4   | 1.6   |
| Mode     | 0.2       | 0.2   | 0.2   | 0.2   | 0.2   |
| Kurtosis | 178       | 14    | 37    | 158   | 53    |
| Skewness | 11        | 3     | 5     | 12    | 6     |

There appears to be a temporal relationship, with the highest concentrations being seen during the warmer months. However, on many dates, one or more of the air monitoring stations have PCB results that appear to be elevated relative to the other sites. Most of the higher PCB concentrations could not immediately be correlated with specific Site activities. Because the original purpose of the air monitoring was to determine compliance with the MOE objective (150 ng/m3) and all samples were below this, no further analysis of the data by P&R was funded by MOE. Some sample extracts from May to July, 1991 that showed elevated

PCB concentrations by GC-ECD analysis were reanalyzed by GC-MS and found to contain PCB and elevated phthalate concentrations, possibly from the sample extraction steps. Unfortunately, quantitative analysis by GC-MS was not possible and the magnitude of the contaminations' effect on the results cannot be determined precisely. Changes were made in the sample cleanup procedures to reduce this problem in later samples.

### 3.3.4 Trace Atmospheric Gas Analysis Polychlorinated Biphenyl Air Monitoring Results

TAGA sampling was performed in the vicinity of the CWML site before, during and after the Phase 3 Cleanup. The highest concentrations (and the only samples to exceed the MOE guideline of 450 ng/m$^3$, ½ hr average) were observed in early February, 1991, **prior** to the incineration of any PCB materials and are believed to be due to fugitive emissions from Site activities, specifically operation of the shredder. As a result of these monitoring results, shredder operations were restricted until a carbon filtration unit (CFU) was installed on the containment building.

During the stack testing the TAGA was able to track the incinerator stack exhaust plume so that on a number of occasions the plume was visibly impinging on the TAGA unit. Polychlorinated biphenyl concentrations observed during these periods of plume impingement were non-detectable.

A total of 251 TAGA air samples were reported. No samples taken by the TAGA during incineration of PCBs exceeded the MOE ½ hr guideline of 450 ng/m$^3$. Descriptive statistics for the TAGA results are summarized in Table XXXVII (below).

Note that the TriPCB was present at the highest concentration in detected samples (67 of 251) and the PentaPCB homolog was only detected in 17 out of 251 samples. The TAGA results have been reported in detail by MOE [229];[224]; [223].

## TABLE XXXVII

### SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
### POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| June 1990 Background | Temperature (°C) | MIN WS (km/hr) | MAX WS (km/hr) | PCBTOT (ng/m³) ½ hr ave. | PCBDI (ng/m³) ½ hr ave. | PCBTRI (ng/m³) ½ hr ave | PCBTET (ng/m³) ½ hr ave | PCBPNT (ng/m³) ½ hr ave |
|---|---|---|---|---|---|---|---|---|
| n for number | 23 | 23 | 23 | 23 | 0 | 0 | 0 | 0 |
| Mean | 22.4 | 17.4 | 31.1 | 66.2 | | | | |
| Standard Error | 0.6 | 2.1 | 2.6 | 4.1 | | | | |
| Median | 23 | 15 | 30 | 58.8 | | | | |
| Mode | 23 | 10 | 25 | 85.6 | | | | |
| Std. Dev. | 2.9 | 9.9 | 12.7 | 19.6 | | | | |
| Sample Variance | 8.2 | 97.4 | 161.3 | 382.2 | | | | |
| Kurtosis | 0.05 | -0.86 | -0.87 | -1.13 | | | | |
| Skewness | -1.0 | 0.27 | 0.28 | -0.4 | | | | |
| Range | 9 | 35 | 45 | 52.8 | | | | |
| Minimum | 17 | 0 | 10 | <34.2 (DL) | <5.2 (DL) | <6.5 (DL) | <7.5 (DL) | <15 (DL) |
| Maximum | 26 | 35 | 55 | <87 (DL) | <24 (DL) | <18 (DL) | <23 (DL) | <42 (DL) |

**Notes:**

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

# TABLE XXXVII (Continued)

## SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
## POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| January 1991 Prior To Incineration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Statistic | Temperature (°C) | MIN. WS (km/hr) | MAX. WS (km/hr) | PCBTOT (ng/m³) ½ hr. ave. | PCBDI (ng/m³) ½ hr. ave | PCBTRI (ng/m³) ½ hr. ave | PCBTET (ng/m³) ½ hr. ave | PCBPNT (ng/m³) ½ hr. ave |
| n | 26 | 26 | 26 | 26 | 0 | 0 | 0 | 0 |
| Mean | 2.6 | 10.8 | 26.2 | 75.8 | | | | |
| Standard Error | 0.42 | 2.2 | 4.3 | 12.5 | | | | |
| Median | 3 | 5 | 17.5 | 53.4 | | | | |
| Mode | 5 | 0 | 10 | 53.4 | | | | |
| Std. Dev. | 2.12 | 11.29 | 21.8 | 63.9 | | | | |
| Sample Variance | 4.49 | 127.4 | 476.6 | 4084.7 | | | | |
| Kurtosis | -1 | -1 | -1 | 6 | | | | |
| Skewness | 0 | 0 | 0 | 2 | | | | |
| Range | 6 | 30 | 65 | 243.4 | 12.6 | 7.6 | 4.5 | 5.6 |
| Minimum | -1 | 0 | 0 | <36.6 (DL) | <6.4 | <7.4 | <6.5 | <9.4 |
| Maximum | 5 | 30 | 65 | <280 | <19 | <15 | <11 | <15 |

<u>Notes:</u>

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

**TABLE XXXVII (Continued)**

SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| January-February 1991 Incinerator on Hot Standby | Temperature (°C) | MIN WS (km/hr) | MAX WS (km/hr) | PCBTOT Reported (ng/m³) 1/2 hr ave. | PCBTOT Detected (ng/m³) 1/2 hr ave. | PCBDI Detected (ng/m³) 1/2 hr ave. | PCBTRI Detected (ng/m³) 1/2 hr ave. | PCBTET Detected (ng/m³) 1/2 hr ave. | PCBPNT Detected (ng/m³) 1/2 hr ave. |
|---|---|---|---|---|---|---|---|---|---|
| n | 61 | 61 | 61 | 61 | 13 | 10 | 11 | 11 | 4 |
| Mean | 4.6 | 12.6 | 25.4 | 78.2 | 217.4 | 50.2 | 106.3 | 78.3 | 54.5 |
| Standard Error | 0.4 | 1.3 | 2.1 | 10.1 | 57.6 | 12.2 | 26.0 | 20.9 | 12.38416 |
| Median | 5 | 10 | 25 | 53.4 | 117.8 | 33.4 | 61 | 56 | 54.5 |
| Mode | 6 | 0 | 10 | 32.6 | 0 | 15.5 | 36.3 | 33 | 75.9 |
| Std. Dev. | 3.0 | 10.23094 | 16.6 | 79.0 | 207.6 | 38.7 | 86.5 | 69.3 | 24.8 |
| Sample Variance | 9.1 | 104. | 277.7 | 6253. | 43096.8 | 1496.7 | 7476.5 | 4802.8 | 613.5 |
| Kurtosis | 1.4 | -0.99 | -0.49 | 4.2 | -0.32 | -1.2 | -0.75 | 3.17 | -6 |
| Skewness | 0.66 | 0.3 | 0.5 | 2.2 | 0.98 | 0.74 | 0.93 | 1.7 | 0 |
| Range | 14 | 35 | 65 | 354.1 | 600 | 94.49 | 223.7 | 232.5 | 42.9 |
| Minimum | -1 | 0 | 0 | < 25.9 (DL) | 21.1 | 15.5 | 36.3 | 17.4 | 33 |
| Maximum | 13 | 35 | 65 | 600 | 600 | 110 | 260 | 250 | 75.9 |

**Notes:**

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

TABLE XXXVII (Continued)

SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| February, 1991 during Incineration | Temperature (°C) | MIN. WS (km/hr) | MAX. WS (km/hr) | PCBTOT Reported (ng/m³) 1/2 hr ave. | PCBTOT Detected (ng/m³) 1/2 hr ave. | PCBDI (ng/m³) 1/2 hr ave. | PCBTRI (ng/m³) 1/2 hr ave. | PCBTET (ng/m³) 1/2 hr ave. | PCBPNT (ng/m³) 1/2 hr ave. |
|---|---|---|---|---|---|---|---|---|---|
| n | 109 | 109 | 109 | 109 | 30 | 25 | 34 | 13 | 2 |
| Mean | -1.8 | 11.3 | 21.4 | 47.2 | 68.6 | 26.8 | 33.6 | 24.3 | 18.7 |
| Standard Error | 0.55 | 1.0 | 1.3 | 3.4 | 8.4 | 2.40 | 3.36 | 2.9 | 1.3 |
| Median | -1 | 10 | 20 | 29.1 | 47.7 | 23.43 | 26.4 | 18.8 | 18.8 |
| Mode | 0 | 10 | 20 | 29.1 | 41.7 | 15.18 | 20.79 | 18.81 | |
| Std. Dev. | 5.7 | 10.6 | 13.4 | 35.3 | 46 | 12.0 | 19.61 | 10.4 | 1.8 |
| Sample Variance | 32.8 | 112. | 180.0 | 1243.0 | 2112 | 144.4 | 384.6 | 108.3 | 3.2 |
| Kurtosis | -0.26 | 0.92 | 0.3 | 5.0 | 2.6 | -0.73 | 4.10 | -0.93 | |
| Skewness | 0.36 | 1.1 | 0.7 | 2.05 | 1.6 | 0.80 | 2.09 | 0.71 | |
| Range | 23 | 40 | 60 | 192.7 | 189.9 | 36.15 | 78 | 30.8 | 2.5 |
| Minimum | -12 | 0 | 0 | <17.3 (DL) | 21.1 | 14.85 | 19 | 12.2 | 17.5 |
| Maximum | 11 | 40 | 60 | 211 | 211 | 51 | 97 | 43 | 20 |

**Notes:**

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

## TABLE XXXVII (Continued)

SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| April 1991 During Incineration Statistic | Temperature (°C) | MIN. WS (km/hr) | MAX. WS (km/hr) | PCBTOT (ng/m³) ½ hr. ave. | PCBDI (ng/m³) ½ hr. ave | PCBTRI (ng/m³) ½ hr. ave | PCBTET (ng/m³) ½ hr. ave | PCBPNT (ng/m³) ½ hr. ave |
|---|---|---|---|---|---|---|---|---|
| n | 28 | 28 | 28 | 27 | 21 | 22 | 19 | 11 |
| Mean | 11.8 | 21.4 | 38.2 | 124.6 | 35.02 | 69.4 | 37.4 | 38.1 |
| Standard Error | 0.55 | 2.6 | 3.7 | 16.6 | 4.0 | 8.5 | 3.9 | 3.7 |
| Median | 12 | 17.5 | 35 | 96 | 38 | 69 | 37 | 42.9 |
| Mode | 9 | 10 | 60 | 33.6 | 13.9 | 120 | 16.8 | 25.08 |
| Standard Deviation | 2.89 | 13.67 | 19.54 | 86.2 | 18.19 | 39.63 | 16.89 | 12.37 |
| Sample Variance | 8.32 | 186.77 | 381.88 | 7430.8 | 330.93 | 1570.61 | 285.31 | 153.04 |
| Kurtosis | -1 | -1 | 0 | -1 | -2 | -2 | -1 | -1 |
| Skewness | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 |
| Range | 10 | 50 | 80 | 273.4 | 54 | 112.5 | 54 | 36.9 |
| Minimum | 6 | 0 | 10 | <26.6 (DL) | 13 | 17.5 | 15 | 25.1 |
| Maximum | 16 | 50 | 90 | 300 | 67 | 130 | 69 | 62 |

**Notes:**

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

**TABLE XXXVII (Continued)**

SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| All Samples During Incineration Statistic | Temperature (°C) | MIN. WS (km/hr) | MAX. WS (km/hr) | PCBTOT (ng/m³) ½ hr. ave. | PCBDI (ng/m³) ½ hr. ave | PCBTRI (ng/m³) ½ hr. ave | PCBTET (ng/m³) ½ hr. ave | PCBPNT (ng/m³) ½ hr. ave |
|---|---|---|---|---|---|---|---|---|
| n | 137 | 137 | 137 | 137 | 46 | 56 | 32 | 13 |
| Mean | 1.0 | 13.4 | 24.8 | 62.4 | 30.6 | 47.7 | 32.1 | 35.1 |
| Standard Error | 0.65 | 1.02 | 1.39 | 4.96 | 2.29 | 4.52 | 2.8 | 3.73 |
| Median | 0 | 10 | 20 | 33 | 25.6 | 29.5 | 27.5 | 32 |
| Mode | 0 | 10 | 20 | 29.1 | 15.2 | 20 | 18.8 | 25.08 |
| Std. Dev. | 7.62 | 11.96 | 16.29 | 58.03 | 15.53 | 33.79 | 15.81 | 13.43 |
| Sample Variance | 57.99 | 142.99 | 265.22 | 3367.2 | 241.23 | 1142.03 | 249.93 | 180.49 |
| Kurtosis | -1 | 0 | 1 | 4 | -1 | 0 | -1 | -1 |
| Skewness | 0 | 1 | 1 | 2 | 1 | 1 | 1 | 0 |
| Range | 28 | 50 | 90 | 282.7 | 54 | 112.5 | 56.8 | 44.5 |
| Minimum | -12 | 0 | 0 | <17.3 (DL) | 13 | 17.5 | 12.2 | 17.5 |
| Maximum | 16 | 50 | 90 | 300 | 67 | 130 | 69 | 62 |

**Notes:**

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

**TABLE XXXVII (Continued)**

SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| April 1993 After Incineration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Statistic | Temperature ($^o$C) | MIN. WS (km/hr) | MAX. WS (km/hr) | PCBTOT (ng/m$^3$) ½ hr. ave. | PCBDI (ng/m$^3$) ½ hr. ave | PCBTRI (ng/m$^3$) ½ hr. ave | PCBTET (ng/m$^3$) ½ hr. ave | PCBPNT (ng/m$^3$) ½ hr. ave |
| n | 30 | 30 | 30 | 30 | 0 | 0 | 0 | 0 |
| Mean | 8.4 | 29.5 | 44.5 | 64.7 | | | | |
| Standard Error | 1.13 | 2.09 | 2.6 | 2.56 | | | | |
| Median | 10 | 30 | 45 | 58 | | | | |
| Mode | 0 | 30 | 30 | 71 | | | | |
| Std. Dev. | 6.19 | 11.47 | 14.22 | 14.03 | | | | |
| Sample Variance | 38.32 | 131.64 | 202.33 | 196.71 | | | | |
| Kurtosis | -1 | -1 | -1 | 3 | | | | |
| Skewness | 0 | 0 | 0 | 2 | | | | |
| Range | 18 | 40 | 50 | 54.1 | | | | |
| Minimum | -1 | 10 | 20 | <50.9 (DL) | | | | |
| Maximum | 17 | 50 | 70 | <105 (DL) | | | | |

**Notes:**

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

## TABLE XXXVII (Concluded)

### SUMMARY OF BASIC STATISTICS FOR TRACE ATMOSPHERIC GAS ANALYSIS
### POLYCHLORINATED BIPHENYL AIR MONITORING RESULTS

| All Data Combined Statistic | Temperature (°C) | MIN. WS (km/hr) | MAX. WS (km/hr) | PCBTOT (ng/m³) ½ hr. ave. | PCBDI (ng/m³) ½ hr. ave | PCBTRI (ng/m³) ½ hr. ave | PCBTET (ng/m³) ½ hr. ave | PCBPNT (ng/m³) ½ hr. ave |
|---|---|---|---|---|---|---|---|---|
| n | 251 | 251 | 251 | 251 | 56 | 67 | 43 | 17 |
| Mean | 4.7 | 15.5 | 27.9 | 66.7 | 34.07 | 57.3 | 43.9 | 39.7 |
| Standard Error | 0.55 | 0.79 | 1.07 | 3.69 | 2.99 | 6.19 | 6.37 | 4.35 |
| Median | 4 | 15 | 25 | 52.1 | 25.6 | 36.3 | 33 | 33 |
| Mode | 0 | 10 | 20 | 29.1 | 15.2 | 20 | 18.8 | 25.1 |
| Std. Dev. | 8.77 | 12.45 | 17.01 | 58.43 | 22.36 | 50.63 | 41.77 | 17.94 |
| Sample Variance | 76.98 | 155.05 | 289.32 | 3414.41 | 500.10 | 2563.35 | 1744.39 | 321.96 |
| Kurtosis | 0 | 0 | 0 | 7 | 3 | 5 | 14 | 0 |
| Skewness | 0 | 1 | 1 | 3 | 2 | 2 | 3 | 1 |
| Range | 38 | 50 | 90 | 362 | 97 | 243 | 238 | 58 |
| Minimum | -12 | 0 | 0 | <17.3 (DL) | 13 | 17.5 | 12.2 | 17.5 |
| Maximum | 26 | 50 | 90 | 600 | 110 | 260 | 250 | 75.9 |

**Notes:**

n = the number of samples reported for the PCB homologs

n = 0 if the homolog was not detected in any of the samples

WS = wind speed

DL = detection limit

## 3.4    Polychlorinated Dibenzo-p-dioxin/Dibenzofuran Air Sampling Results

The MOE air sampler with a rotary vane gas meter (see Figure 14) was used exclusively for the PCDD/DF air samples at the off-site monitoring stations. These PCDD/DF air samples were analyzed for the seventeen (17) 2,3,7,8 isomers (see Table XXXVIII) and the tetra-octa homolog groups. Unfortunately, the Dioxins Analysis Section of LSB did not report the data to the LIS in electronic format, so the PCDD/DF data was only available in printed format. A preliminary, visual, review of the data showed that no samples exceeded the MOE guidelines (20 pg/m$^3$ I-TEQ, for 24-72 hr samples), most samples were ND for many of the 2,3,7,8 isomers, or had only low levels detected. It was also discovered during this preliminary review that the many of the early MOE data (prior to April 1991), had been over-reported by 1000X due to an error in converting from picograms (pg) to femtograms (fg). In order to perform some statistical analysis and correct the reported I-TEQ value, only those isomers that were detected in a sample were entered into an Excel™ spreadsheet. Non-detected isomers were given a value of 0. Because of time considerations (for data entry), the homolog data was not used for this research.

The PCDD/DF air samples for the project are summarized by site location in Table XXXIX. The off-site PCDD/DF air sampling results (in pg/m$^3$, TEQ) for the Phase 3 Cleanup are provided in Table XL. The PCDD/DF results as a function of sample date are shown in Figure 24. Some summary statistics for the 2,3,7,8–PCDD/DF data (all sites) are provided in Table XLI. Summary statistics for the PCDD/DF I TEQ are provided for all data combined and each site in Table XLII.

**TABLE XXXVIII**

2, 3, 7, 8 POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN ISOMERS
AND SAS™ ANALYTE CODES

| | Compound | TEF | SAS Analyte Code |
|---|---|---|---|
| 1 | 2, 3, 7, 8-TeCDD | 1 | Cl4DD1 |
| 2 | 1, 2, 3, 7, 8-PeCDD | 0.5 | Cl5DD1 |
| 3 | 1, 2, 3, 4, 7, 8-HxCDD | 0.1 | Cl6DD1 |
| 4 | 1, 2, 3, 6, 7, 8-HxCDD | 0.1 | Cl6DD2 |
| 5 | 1, 2, 3, 7, 8, 9-HxCDD | 0.1 | Cl6DD3 |
| 6 | 1, 2, 3, 4, 6, 7, 8-HPCDD | 0.01 | Cl7DD1 |
| 7 | OCDD | 0.001 | Cl8DD1 |
| 8 | 2, 3, 7, 8-TeCDF | 0.1 | Cl4DF1 |
| 9 | 1, 2, 3, 7, 8-PeCDF | 0.05 | Cl5DF1 |
| 10 | 2, 3, 4, 7, 8-PeCDF | 0.5 | Cl5DF2 |
| 11 | 1, 2, 3, 4, 7, 8-HxCDF | 0.1 | Cl6DF1 |
| 12 | 1, 2, 3, 6, 7, 8-HxCDF | 0.1 | Cl6DF2 |
| 13 | 2, 3, 4, 6, 7, 8-HxCDF | 0.1 | Cl6DF3 |
| 14 | 1, 2, 3, 7, 8, 9-HxCDF | 0.1 | Cl6DF4 |
| 15 | 1, 2, 3, 4, 6, 7, 8-HPCDF | 0.01 | Cl7DF1 |
| 16 | 1, 2, 3, 4, 7, 8, 9-HPCDF | 0.01 | Cl7DF2 |
| 17 | OCDF | 0.001 | Cl8DF1 |
| | Sum of 2, 3, 7, 8 PCDD/DF compounds | | 2378TOT |

**TABLE XXXIX**

SUMMARY OF POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN
AMBIENT AIR SAMPLES

|  | 23007 | 23009 | 23011 | 23013 | All Sites |
|---|---|---|---|---|---|
| Before Incineration | 1 | 2 | 2 | 1 | 6 |
| During Incineration | 58 | 42 | 40 | 38 | 178 |
| After Incineration | 0 | 0 | 0 | 1 | 1 |
| Total For Project | 59 | 44 | 42 | 40 | 185 |

**Notes:**

1)   Based on reported results

2)   Does not include spikes, blanks, and duplicates

3)   A number of PCDD/DF air samples were taken on-site during the Phase 3
     Cleanup. However, these results were only available in printed format and
     were not used in this research.

**TABLE XL**

POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN DATA[a]
FOR OFF-SITE AIR MONITORING STATIONS

| Sample Date (mm/dd/yy) | 23007 | 23009 | 23011 | 23013 |
|---|---|---|---|---|
| 01/29/91 | 2.71E-03 | 2.21E-04 | 3.31E-04 | 4.07E-04 |
| 02/01/91 | | 2.35E-04 | 2.35E-04 | |
| 02/14/91 | 1.27E-02 | 1.21E-02 | 1.12E-02 | 1.25E-02 |
| 02/26/91 | 2.02E-02 | 3.51E-03 | | 1.82E-02 |
| 03/16/91 | 2.16E-03 | 1.54E-03 | 8.47E-03 | 1.10E-03 |
| 03/31/91 | 5.01E-04 | 5.89E-04 | ND | 5.85E-04 |
| 04/05/91 | 2.07E-03 | 5.52E-02 | 3.46E-02 | 5.43E-03 |
| 04/16/91 | 1.11E-03 | 1.05E-03 | 8.76E-04 | 9.73E-04 |
| 04/21/91 | 1.41E-03 | 2.31E-03 | 8.07E-03 | 2.48E-01 |
| 05/03/91 | 9.04E-02 | 4.74E-03 | 3.02E-02 | 4.99E-03 |
| 05/07/91 | 7.65E-03 | 8.92E-02 | 1.32E-03 | |
| 05/14/91 | 1.10E-03 | 4.86E-03 | 1.64E-03 | 1.35E-03 |
| 05/24/91 | 3.04E-02 | 5.81E-02 | 2.37E-02 | 6.33E-03 |
| 05/31/91 | 8.49E-03 | 6.91E-04 | 1.87E-02 | 1.82E-02 |
| 06/12/91 | ND | 4.97E-04 | ND | ND |
| 06/20/91 | 3.57E-03 | 3.91E-03 | 4.62E-03 | 6.27E-03 |
| 06/30/91 | 9.55E-03 | 2.16E-02 | 1.89E-02 | 2.78E-02 |
| 07/11/91 | 1.67E-03 | 5.76E-03 | 1.23E-02 | 1.95E-03 |
| 07/21/91 | 5.70E-04 | 1.51E-02 | 2.84E-04 | 3.59E-04 |
| 07/29/91 | 4.70E-04 | 5.40E-04 | 1.21E+00 | 2.24E-04 |
| 08/05/91 | 1.08E-02 | 1.76E-02 | 1.38E-03 | 1.33E-02 |
| 08/13/91 | | 7.76E-04 | | |
| 08/21/91 | 3.09E-04 | 5.56E-04 | 1.84E-04 | 2.52E-04 |
| 09/25/91 | 6.12E-03 | 3.54E-02 | 1.20E-02 | |
| 10/04/91 | 1.24E-02 | 2.10E-02 | 1.05E-02 | |
| 10/11/91 | 1.28E-02 | 2.25E-02 | 1.26E-02 | |
| 10/19/91 | ND | | ND | ND |
| 10/27/91 | | 1.67E-03 | ND | ND |
| 11/07/91 | 2.59E+00 | 9.90E-03 | 1.37E-02 | ND |
| 11/14/91 | 2.12E-02 | 2.23E-02 | 1.89E-02 | 9.53E-03 |
| 11/21/91 | 8.55E-03 | 1.00E-02 | 5.88E-01 | 5.17E-03 |
| 12/13/91 | 1.12E-02 | | | |
| 12/24/91 | ND | ND | 8.87E-02 | |

**Notes:**

ND = not detected for all 2,3,7,8 isomers

[a]      Data in $pg/m^3$ I-TEQ

Limit of detection was different for each sample but typically 1E-3 to 1 E-4 $pg/m^3$ I-TEQ

**TABLE XL (Continued)**

POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN DATA[a]
FOR OFF-SITE AIR MONITORING STATIONS

| Sample Date (mm/dd/yy) | 23007 | 23009 | 23011 | 23013 |
|---|---|---|---|---|
| 01/05/92 | | | 9.10E-02 | 1.48E-02 |
| 01/13/92 | 1.87E-02 | | | |
| 01/25/92 | 3.01E-03 | | 2.01E-03 | 2.32E-03 |
| 02/04/92 | 1.41E-02 | 2.99E-02 | 2.50E-02 | 1.57E-02 |
| 02/09/92 | | 2.18E-03 | 9.10E-03 | |
| 02/22/92 | 2.39E-03 | 4.13E-03 | 7.34E-03 | |
| 03/10/92 | 1.14E-03 | | | |
| 03/15/92 | | 7.86E-04 | | |
| 03/21/92 | | 3.54E-02 | 2.35E-02 | |
| 03/31/92 | 1.56E-02 | 9.77E-03 | | |
| 04/06/92 | | | 1.68E-03 | |
| 04/12/92 | | 2.42E-03 | | 5.86E-04 |
| 04/20/92 | | | | 4.86E-03 |
| 04/26/92 | 8.51E-04 | | 9.53E-04 | 2.95E-03 |
| 05/01/92 | 3.76E-03 | | | 5.28E-03 |
| 05/10/92 | | | | 5.08E-03 |
| 05/18/92 | 6.15E-03 | | | ND |
| 05/24/92 | 4.43E-03 | | | 6.26E-03 |
| 05/30/92 | 4.08E-03 | | | |
| 06/08/92 | 2.09E-03 | | | |
| 06/13/92 | 1.93E-03 | | | |
| 06/26/92 | 1.11E-03 | | | |
| 07/13/92 | 3.02E-03 | 1.84E-03 | | |
| 07/22/92 | ND | | 2.70E-03 | |
| 07/30/92 | | | 8.57E-04 | 2.85E-03 |
| 08/07/92 | | | 1.10E-03 | |
| 08/14/92 | | | | 5.46E-03 |
| 08/22/92 | 3.39E-03 | | | |
| 08/29/92 | | ND | | 7.00E-04 |

**Notes:**

ND = not detected for all 2,3,7,8 isomers

[a]     Data in $pg/m^3$ I-TEQ

Limit of detection was different for each sample but typically 1E-3 to 1 E-4 $pg/m^3$ I-TEQ

**TABLE XL (Concluded)**

POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN DATA[a]
FOR OFF-SITE AIR MONITORING STATIONS

| Sample Date (mm/dd/yy) | 23007 | 23009 | 23011 | 23013 |
|---|---|---|---|---|
| 09/11/92 | 4.93E-02 | 3.95E-02 | | |
| 09/19/92 | 4.81E-02 | | | |
| 09/19/92 | 6.54E-04 | | | |
| 10/03/92 | | 1.33E-01 | | |
| 10/11/92 | 1.80E-03 | | | |
| 10/11/92 | ND | | | |
| 10/21/92 | 1.78E-03 | | 2.68E-03 | |
| 10/30/92 | 5.04E-03 | | 6.33E-03 | |
| 11/05/92 | 5.42E-03 | | | |
| 11/11/92 | 2.82E-02 | | | |
| 11/18/92 | 3.07E-02 | | | |
| 12/03/92 | 2.78E-03 | | | |
| 12/10/92 | | 1.38E-01 | | 6.62E-02 |
| 12/17/92 | 2.22E-02 | | | |
| 01/10/93 | | | | 1.95E-03 |

**Notes:**

ND = not detected for all 2,3,7,8 isomers

[a]    Data in pg/m$^3$ I-TEQ

Limit of detection was different for each sample but typically 1E-3 to 1 E-4 pg/m$^3$ I-TEQ
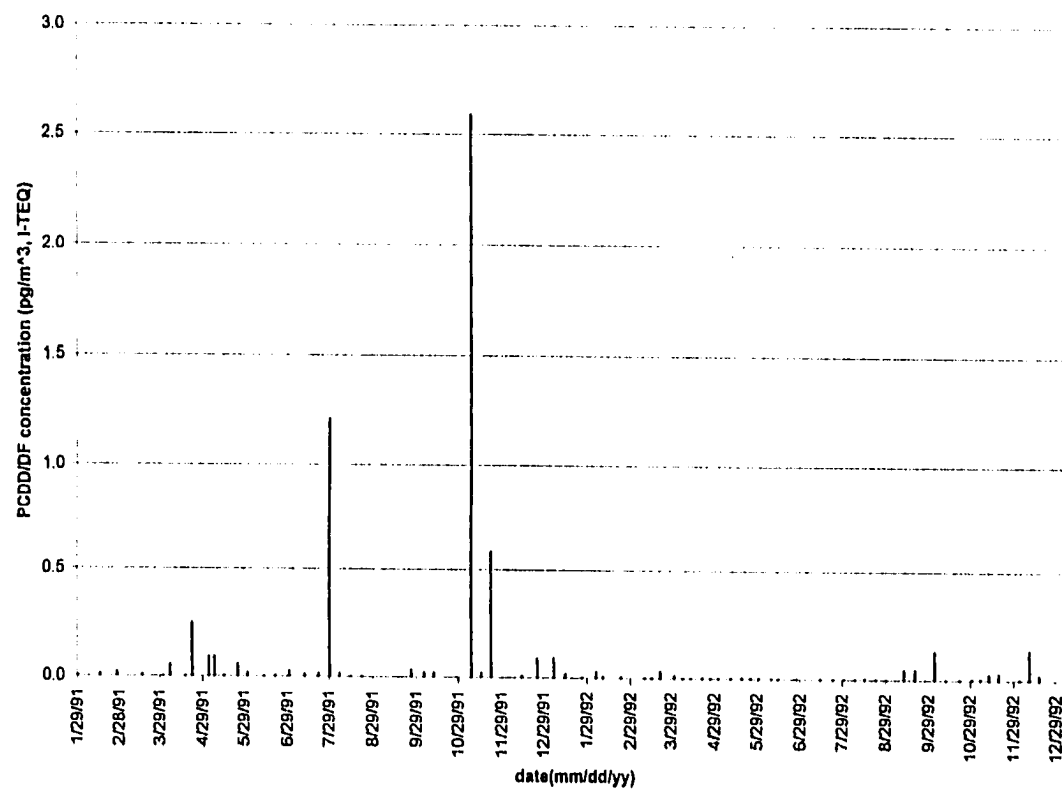
Figure 24.  Ambient air polychlorinated dibenzo-p-dioxin/dibenzofuran toxic equivalency concentration versus date. (MOE Guideline = 20 pg/m³.)

## TABLE XLI

### BASIC STATISTICS FOR OFF-SITE AMBIENT AIR POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN 2, 3, 7, 8 ISOMER ANALYSIS (DETECTS ONLY)

| 2378 PCDD/DF Compound | Cl4DF1 | Cl4DD1 | Cl5DF1 | Cl5DF2 | Cl5DD1 | Cl6DF1 | Cl6DF2 | Cl6DF3 | Cl6DF4 |
|---|---|---|---|---|---|---|---|---|---|
| n Detected | 80 | 1 | 13 | 22 | 3 | 41 | 18 | 15 | 2 |
| n Non-Detected | 105 | 184 | 172 | 163 | 182 | 144 | 167 | 170 | 183 |
| Minimum | 1.45E-03 | 2.91E-01 | 5.81E-04 | 5.17E-03 | 5.06E-03 | 1.04E-03 | 1.54E-03 | 1.85E-03 | 1.70E-02 |
| Maximum | 2.55E-01 | 2.91E-01 | 5.89E-02 | 8.50E-01 | 6.68E-01 | 1.30E-01 | 4.37E-02 | 2.20E-01 | 1.49E-01 |
| Range | 2.54E-01 | 0.00E+00 | 5.83E-02 | 8.45E-01 | 6.62E-01 | 1.29E-01 | 4.22E-02 | 2.18E-01 | 1.32E-01 |
| Mean | 1.61E-02 | 2.91E-01 | 1.29E-02 | 9.52E-02 | 2.31E-01 | 1.10E-02 | 7.26E-03 | 2.59E-02 | 8.31E-02 |
| 99% Confidence Interval | 7.16E-03 |  | 9.15E-03 | 7.29E-02 | 3.59E-01 | 5.35E-03 | 3.94E-03 | 2.39E-02 | 1.09E-01 |
| 95% Confidence Interval | 8.53E-03 |  | 1.09E-02 | 8.69E-02 | 4.27E-01 | 6.38E-03 | 4.69E-03 | 2.85E-02 | 1.30E-01 |
| 90% Confidence Interval | 1.12E-02 |  | 1.43E-02 | 1.14E-01 | 5.62E-01 | 8.38E-03 | 6.17E-03 | 3.75E-02 | 1.70E-01 |
| Standard Deviation | 3.89E-02 |  | 2.01E-02 | 2.08E-01 | 3.78E-01 | 2.08E-02 | 1.02E-02 | 5.64E-02 | 9.35E-02 |
| Sample Variance | 1.52E-03 |  | 4.03E-04 | 4.33E-02 | 1.43E-01 | 4.34E-04 | 1.03E-04 | 3.18E-03 | 8.74E-03 |
| Standard Error | 4.35E-03 | 0.00E+00 | 5.57E-03 | 4.43E-02 | 2.18E-01 | 3.25E-03 | 2.39E-03 | 1.46E-02 | 6.61E-02 |
| Median | 6.80E-03 | 2.91E-01 | 2.60E-03 | 2.14E-02 | 2.17E-02 | 5.82E-03 | 3.28E-03 | 5.69E-03 | 8.31E-02 |
| Mode |  |  |  |  |  |  |  |  |  |
| Kurtosis | 2.86E+01 |  | 2.12E+00 | 9.57E+00 |  | 2.75E+01 | 1.05E+01 | 1.17E+01 |  |
| Skewness | 5.27E+00 |  | 1.82E+00 | 3.16E+00 | 1.73E+00 | 4.98E+00 | 3.08E+00 | 3.35E+00 |  |

**Notes:**

See TABLE XXXVIII for 2,3,7,8 PCDD/DF Analyte Code

ND values (='.') not considered in statistical analysis

Dark shaded areas indicate insufficient data

# TABLE XLI (Continued)

## BASIC STATISTICS FOR OFF-SITE AMBIENT AIR POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN 2, 3, 7, 8 ISOMER ANALYSIS (DETECTS ONLY)

|  | Cl6DD1 | Cl6DD2 | Cl6DD3 | Cl7DF1 | Cl7DF2 | Cl7DD1 | Cl8DF1 | Cl8DD1 | 2378TOT |
|---|---|---|---|---|---|---|---|---|---|
| n Detected | 6 | 11 | 12 | 42 | 8 | 140 | 92 | 162 | 169 |
| n Non-Detected | 179 | 174 | 173 | 143 | 177 | 45 | 93 | 23 | 16 |
| Minimum | 1.09E-03 | 1.34E-03 | 1.18E-03 | 3.20E-04 | 6.48E-05 | 4.14E-04 | 2.01E-05 | 6.17E-05 | 1.84E-04 |
| Maximum | 1.57E-01 | 1.41E-01 | 2.12E-01 | 2.51E-02 | 1.26E-02 | 1.73E-02 | 3.56E-03 | 3.18E-03 | 2.59E+00 |
| Range | 1.56E-01 | 1.40E-01 | 2.11E-01 | 2.48E-02 | 1.25E-02 | 1.69E-02 | 3.54E-03 | 3.12E-03 | 2.59E+00 |
| Mean | 2.82E-02 | 1.59E-02 | 2.29E-02 | 2.05E-03 | 2.60E-03 | 2.13E-03 | 2.07E-04 | 5.25E-04 | 4.02E-02 |
| 99% Confidence Interval | 4.24E-02 | 2.06E-02 | 2.83E-02 | 9.91E-04 | 2.54E-03 | 3.17E-04 | 8.29E-05 | 5.97E-05 | 2.83E-02 |
| 95% Confidence Interval | 5.05E-02 | 2.46E-02 | 3.37E-02 | 1.18E-03 | 3.02E-03 | 3.78E-04 | 9.87E-05 | 7.11E-05 | 3.38E-02 |
| 90% Confidence Interval | 6.64E-02 | 3.23E-02 | 4.43E-02 | 1.55E-03 | 3.97E-03 | 4.97E-04 | 1.30E-04 | 9.35E-05 | 4.44E-02 |
| Standard Deviation | 6.31E-02 | 4.16E-02 | 5.96E-02 | 3.90E-03 | 4.36E-03 | 2.28E-03 | 4.83E-04 | 4.62E-04 | 2.24E-01 |
| Sample Variance | 3.99E-03 | 1.73E-03 | 3.56E-03 | 1.52E-05 | 1.90E-05 | 5.22E-06 | 2.34E-07 | 2.13E-07 | 5.02E-02 |
| Standard Error | 2.58E-02 | 1.26E-02 | 1.72E-02 | 6.02E-04 | 1.54E-03 | 1.93E-04 | 5.04E-05 | 3.63E-05 | 1.72E-02 |
| Median | 3.04E-03 | 3.55E-03 | 6.05E-03 | 1.09E-03 | 4.59E-04 | 1.42E-03 | 8.68E-05 | 3.81E-04 | 5.17E-03 |
| Mode |  |  |  |  |  | 1.00E-03 |  | 2.68E-04 |  |
| Kurtosis | 5.99E+00 | 1.10E+01 | 1.19E+01 | 3.13E+01 | 4.62E+00 | 1.67E+01 | 3.09E+01 | 1.17E+01 | 1.06E+02 |
| Skewness | 2.45E+00 | 3.31E+00 | 3.45E+00 | 5.34E+00 | 2.17E+00 | 3.58E+00 | 5.34E+00 | 3.01E+00 | 9.86E+00 |

**Notes:**
See TABLE XXXVIII for 2378 PCDD/DF Analyte Code

Non-detected Values (='.') not considered in Statistics

Dark Shaded areas indicate insufficient data

**TABLE XLII**

SUMMARY OF BASIC STATISTICS FOR TOXIC EQUIVALENCY BY SITE

| Statistical Parameter | 23007 | 23009 | 23011 | 23013 |
|---|---|---|---|---|
| n for samples | 59 | 43 | 43 | 40 |
| n Detected | 54 | 41 | 39 | 35 |
| n Non-Detected | 5 | 2 | 4 | 5 |
| Minimum | 3.09E-04 | 2.21E-04 | 1.84E-04 | 2.24E-04 |
| Maximum | 2.59E+00 | 1.38E-01 | 1.21E+00 | 2.48E-01 |
| Range | 2.59E+00 | 1.37E-01 | 1.21E+00 | 2.48E-01 |
| Mean | 5.84E-02 | 2.00E-02 | 5.92E-02 | 2.65E-02 |
| 99% Confidence Interval | 7.87E-02 | 8.39E-03 | 5.58E-02 | 1.18E-02 |
| 95% Confidence Interval | 9.38E-02 | 9.99E-03 | 6.64E-02 | 1.40E-02 |
| 90% confidence interval | 1.23E-01 | 1.14E-02 | 7.60E-02 | 1.60E-02 |
| Standard Deviation | 3.52E-01 | 3.26E-02 | 2.12E-01 | 4.23E-02 |
| Sample Variance | 1.24E-01 | 1.07E-03 | 4.48E-02 | 1.79E-03 |
| Standard Error | 4.78E-02 | 5.10E-03 | 3.39E-02 | 7.15E-03 |
| Median | 4.25E-03 | 4.86E-03 | 8.47E-03 | 5.08E-03 |
| Mode | | | | |
| Kurtosis | 5.38E+01 | 6.59E+00 | 2.51E+01 | 2.91E+01 |
| Skewness | 7.33E+00 | 2.56E+00 | 4.91E+00 | 5.26E+00 |

**Notes:**

ND values not included

Concentrations in pg/m$^3$ as I-TEQ

## 3.5     Meteorology

During the Phase 3 Cleanup, a meteorological station (station id=23005) was established in the West Lincoln Township Public Works yard located approximately 1 km NW of the CWML SV Site (see Figure 15). This meteorological station monitored for wind speed (in kilometers per hour (km/hr or kmph)) and wind direction (in degrees) at a height of 10m. Although it was supposed to be carried out, air temperature data was not available

from this station. However, the MOE WCR had a multilevel meteorological station located at Allanburg, ON, approximately 15 km E from the Smithville Site (see Figure 8) that was operational during the Phase 3 Cleanup.

It was expected that the Allanburg data could be used to supplement the Smithville data (for windspeed and direction) and to provide the temperature data.

The one hour averaged data for the Smithville (23005) and Allanburg (27011) meteorological stations for the December, 1990 through January, 1993 time period (19032 records) were obtained from MOE [230] in Excel™ files.

A completeness review of the Smithville meteorological data showed that there were periods of missing or invalid data in the Smithville station data. It was decided to evaluate the correlation between the Smithville and Allanburg data to see if data substitution (i.e., Allanburg Level 1 or Level 2 data for missing/invalid Smithville data) might be a viable option. The first step was to replace known invalid or missing (coded as 9999 or -999) Smithville Met data as a missing value ('.'). The criteria used were a windspeed of <0 or >100 km/hr, or wind direction of <0 or >360 degrees. Using these criteria, 16104 valid observations remained in the data set (i.e., 2928 (15%) missing or invalid data records).

Summary statistics for the Smithville and Allanburg meteorological data is provided below in Table XLIII.

# TABLE XLIII

## SUMMARY STATISTICS FOR METEOROLOGICAL DATA

| | WINDSPD (km/hr) | WINDDIR (degrees) | WINDSPD1 (km/hr) | WINDDIR1 (degrees) | WINDSPD2 (km/hr) | WINDDIR2 (degrees) | ALLANTEMP (0.1 °C) |
|---|---|---|---|---|---|---|---|
| n valid records | 18897 | 18916 | 18678 | 18678 | 18736 | 18736 | 18985 |
| n Blank or Invalid | 135 | 116 | 354 | 354 | 296 | 296 | 47 |
| n Total Records | 19032 | 19032 | 19032 | 19032 | 19032 | 19032 | 19032 |
| MIN. | 0.00 | | 0.00 | | 0.00 | | -189.00 |
| MAX. | 85.00 | | 43.00 | | 63.00 | | 308.00 |
| Range | 85.00 | | 43.00 | | 63.00 | | 497.00 |
| Median | 11.00 | | 8.00 | | 14.00 | | 71.00 |
| Mode | 10.00 | | 7.00 | | 14.00 | | 0.00 |
| Mean | 12.79 | | 9.19 | | 15.42 | | 82.37 |
| Std. Dev. | 8.71 | | 6.11 | | 8.28 | | 99.59 |
| Variance. | 75.91 | | 37.34 | | 68.52 | | 9917.48 |
| Std. Error of Mean | 0.06 | | 0.04 | | 0.06 | | 0.72 |
| Skewness | 1.07 | | 0.90 | | 0.86 | | 0.03 |
| Kurtosis | 1.90 | | 0.92 | | 1.18 | | -0.88 |

**Notes:**

Winddir:  Wind direction (in degrees) from Smithville Meteorological Tower at 10 m

Winddir1:  Wind direction (in degrees) from Allanburg Meteorological Tower at 10 m

Winddir2:  Wind direction (in degrees) from Allanburg Meteorological Tower at 30 m

Windspd:  Wind speed (in km/hr) from Smithville Meteorological Tower at 10 m

Windspd1:  Wind speed (in km/hr) from Allanburg Meteorological Tower at 10 m

Windspd2:  Wind speed (in km/hr) from Allanburg Meteorological Tower at 30 m

Allantemp:  Temperature (in 0.1° C) at Allanburg Meteorological Tower, height not given

# 4.    RESULTS AND DISCUSSION

## 4.1    Description of Chapter

This Results and Discussion Chapter (R&D) describes the actual data analysis work carried out for the raw environmental monitoring data for meteorology, ambient air PCB, and ambient air PCDD/DF. This chapter also provides the interpretation of the data, including the conclusions and suggestions for further work. The work carried out for the data analysis and interpretation is laid out schematically in Figure 25 (below).

The first tasks that were undertaken were to evaluate the available electronic data for meteorology and PCB and PCDD/DF air samples. The Smithville and Allanburg electronic meteorological data (see section 3.5 above) were evaluated for completeness and formatting issues. Further data manipulation and analysis were carried out on these data, including calculations of wind speed in meters per second (m/s or mps), mile per hour (mi/hr or mph), temperatures in degrees Celsius (°C) and Kelvin (°K), and correlations of Smithville wind direction and wind speed with the Allanburg data.

The ambient air PCB sample data in electronic format (MS-Access[tm] database) for the project were evaluated for completeness, detection limit handling issues, data reporting format, overall descriptive statistics, descriptive statistics by sampling location, and analyte correlations. The conclusions resulting from this analysis are represented by italicized text in Section 4.1.
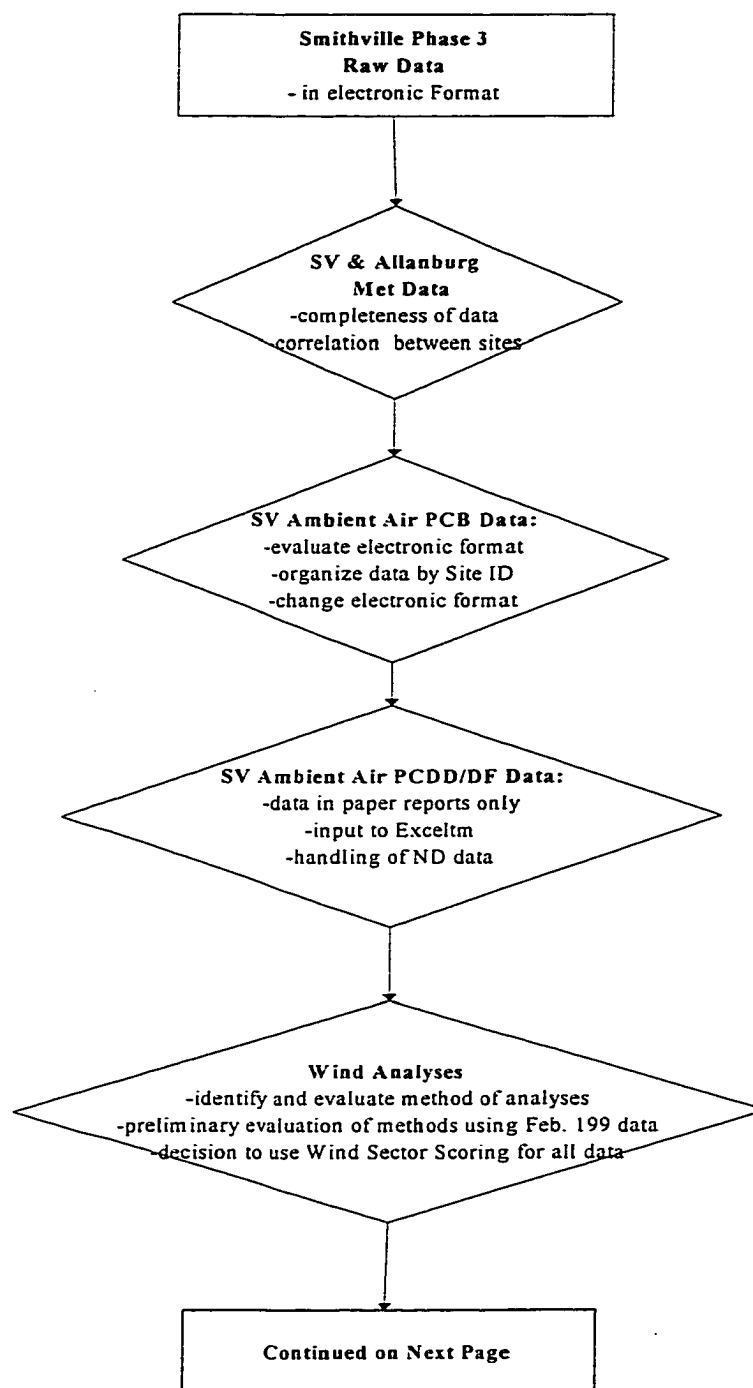
Figure 25.    Schematic for results and discussion chapter.
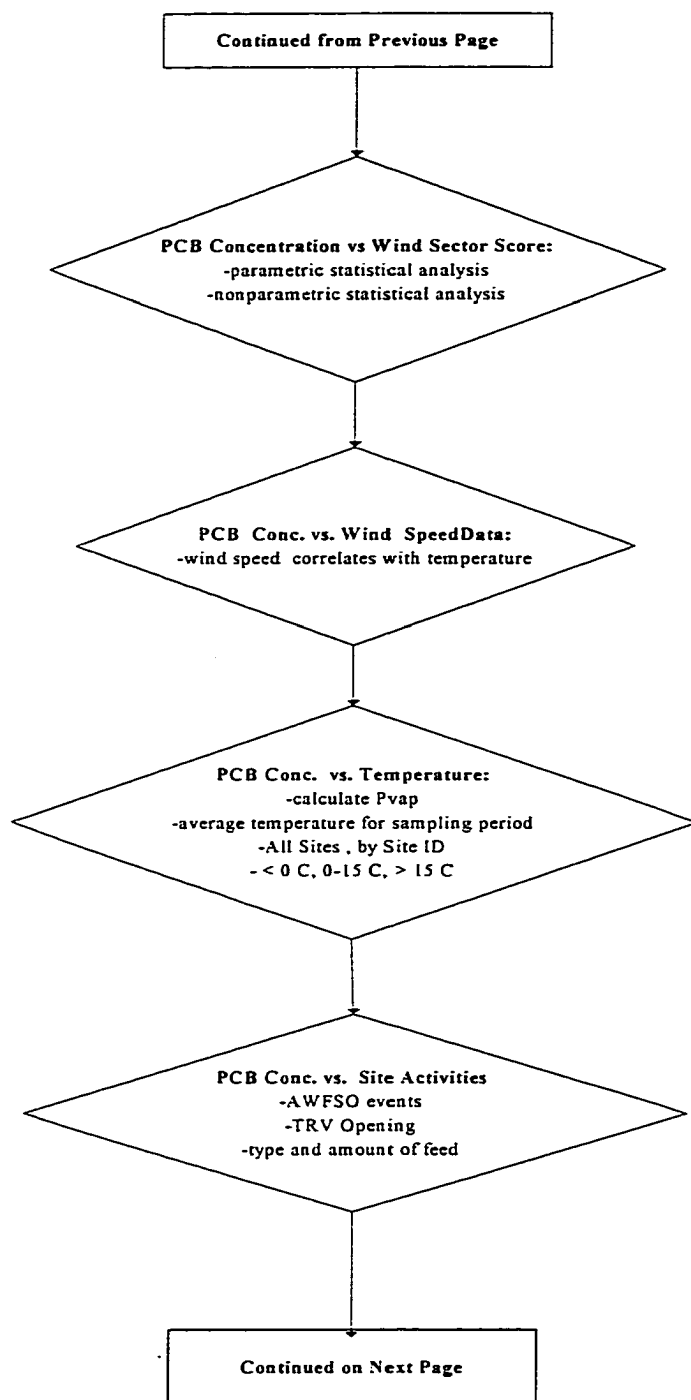
Figure 25.    Schematic for results and discussion chapter (continued).
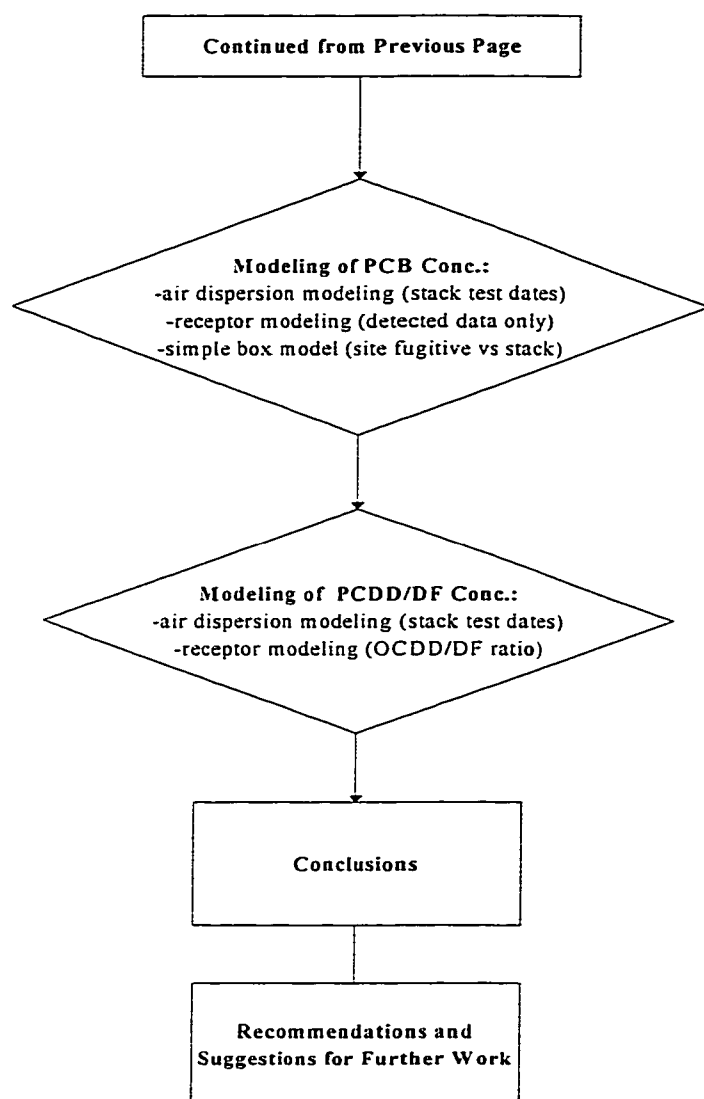
Figure 25. Schematic for results and discussion chapter (concluded).

*The analyte correlation evaluation indicated that total PCB (PCBTOT) concentrations were well correlated with many of the other analytes and therefore PCBTOT could be used as a surrogate for the other analytes in further work.* See Section 4.2.2.2.

The ambient air PCDD/DF data (detected values only) that were available electronically in Microsoft Excel$^{tm}$ (see Section 3.5 above) were evaluated for handling of ND data, and for homolog vs. 2,3,7,8-substituted congener specific data, including descriptive statistics and electronic formatting issues. See Section 4.2.3.

In this project, the relationship between wind direction and observed air concentrations of PCB (and possibly PCDD/DF) was of interest. However, the manner in which to evaluate this relationship was not clear. Before the relationship between air concentrations and wind direction could be evaluated, the meteorological data required additional processing and calculations in order to provide the required data. Three methods of analyzing the wind data were identified from the literature and evaluated on a subset of the meteorology data for February, 1991. *Based on this work, wind Sector scoring was determined to be a superior method of data analysis for this dataset and was used for evaluating the correlation between wind direction and ambient air PCB concentrations.* See Section 4.4.

The correlation between ambient air PCBTOT concentrations and wind sector scores was analyzed in further detail, using parametric and non-parametric statistics, looking at the data in terms of: all data combined, data by sampling station, data by month, and data with

and without ND values. *A weak correlation was observed for the dataset as a whole. However, stronger correlations were observed between wind score and PCBTOT concentrations for the warmer months. Because there were more detected PCBTOT values in the warmer months, there were more data to work with in these time periods.* See Section 4.4.2.3.

The effect of wind speed on observed PCBTOT concentrations was evaluated looking at the data for all sites, by site id, and for all wind speeds and stratified wind speeds, as well as for temperature. Once again the effect of using all data (i.e., including ND) vs. detects only was examined. See Section 4.6.

The effect of temperature was examined looking at the PCBTOT data for all sites, by site id, and for stratified by temperatures; again, the effect of using all data (i.e., including ND) vs. detects only was examined. *A clear temperature relationship was observed, with the highest concentration occurring during the warmest months, especially in the summer of 1991. A statistically significant correlation between temperature and concentration (as vapor pressure) was observed for temperatures above approximately 0°C.* See Section 4.5.

For the Smithville project there was some information available about on-site activities. This information was used to evaluate Site activities with respect to observed ambient air PCBTOT concentrations. Parameters that were examined included type of feed material, feed rate, amount of material treated to date, spill reports, openings of the TRV, AWFSO events, etc. *The single major factor that was identified was the amount of high level*

*PCB liquids remaining on-site. Once the high level PCB liquid in the tank farm was destroyed in September, 1991, the ambient air concentrations decreased significantly.* See Section 4.7.

Some air modeling was carried out for the PCB air data. Air dispersion modeling (ADM) was carried out for the nine (9) dates of source testing with PCB emissions data using the ISCVIEW interface for the ISC3ST model [231, 232]. Receptor modeling was carried out using source profiles derived from on-site monitoring and source testing. Receptor modeling was carried out for air samples with detected PCBTOT only. The results from the air modeling were evaluated in conjunction with the previous data analyses. Some simple box modeling was also carried out for the on-site air results. *The air modeling results indicated that the incinerator emissions were a minor contributor to the observed ambient air concentrations.* See Section 4.8.

Air modeling was also performed for the ambient air PCDD/DF data. The ISC3ST model results were used in conjunction with the PCDD/DF emissions data to calculate a predicted PCDD/DF concentration (I-TEQ) for the 9 source testing dates. Some preliminary receptor modeling work was performed using the ratio of OCDF/OCDD. *This modeling work indicated that the incineration project and associated activities did not have an identifiable impact on the ambient air PCDD/DF.* See Section 4.9.

The results of the various data analyses, carried out above, were utilized to develop a series of conclusions for this dataset, some of which can be applied on a general basis to PCB

behavior in the environment. In addition to these conclusions, a number of issues were identified that need additional investigation. These issues were incorporated into a Suggestions for Further Work Section.

## 4.2 Data Preparation

### 4.2.1 Meteorological Data

The initial meteorological data could not be used for data analysis due to the format of the data file. Eventually, the one-hour averaged meteorological data for the Smithville and Allanburg stations were obtained from MOE [230] in Excel$^{tm}$ files. The data files for the Smithville and Allanburg stations were merged to create a file with hourly averaged data for Smithville wind speed, Smithville wind direction, Allanburg Level 1 (10 m), Allanburg Level 1 wind direction, Allanburg Level 1 temperature Allanburg Level 2 (30 m) wind speed, Level2 wind direction and temperature difference for Allanburg Level 1 – Level 2, for the December 1, 1990 to January 31, 1993 time period (a total of 19,032 data records). A program was written in SAS$^{tm}$ to detect and replace known invalid (i.e., wind direction <0 or >360 ) or missing (coded as 999, 9999 or -999) Smithville meteorological data as a missing value ('.') (see Section 3.5 above). A total of 2928 (~ 15% of the 19032 records) missing values resulted.

The correlation between the Smithville and Allanburg data was evaluated to see if data substitution (i.e., Allanburg Level 1 or Level 2 data substituted for missing/invalid Smithville data) was a viable option. The Smithville wind speed and wind direction data were analyzed vs. the Allanburg wind speed and wind direction. Figure 26 shows a plot of

the Smithville wind direction vs. Allanburg Level 1 wind direction. Figure 27 shows a plot of Smithville wind direction vs. Allanburg Level 2 wind direction. In Figure 28, the Smithville wind speed vs. Allanburg Level 1 wind speed is plotted. Figure 29 shows a plot of Smithville wind speed vs. Allanburg Level 2 wind speed. A visual review of these data indicated that there was a correlation between the Smithville and Allanburg Level 1 wind data. Although linear regression equations and correlation coefficients are shown in these figures, the reader is cautioned that the equations cannot be used quantitatively for wind direction because of the nature of circular data; any value of 0-20° and 340-360° is within +/- 20° of 360° (i.e., due north), but will be plotted and be handled by linear regression much differently depending on which side of 360° they fall. There is strong correlation for the wind speed data, with the Smithville data generally being in between the Level 1 and Level 2 data. This result would be expected due to the difference in the sites. Smithville is a rural site with a long wind "fetch" and less surface roughness to reduce wind speed. Because the Smithville and Allanburg data were clearly correlated, the Allanburg 10 m data was directly substituted for the missing or invalid Smithville data. After this substitution was carried out, there were still 135 records with missing or invalid Smithville data. These remaining data were then substituted with Allanburg 30 m data where possible. The final meteorological data set had 116 missing or invalid records (0.61% of the 19032 records), which was considered to be inconsequential and acceptable for use for data analysis for this Thesis. Direct substitution was used for both wind speed and wind direction, rather than the calculated regression equation because of concerns about the validity of the regression equation (for circular data especially) or quantifying the error from using the equations. Extrapolation (from the data immediately prior to, and after the data gaps) as recommended

by USEPA [233] was considered, but some of the invalid Smithville data gaps span several days and it is believed that direct substitution with Allanburg data was more accurate.

The meteorological data were collected for each hour of the day using the 1 to 24 hour time scale (i.e., 0100-2400). However, the ambient air monitoring was carried out on a mid-morning (day n) to mid-morning (day n +1, n+2 for PCDD/DF samples) schedule. While the times for start and finish for each sample were recorded on the sample information sheets, these times were not part of the information in the electronic database. Rather than enter the start and finish times for each of the 1600+ ambient air samples for PCBs, it was decided to use a 1200 hrs (day n) start to 1100 hrs (day n+1) finish as the standard "sampling day". Additional calculations and conversions were carried out as follows: 1) the temperature values were calculated in °C (variable = tempC) by multiplying Allantemp (in 0.1°C) by 10; 2) degrees C were converted to degrees Kelvin; (variable tempK); and 3) the wind speed (in km/hr) was converted to wind speeds in meters per second (m/s or mps) and miles per hour (mph). These data manipulations yielded a meteorological data set with hourly temperature, wind speed, and wind direction data. The data set was then analyzed further to provide MIN., MAX., average and std. dev. data for the wind speed and temperatures.
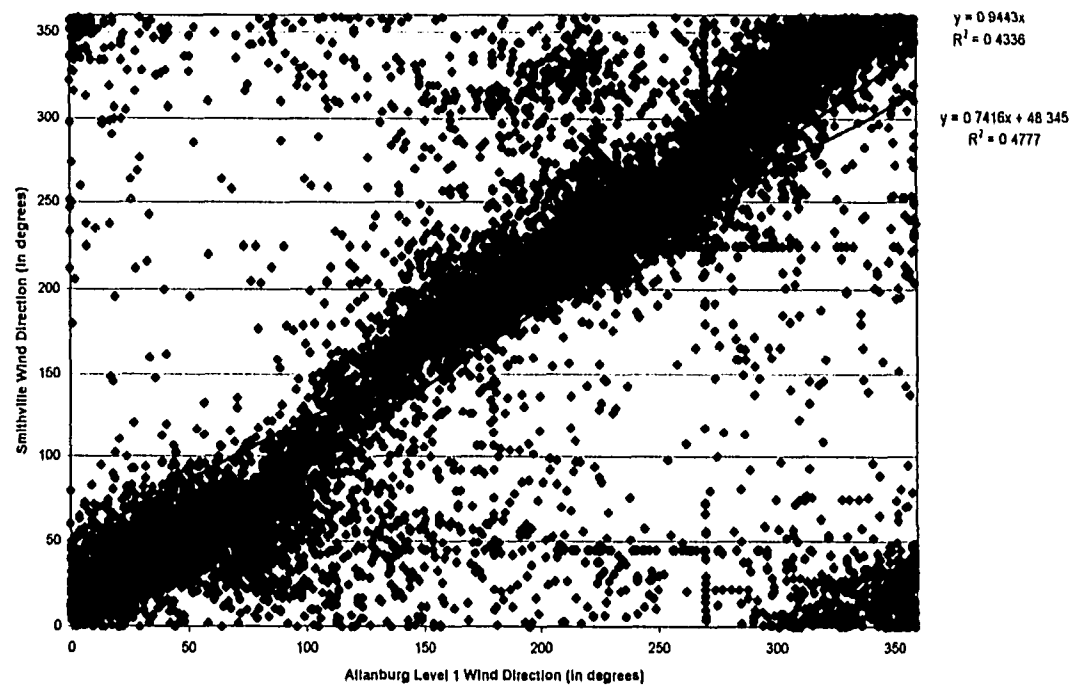
Figure 26. Smithville wind direction versus Allanburg Level 1 (ten meter) wind direction.

The scatter plot includes the following annotations:

$y = 0.8999x$
$R^2 = 0.4326$

$y = 0.7042x + 49.065$
$R^2 = 0.4783$

Y-axis: Smithville Wind Direction (in degrees)

X-axis: Allanburg L2 Wind Direction (in degrees)
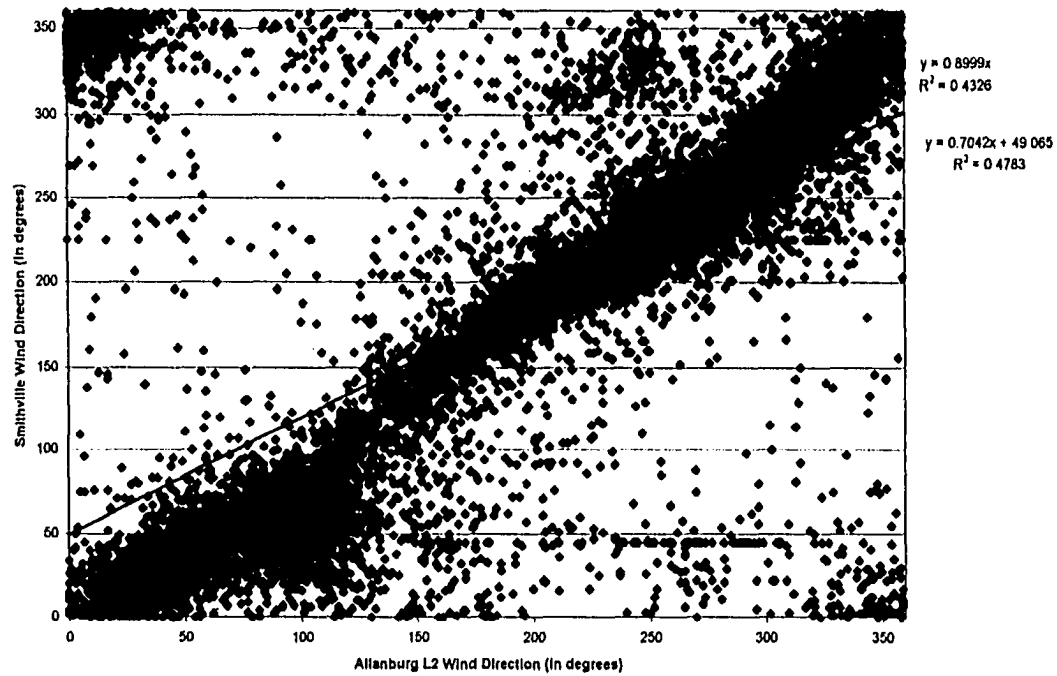
Figure 27. Smithville wind direction versus Allanburg Level 2 (thirty meter) wind direction.
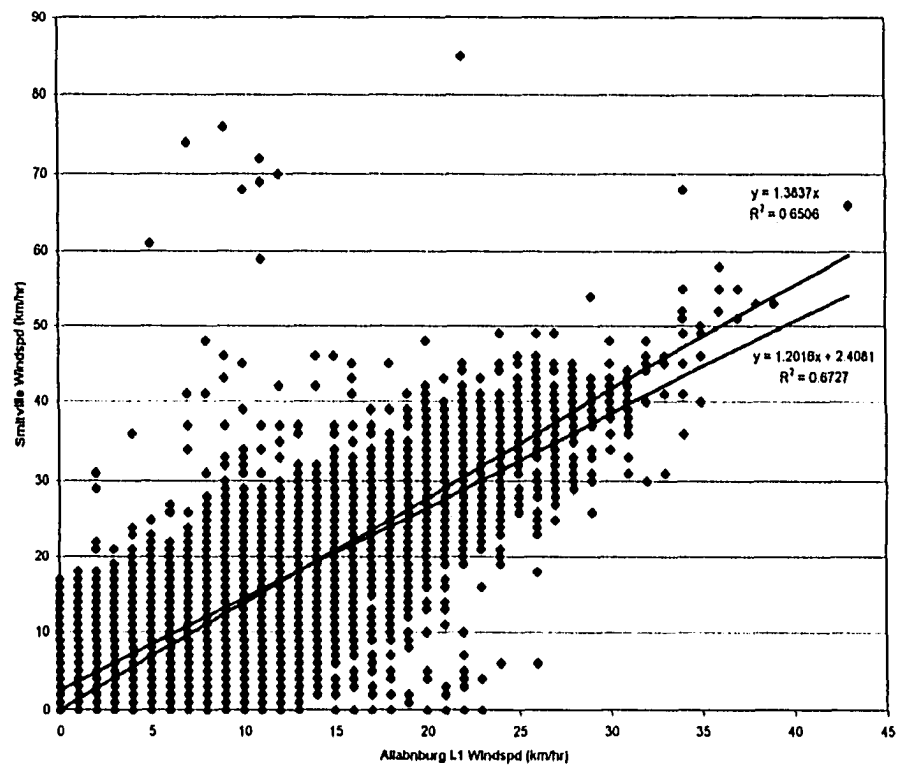
Figure 28.   Smithville wind speed versus Allanburg Level 1 (ten meter) wind speed.
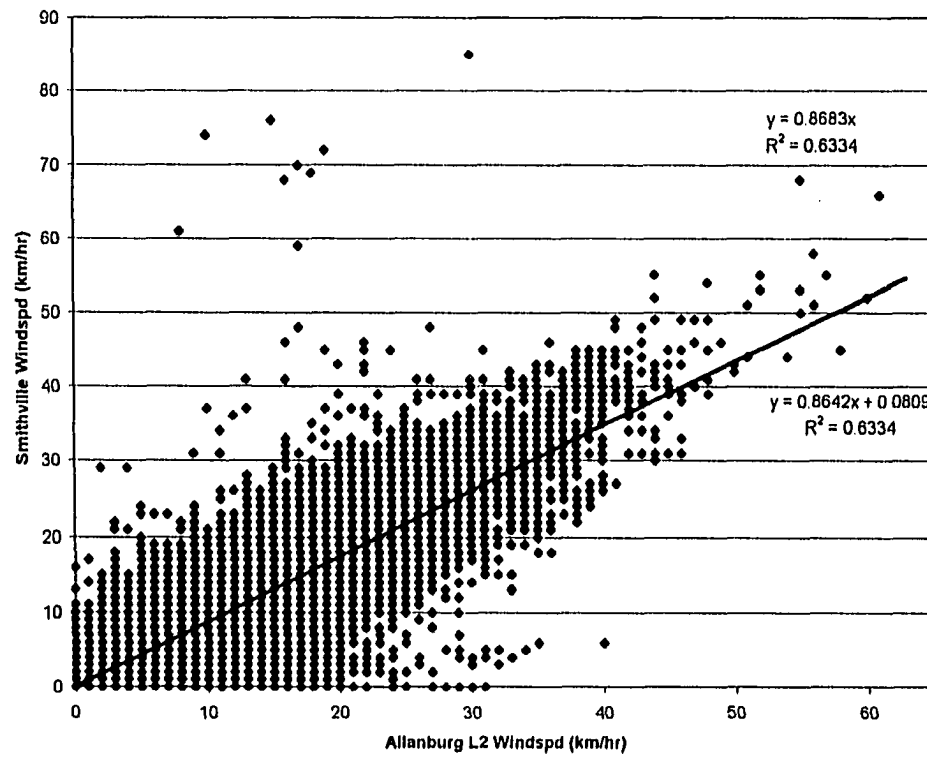
Figure 29.    Smithville wind speed versus Allanburg Level 2 (thirty meter) wind speed.

### 4.2.2 Data Preparation and Additional Statistical Analysis for Polychlorinated Biphenyl/Chlorobenzene Air Samples

The PCB/CB air sample data in electronic format was received from P&R in dbaseIV$^{tm}$ format. The data format had one record per analyte, which duplicated most of the sample information and resulted in 24 records (1 for each of the 24 analytes) per sample. The following additional statistical analyses (in addition to those in Section 3.3.3) were performed for the PCB/CB data. The purposes of the additional statistical analyses included:

1) ·    to evaluate the effect of different methods for treating data that were below the quantitation limit (QL) and/or detection limit (DL) (or ND values); and


2)    to determine the type of distribution (normal, log-normal, etc.) for the PCB/CB data using indicators such as the kurtosis, skewness, etc. [228, 234]. Kurtosis characterizes the relative peakedness or flatness of a distribution compared with the normal distribution. Positive kurtosis indicates a relatively peaked distribution. Negative kurtosis indicates a relatively flat distribution. Skewness characterizes the degree of asymmetry of a distribution around its mean. Positive skewness indicates a distribution with an asymmetric tail extending toward more positive values. Negative skewness indicates a distribution with an asymmetric tail extending toward more negative values.

**4.2.2.1 Detection and Quantitation Limit Issues**

Data for PCB/CB analytes in ambient air samples taken during Phase 3 were reported using the <W and/or <T flags [235] for low level data. The description of these two terms is reprinted from the MOE source document [235] as follows:

W represents the value below which there is no analytical response. Results coded <W are equivalent to 'zero'. The reported value is then the value of W to indicate the sensitivity of the method. T is a factor of 5, 10, or 20 times W. It is equal to or larger than the analytical detection limit (three times standard deviations based on duplicate analysis of low-level samples or 'spiked blanks'). It represents a value below which the analytical result is considered somewhat unreliable due to imprecision or bias. Results coded <T are measured results; but are reported for information purposes only.

The <W and <T flag system used by MOE is unique in experience in the author's experience. Basically, W can be considered to be similar to (but not exactly the same as) the DL; and T can be considered to be similar to (but not exactly the same as) the QL for a sample analysis. Typically, W varied between 0.2 to 1.0 ng/m$^3$ (depending on the analyte) and T varied between 0.4 to 1.4 ng/m$^3$. Samples with <W and/or <T flags for PCBTOT provide little useful information in terms of PCB homolog, profiles, etc. The majority of analytes for PCB/CB air samples for the Phase 3 Cleanup are reported in the database with <W or <T flags. These data are referred to as censored data [236] or truncated datasets [237]. The actual concentration of the censored data can lie anywhere between zero and the DL, or between DL and QL.

The issue of how to deal with data below the DL and/or QLs has received considerable attention in the literature [237, 238]. Approaches that have been identified for handling censored data include:

1)    Take data at DL; this may or may not give a biased estimate of the mean.

2)    Data at ½ DL; this may or may not give a biased estimate of the mean.

3)    DL data = 0; this gives a biased underestimate for the mean.

4)    Ignore (i.e., do not include) censored values. This gives a biased overestimate of the mean.

5)    Other alternative procedures for handling censored data are outlined in Haas and Scheff [237] and McBean and Rovers [236].


Initial statistical analysis of the PCB/CB data was carried out in Section 3.3.3 using the first approach. The ambient air PCB/CB data was reanalyzed statistically using the second, third and fourth approaches. The results for the additional statistical analyses for PCBTOT are shown in Table XLIV below. The same analysis was performed for each of the 24 PCB/CB analytes; however, the results are not shown here. For the first three approaches, there was only a small effect on the mean for PCBTOT, with a maximum value of 1.32 ng/m$^3$ with data included at the reported values (including <W and <T), and a minimum of 1.11 ng/m$^3$ for <W and <T = 0 (the third approach above). The mean value for the fourth approach was much higher: 4.83 ng/m$^3$. Because there were 1216 non-quantified (i.e., <W or <T) values, the median and mode values varied with the assumptions made for <W and <T values. The skewness value indicates the data distribution is skewed with a tail extending to

the right and the kurtosis value indicates that it is a peaked distribution, both of which are

characteristic of log-normal data distribution.

193

**TABLE XLIV**

DESCRIPTIVE STATISTICS FOR TOTAL POLYCHLORINATED BIPHENYLS WITH
VARIOUS TREATMENTS OF "<W" & "<T" VALUES

| | PCBTOT | PCBTOT_3 | PCBTOT_1 | PCBTOT_2 | PCBTOTDET |
|---|---|---|---|---|---|
| | Raw Data (with errors corrected) | <W & <T @ ½ the limit value | <W = 0 | <W & <T = 0 | Not <W or <T |
| n | 1584 | 1584 | 1584 | 1584 | 366 |
| n = 0 | 0 | 0 | 1034 | 1218 | 0 |
| n blank | 0 | 0 | 0 | 0 | 0 |
| n for non-detected (<W) | 1034 | | | | 36 |
| n for quantified | 366 | | | | |
| n for detected but not quantified | 184 | | | | |
| n for detected and/or quantified | 550 | | 550 | | |
| MIN. | 0.2 | 0.1 | 0.0 | 0.0 | 0.2 |
| MAX. | 83.2 | 83.2 | 83.2 | 83.2 | 83.2 |
| Range | 83.0 | 83.1 | 83.2 | 83.2 | 83.0 |
| Median | 0.2 | 0.1 | 0.0 | 0.0 | 2.9 |
| Mode | 0.2 | 0.1 | 0.0 | 0.0 | 1.2 |
| Mean | 1.32 | 1.22 | 1.19 | 1.11 | 4.83 |
| 95% CL | 0.19 | 0.19 | 0.19 | 0.19 | 0.7 |
| Std. Dev. | 3.79 | 3.82 | 3.83 | 3.84 | 6.79 |
| Var. | 14.37 | 14.56 | 14.66 | 14.77 | 46.14 |
| Std. Error of Mean | 0.1 | 0.1 | 0.1 | 0.1 | 0.36 |
| Skewness | 11 | 11 | 10 | 10 | 6 |
| Kurtosis | 178 | 174 | 172 | 170 | 59 |

**Notes:**

The Mean for the raw data was calculated using the reported value for <W and <T flagged samples.

PCBTOT_1 = total polychlorinated biphenyl, <W flagged values = 0

PCBTOT_2 = total polychlorinated biphenyl, <W and <T flagged values = 0

PCBTOT_3 = total polychlorinated biphenyl, <W and <T values assumed present at half the specified limit value

PCBTOTDET = total polychlorinated biphenyl, detected values only (no <W or <T values)

A histogram plot is provided for PCBTOT in Figure 30 below. Histogram plots of data can be used to determine if there are any other interesting aspects or to confirm conclusions from other statistical analyses [239]. In this case, the histogram plot confirms the conclusions suggested by the skewness and kurtosis values.
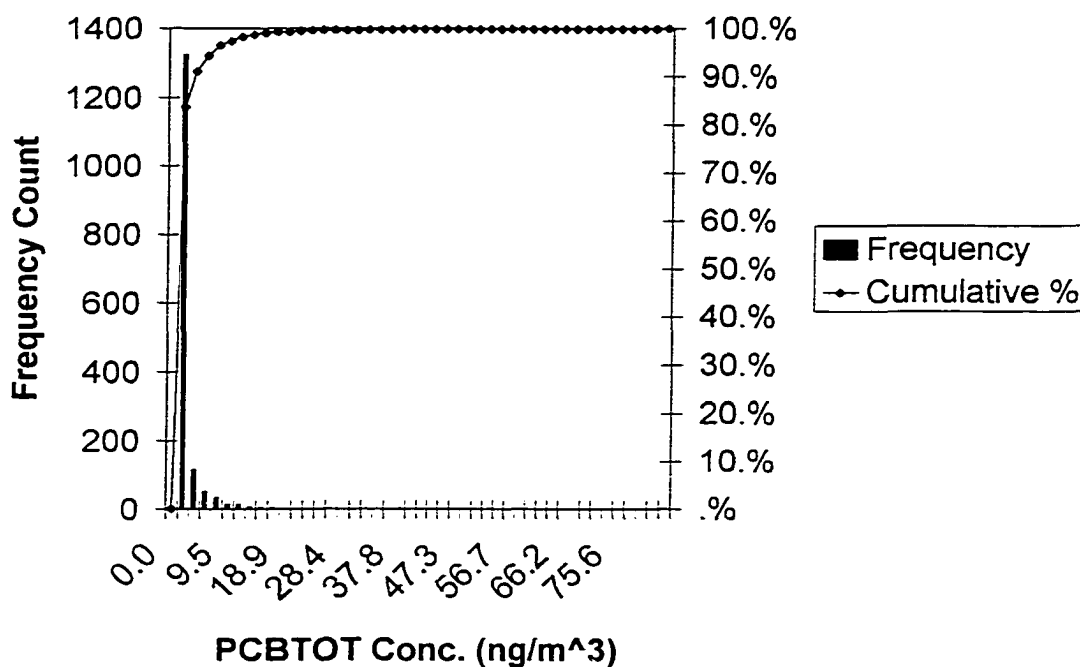


Figure 30.    Histogram frequency plot for total polychlorinated biphenyl data.

## 4.2.2.2 Correlations With Total Polychlorinated Biphenyls

The correlations between the 24 PCB/CB analytes were examined. The slope for the correlations was determined by linear regression (LR) using the least squares fit model [240]. Table XLV shows the Pearson correlation coefficients for the off-site PCB/CB data, where the <W and <T values were used as reported. The analytes PCBDI, PCBTRI, PCBTET, PCBPNT, PCBHEX, X2124, X2123, X21245, X21234, and X2PNCB were found to be significantly correlated with PCBTOT at the 99.5% significance level (e.g., p<0.005). Dot plots were also made of the data and examined individually to ensure that correlations observed were not artificially influenced by outliers. The LR results indicated that while some data points were outliers (based on Studentized Residual), exhibited large leverage (based on Leverage), or had large influence (based on Cook Distance), the correlations were still statistically valid.

Non-parametric correlation analysis (Spearman's correlation coefficient) was also performed on the data [236], but is not shown. While the non-parametric analysis changed some of the correlation coefficients and probabilities, it did not change the interpretation of the data (i.e., the same analytes were found to be correlated).

The correlation analysis was also carried out on the data set for the cases where PCBTOT was reported as >T (366 samples). This analysis is shown in Table XLVI below. This analysis changed some of the correlation coefficients and probabilities, but did not change the interpretation of the data (i.e., the same analytes were found to be significantly correlated), with the exception that PCBHEX was no longer significantly correlated.

**TABLE XLV**

CORRELATION MATRIX FOR OFF-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AIR MONITORING DATA, n=1584

| | PCBDI | PCBTRI | PCBTET | PCBPNT | PCBHEX | PCBHEPT | PCBOCT | PCBNON | PCBDEC | PCBTOT |
|---|---|---|---|---|---|---|---|---|---|---|
| PCBDI | 1.000 | | | | | | | | | |
| PCBTRI | r=0.854 p<0.000 | 1.000 | | | | | | | | |
| PCBTET | r=0.334 p<0.000 | 0.362 0.000 | 1.000 | | | | | | | |
| PCBPNT | r=0.126 p<0.000 | 0.117 0.001 | 0.367 0.000 | 1.000 | | | | | | |
| PCBHEX | r=0.013 p=1.000 | 0.005 1.000 | 0.221 0.000 | 0.077 0.608 | 1.000 | | | | | |
| PCBHEPT | r=0.008 p<1.000 | -0.010 1.000 | 0.035 1.000 | 0.013 1.000 | 0.103 0.012 | 1.000 | | | | |
| PCBOCT | r=-0.001 p<1.000 | -0.000 1.000 | 0.136 1.000 | 0.046 1.000 | 0.180 0.000 | 0.011 1.000 | 1.000 | | | |
| PCBNON | r=0.008 p<1.000 | 0.007 1.000 | 0.039 1.000 | 0.012 1.000 | 0.029 1.000 | 0.088 1.000 | 0.222 1.000 | 1.000 | | |
| PCBDEC | r=0.013 p< 1.000 | 0.012 1.000 | 0.012 1.000 | 0.015 1.000 | 0.036 1.000 | 0.045 1.000 | 0.273 1.000 | 0.817 0.000 | 1.000 | |
| PCBTOT | M=0.222 r=0.796 p<0.000 | 0.332 0.826 0.000 | 0.267 0.735 0.000 | 0.144 0.509 0.000 | 0.010 0.174 0.000 | 0.003 0.060 0.017 | 0.001 0.081 1.000 | 0.000 0.023 1.000 | 0.000 0.012 1.000 | 1.000 |

# TABLE XLV (Concluded)

## CORRELATION MATRIX FOR OFF-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE AIR MONITORING DATA, n=1584

| | PCBDI | PCBTRI | PCBTET | PCBPNT | PCBHEX | PCBHEPT | PCBOCT | PCBNON | PCBDEC | PCBTOT |
|---|---|---|---|---|---|---|---|---|---|---|
| X2HCE | 0.013 1.000 | 0.012 | 0.012 | 0.015 | 0.036 | 0.045 | 0.273 0.000 | 0.817 | 1.000 | 0.012 1.000 |
| X2135 | 0.065 1.000 | 0.090 | 0.036 | -0.023 | -0.003 | 0.001 | 0.020 | 0.083 | 0.084 | 0.062 1.000 |
| X2124 | r=0.293 p<0.000 | 0.332 | 0.165 | 0.075 | 0.008 | 0.011 | -0.002 | 0.016 | 0.018 | 0.309 0.000 |
| X1HCBD | 0.004 1.000 | 0.024 | 0.069 | 0.021 | 0.019 | 0.024 | 0.152 | 0.456 | 0.559 | 0.041 1.000 |
| X2123 | r=0.492 p<0.000 | 0.479 | 0.187 | 0.101 | 0.005 | -0.008 | 0.004 | 0.023 | 0.032 | 0.437 0.000 |
| X2T245 | 0.013 1.000 | 0.012 | 0.012 | 0.015 | 0.036 | 0.045 | 0.273 | 0.817 | 1.000 | 0.012 1.000 |
| X2T236 | 0.013 1.000 | 0.012 | 0.012 | 0.015 | 0.036 | 0.045 | 0.273 | 0.817 | 1.000 | 0.012 1.000 |
| X21235 | 0.013 1.000 | 0.012 | 0.012 | 0.015 | 0.036 | 0.045 | 0.273 | 0.817 | 1.000 | 0.012 1.000 |
| X21245 | r=0.760 p<0.000 | 0.724 | 0.350 | 0.084 | 0.025 | -0.001 | 0.025 | 0.082 | 0.102 | 0.666 0.000 |
| X2T26A | 0.013 1.000 | 0.012 | 0.012 | 0.015 | 0.036 | 0.045 | 0.273 | 0.817 | 1.000 | 0.012 1.000 |
| X21234 | 0.825 0.000 | 0.824 | 0.360 | 0.092 | 0.015 | -0.008 | 0.003 | 0.018 | 0.025 | 0.735 0.000 |
| X2PNCB | 0.764 0.000 | 0.645 | 0.352 | 0.120 | 0.038 | 0.008 | 0.065 | 0.197 | 0.242 | 0.641 0.000 |
| X2HCB | 0.013 1.000 | 0.012 | 0.012 | 0.015 | 0.036 | 0.045 | 0.273 | 0.817 | 1.000 | 0.012 |
| X2OCST | 0.013 1.000 | 0.012 | 0.012 | 0.015 | 0.036 | 0.045 | 0.273 | 0.817 | 1.000 | 0.012 |

**Notes:**

r = Correlation coefficient

p = Probability (results <0.005 are significant at 99.5%)

M = Slope of linear regression plot

n = sample population

**Bold text** indicates statistically significant correlations

TABLE XLVI

CORRELATION MATRIX FOR OFF-SITE POLYCHLORINATED BIPHENYL/CHLOROBENZENE
AIR MONITORING DATA GREATER THAN QUANTITATION LIMIT, n = 366

| | PCBDI | PCBTRI | PCBTET | PCBPNT | PCBHEX | PCBHEPT | PCBOCT | PCBNON | PCBDEC | PCBTOT |
|---|---|---|---|---|---|---|---|---|---|---|
| PCBDI | 1.000 | | | | | | | | | |
| PCBTRI | r=0.838 p<0.000 | 1.000 | | | | | | | | |
| PCBTET | r=0.260 p<0.000 | 0.274 0.000 | 1.000 | | | | | | | |
| PCBPNT | r=0.001 p<0.000 | -0.43 1.00 | 0.274 0.000 | 1.000 | | | | | | |
| PCBHEX | r=-0.029 p<1.000 | -0.048 1.000 | 0.191 1.00 | 0.028 1.000 | 1.000 | | | | | |
| PCBHPT | r=-0.039 p<1.000 | -0.049 1.000 | 0.006 1.000 | -0.026 1.000 | 0.103 0.012 | 1.000 | | | | |
| PCBOCT | r=-0.02 p<1.000 | -0.023 1.000 | 0.130 1.000 | 0.027 1.000 | 0.180 0.000 | -0.005 1.000 | 1.000 | | | |
| PCBNON | r=-0.02 <1.000 | -0.025 1.000 | 0.037 1.000 | -0.022 1.000 | 0.029 1.000 | 0.086 1.000 | -0.003 1.000 | 1.000 | | |
| PCBDEC | | | | | | | | | | |
| PCBTOT | **M=0.240** **r=0.781** **p<0.000** | **0.343** **0.632** **0.000** | **0.279** **0.700** **0.000** | **0.115** **0.385** **0.000** | 0.08 0.128 0.015 | 0.001 0.016 0.758 | - | - | - | 1.000 |

**Notes:**

r = Correlation coefficient

p = Probability (results <0.005 are significant at 99.5%)

M = Slope of linear regression plot

n = sample population

**Bold text** indicates statistically significant correlations

Data for 14 non-PCB analytes not shown, as the conclusions (based on their data) did not change

As a result of the correlation analyses reported above, it was determined that PCBTOT could be used as the only analyte for all future data analysis for the following reasons:

1)    PCBTOT were the most frequently detected PCB/CB analyte in air samples (366 samples from off-site monitoring),

2)    PCBTOT concentrations exhibited the greatest range ($\sim$ 83 ng/m$^3$), and

3)    the other analytes can be estimated from the PCBTOT by using the slope from the LR analysis.

### 4.2.2.3 Polychlorinated Biphenyl Homolog Profiles

The least squares fit slope shown in Table XLV represents the average ratio of the analyte to PCBTOT.  For example, the slope (M) of PCBDI vs. PCBTOT was found to be 0.222 with an $r^2$ = 0.633 (r = 0.796) and P <0.000 (two-sided), which is significant at the 95% significance level (p <0.05) and 99.5% significance level (p <0.005).  This means that, on average, 22.2 % of the variability in PCBTOT can be accounted for by the regression of PCBTOT on PCBDI homolog.

Figure 31 shows the average profile for the PCB homolog groups as a fraction of PCBTOT for all of the off-site sampling data (Table XLV).  Figure 32 provides the homolog profile (as relative mass fraction) for Aroclor 1242 liquid, with and without the mono-PCB. Figure 33 shows the calculated vapor homolog profile for Aroclor 1242, with and without mono-PCB.  The data is treated with and without mono-PCB to determine if it makes a difference.  This is an issue because the MOE ambient air data does not include the mono-

PCB homolog. The vapor homolog profile was calculated based on the published homolog profile for Aroclor 1242 and the average $P_{vap}$ for each homolog group in Erickson [19]. The homolog profile for Aroclor 1242 vapor was calculated in the following manner:

1) Converting the relative mass fraction (in oil) to a relative mole fraction by:

   a. dividing by the molecular weight for the homolog group, to give the number of moles in 1 g;

   b. sum the number of moles in 1 g for all homologs to give total moles in 1g; and

   c. divide the number of moles for each homolog by the total moles in 1 g (from b), above).

2) Calculate the partial pressure for each homolog by multiplying relative mole fraction by average $P_{vap}$ for the homolog.

3) Calculate moles per volume from the Ideal Gas Law, Equation (4):

$$PV = nRT \qquad (4)$$

Where:   P = Pressure ($P_a$)

   $n$ = number of moles

   R = Universal Gas Constant, 8.315 Pa $m^3$/K mol

   T = Temperature (K)

   V = Volume ($m^3$)

Equation (4) rearranges to Equation (5) below:

$$n/V = P/RT \qquad (5)$$

For mixtures of gases (which is the case here), P can be replaced with the partial pressure of a gas, $P_v$, to give Equation (6) rearranged as:

$$n/V = P_v/RT \qquad (6)$$

Convert moles/volume for each homolog to air concentration ($C_a$) by multiplying by molecular weight (MW) as shown in Equation (13):

$$C_a = n/V * MW \qquad (13)$$

Where $C_a$ = Air concentration ($g/m^3$)

MW = Molecular Weight (g/mol)

Equation (13) can be rewritten in the form of Equation (14):

$$C_a = P_v/RT \qquad (14)$$

Where T = Temperature, 293.15 K (20 °C) was used

V = volume, 1 $m^3$

4) Sum the $C_a$ for all homologs to give a PCB (total) mass per volume.

5) Divide $C_a$ for each homolog by the total mass per volume to give a relative mass fraction for each homolog.

These calculations are summarized in Table XLVII for the Aroclor 1242 and in Figures 32 and 33. Note that this calculation assumes that only PCBs are in the oil. The calculated concentrations, therefore, are a maximum and will be reduced for the lower PCB concentrations observed when the oils contain chlorobenzenes or mineral oil, etc. However, the relative mass profile should still be very similar.

When the relative concentration profile in Figure 31 (average off-site data) is compared to Figures 32 and 33, it appears to resemble the profile calculated for Aroclor 1242/1260 mixture vapor (Figure 34) more closely.

It is noted that the PCBTRI homolog is the highest relative mass fraction for the observed data, which suggests that either some of the PCB observed in the ambient air was as an aerosol, or that there is a greater amount of a heavier Aroclor.
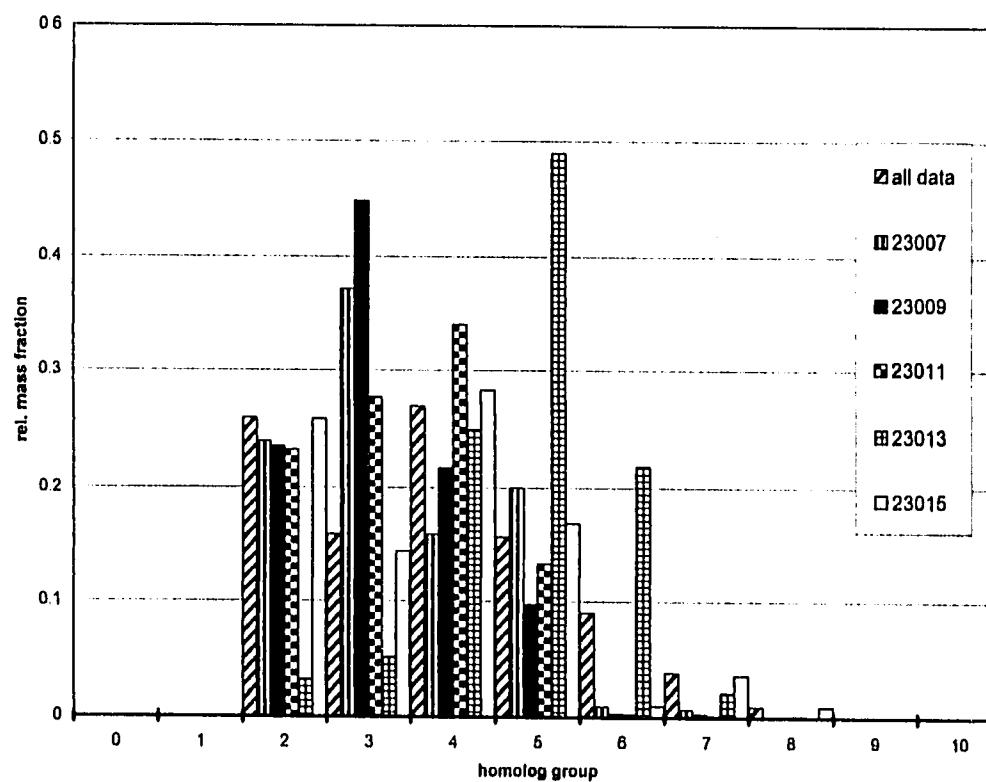
Figure 31.    Average mass fraction for polychlorinated biphenyl homologs for off-site polychlorinated biphenyl air samples (see Table XLV).
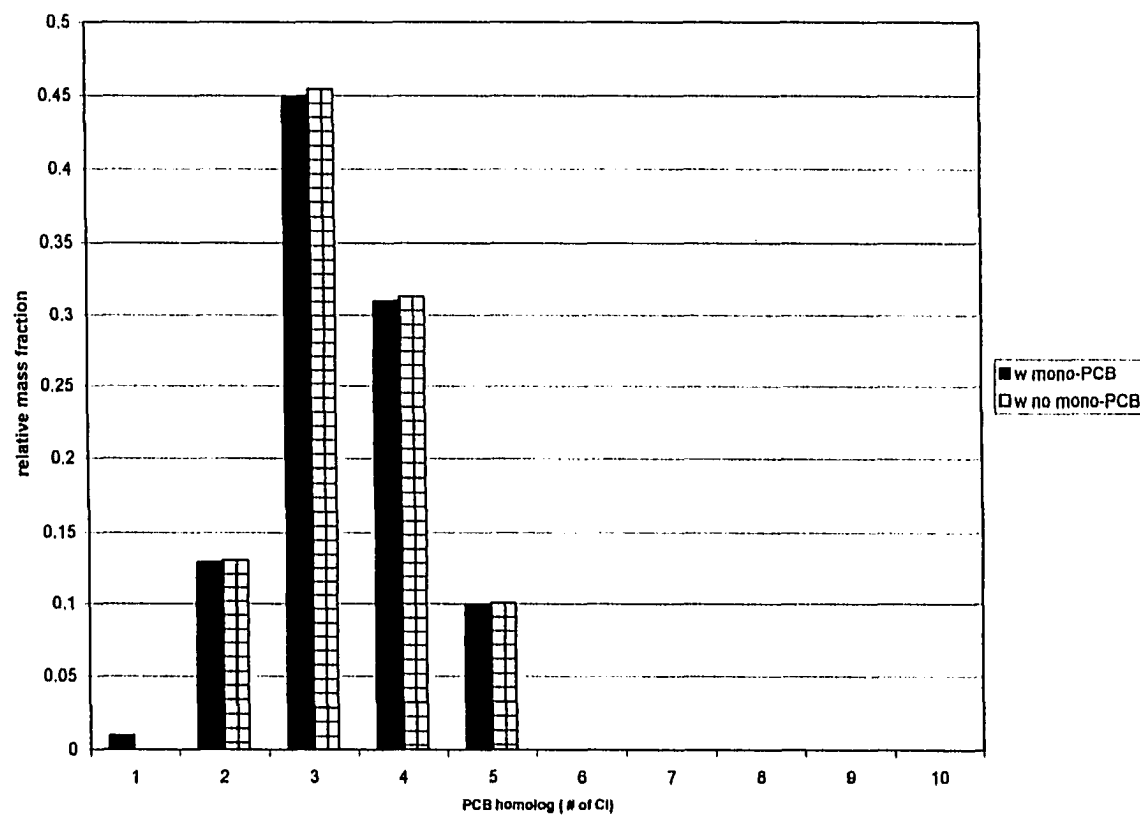
Figure 32. Mass fractions reported for homologs in Aroclor 1242 in oil with and without mono-polychlorinated biphenyls.
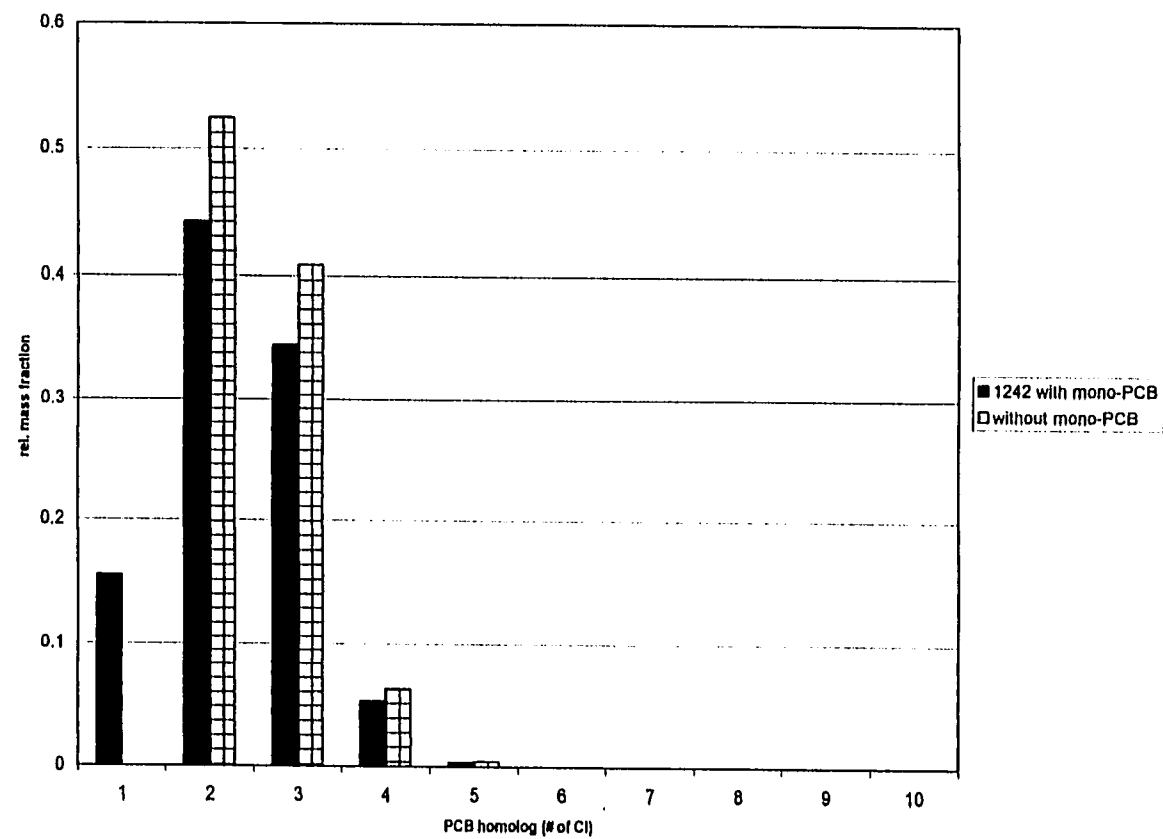
Figure 33.    Calculated mass fractions for homologs from Aroclor 1242 vapor with and without mono-polychlorinated biphenyls.

## TABLE XLVII

### CALCULATIONS FOR AROCLOR 1242 HOMOLOG PROFILE BASED ON VAPOR PRESSURE

| Homolog Group | $P_{vap}$ ($P_a$) | Mean MW (g/mol) | Mass Fraction in Oil INCLUDING Mono | Moles/g | Mol % | Mole Fraction (X) | Calc Partial Pressure $P_v$ $P_v = X*Pvap$ | $n/V = P_v/RT$ | $g/m^3$ | $ng/m^3$ | Mass fraction by wt. in air based on $P_v$ INCLUDING mono | Mass fraction by wt. in air based on EXCLUDING mono |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Biphenyl | 4.9 | 154.2 | | | | | | | | | | |
| 1 | 1.1 | 188.7 | 0.01 | 5.3E-05 | 1.41 | 0.0141 | 0.0155 | 6.26988E-06 | 0.00118 | 1183126 | 0.156 | 0 |
| 2 | 0.24 | 223.1 | 0.13 | 0.000583 | 15.5 | 0.155 | 0.0373 | 1.50416E-05 | 0.00336 | 3355776 | 0.443 | 0.525 |
| 3 | 0.054 | 257.6 | 0.45 | 0.00175 | 46.6 | 0.466 | 0.0252 | 1.01461E-05 | 0.00261 | 2613633 | 0.345 | 0.4085 |
| 4 | 0.012 | 292 | 0.31 | 0.001062 | 28.3 | 0.283 | 0.003397 | 1.37025E-06 | 0.0004 | 400111.7 | 0.0528 | 0.0625 |
| 5 | 2.60E-03 | 326.4 | 0.1 | 0.000306 | 8.17 | 0.0817 | 0.000212 | 8.56765E-08 | 2.8E-05 | 27964.8 | 0.00369 | 0.00437 |
| 6 | 5.80E-04 | 360.9 | | | | | 0 | 0 | 0 | 0 | 0 | 0 |
| 7 | 1.30E-04 | 395.3 | | | | | 0 | 0 | 0 | 0 | 0 | 0 |
| 8 | 2.80E-05 | 429.8 | | | | | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | 6.30E-06 | 464.2 | | | | | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 1.40E-06 | 498.7 | | | | | 0 | 0 | 0 | 0 | 0 | 0 |
| Totals | | | 1 | 0.004 | 100 | 100 | | 3.29135E-05 | 0.007581 | 7580612 | 1 | |
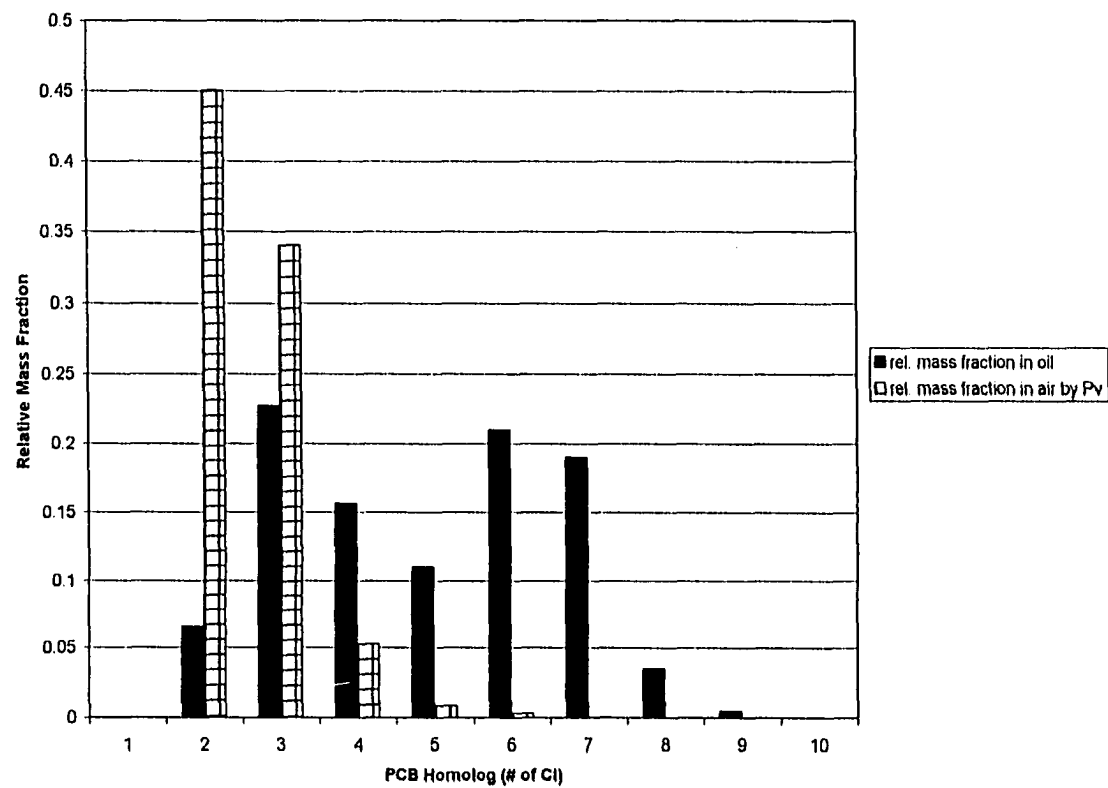
Figure 34.    Mass fractions calculated for Aroclor 1242/1260 one-to-one ratio based on vapor pressure.

## 4.2.2.4 Natural Log Transformed Total Polychlorinated Biphenyl Data

The PCBTOT data were transformed logarithmically using the natural log (LN) of the reported value. The PCB/CB data were then statistically analyzed looking at the data in a number of ways, including by Site ID and time period (i.e., i} before, ii} during, iii} after, and iv} before and after incineration). The descriptive statistics for this data are provided in Table XLVIII. The data appear to fit a log-normal distribution. This is supported by the Kurtosis and Skewness values for the log transformed data, which are much smaller than those for the original data.

Some preliminary comments can be made based on the results in Tables XLIV through XLVIII and Figures 30-34.

1)   Of the 1584 off-site air samples with PCB/CB results, 366 (approximately 33%) of them had concentrations for PCBTOT that were above the <W and/or <T flag concentrations. In other words, approximately 77% of the ambient air samples had PCBTOT results below the QL and/or DL. For the other analytes, the % of ND or <QL data was even greater, with a number of the analytes never observed in any samples.

2)   The descriptive statistics (skewness and kurtosis primarily) and histogram plot (Figure 30) indicate that the data is a log-normal distribution rather than a normal distribution. This result was not surprising and corresponds to the observations of others for many types of environmental data [236], including air pollutants [241, 242].

A series of student's T-tests were performed on the PCBTOT data (combined and by Site ID) to compare sampling periods i}, iii} and iv} with the incineration period ii}, to see if any statistically significant differences existed in the means. The t-test was performed on the reported data and the LN transformed data. The two-tailed t-test was performed, with homeoscadasticity (equal variance for means) and heteroscadasticity (unequal variance for means) assumptions being evaluated. This data is shown below in Table XLIX. A review of the t-test data shows that

- there is *no* difference in the means of all samples taken in periods i} (i.e., before incineration) and ii} (i.e., during incineration); and

- there are differences in the means between samples taken during period ii} (i.e., during) and iii} (i.e., after incineration), although it depends on the exact scenario being considered.

## TABLE XLVIII

### SUMMARY STATISTICS FOR UNTRANSPOSED AND NATURAL LOG TRANSPOSED TOTAL POLYCHLORINATED BIPHENYL DATA

| All Dates | All Sites | LN (All Sites) | 23007 | LN (23007) | 23009 | LN (23009) | 23011 | LN (23011) | 23013 | LN (23013) |
|---|---|---|---|---|---|---|---|---|---|---|
| n | 1584 | 1584 | 396 | 396 | 391 | 391 | 396.0 | 396 | 400 | 400 |
| MIN. | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| MAX. | 83.2 | 4.4 | 22.3 | 3.1 | 37.0 | 3.6 | 83.2 | 4.4 | 18.0 | 2.9 |
| Range | 83.0 | 6.0 | 22.1 | 4.7 | 36.8 | 5.2 | 83.0 | 6.0 | 17.8 | 4.5 |
| Mean | 1.3 | -0.8 | 2.6 | 0.3 | 391.0 | 0.3 | 396.0 | 0.2 | 199.6 | -0.1 |
| Median | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Std. Dev. | 3.79 | 1.23 | 21.09 | 21.02 | 21.15 | 20.92 | 21.63 | 21.04 | 21.04 | 21.11 |
| Mode | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Kurtosis | 178 | 1 | 14 | 0 | 36 | 1 | 158 | 1 | 53 | 2 |
| Skewness | 11 | 1 | 3 | 1 | 5 | 1 | 12 | 2 | 6 | 2 |

| Prior to Incineration | All Sites | LN (All Sites) | 23007 | LN (23007) | 23009 | LN (23009) | 23011 | LN (23011) | 23013 | LN (23013) |
|---|---|---|---|---|---|---|---|---|---|---|
| n | 41 | 41 | 8 | 8 | 11 | 11 | 12 | 12 | 10 | 10 |
| MIN. | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| MAX. | 3.3 | 1.2 | 0.9 | -0.1 | 0.8 | -0.2 | 3.3 | 1.2 | 0.8 | -0.2 |
| Range | 3.1 | 2.8 | 0.7 | 1.5 | 0.6 | 1.4 | 3.1 | 2.8 | 0.6 | 1.4 |
| Mean | 0.5 | -1.2 | 0.3 | -1.3 | 0.3 | -1.4 | 0.9 | -0.8 | 0.3 | -1.3 |
| Median | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.3 | -1.4 | 0.2 | -1.6 |
| Std. Dev. | 0.67 | 0.75 | 0.24 | 0.55 | 0.22 | 0.53 | 1.21 | 1.15 | 0.20 | 0.51 |
| Mode | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Kurtosis | 13 | 3 | 4 | 2 | 3 | 2 | 1 | -1 | 3 | 1 |
| Skewness | 4 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 2 | 1 |

TABLE XLVIII (Continued)

SUMMARY STATISTICS FOR UNTRANSPOSED AND NATURAL LOG TRANSPOSED
TOTAL POLYCHLORINATED BIPHENYL DATA

| During Incineration | All Sites | LN (All Sites) | 23007 | LN (23007) | 23009 | LN (23009) | 23011 | LN (23011) | 23013 | LN (23013) |
|---|---|---|---|---|---|---|---|---|---|---|
| n | 1483 | 1483 | 373 | 373 | 365 | 365 | 370 | 370 | 375 | 375 |
| MIN. | 0.2 | -1.6 | 0.2 | -1.6 | 0 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| MAX. | 83.2 | 4.4 | 22.3 | 3.1 | 37 | 3.6 | 83.2 | 4.4 | 18 | 2.9 |
| Range | 83.0 | 6.0 | 22.1 | 4.7 | 37 | 5.2 | 83 | 6.0 | 17.8 | 4.5 |
| Mean | 1.4 | -0.8 | 1.7 | -0.6 | 1.7 | -0.7 | 1.5 | -0.8 | 0.7 | -1.1 |
| Median | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Std. Dev. | 3.89 | 1.25 | 3.16 | 1.37 | 4.062 | 1.3 | 5.56 | 1.23 | 1.603 | 0.967 |
| Mode | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Kurtosis | 169 | 1 | 13 | 0 | 35 | 0 | 150 | 1 | 50 | 2 |
| Skewness | 10 | 1 | 3 | 1 | 5 | 1 | 11 | 1 | 6 | 2 |

| After Incineration | All Sites | LN (All sites) | 23007 | LN (23007) | 23009 | LN (23009) | 23011 | LN (23011) | 23013 | LN (23013) |
|---|---|---|---|---|---|---|---|---|---|---|
| n | 60 | 60 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| MIN. | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| MAX. | 1.6 | 0.5 | 0.2 | -1.6 | 0.2 | -1.6 | 1.6 | 0.47 | 0.2 | -1.6 |
| Range | 1.4 | 2.1 | 0 | 0 | 0 | 0 | 1.4 | 2.1 | 0 | 0 |
| Mean | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.3 | -1.4 | 0.2 | -1.6 |
| Median | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Std. Dev. | 0.21 | 0.31 | 5.27E-09 | 2.66E-08 | 3.04E-09 | 2.43E-08 | 0.4042 | 0.627 | 2.82E-09 | 2.25E-08 |
| Mode | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Kurtosis | 45 | 45 | -3 | -3 | -3 | -3 | 12 | 11 | -2 | -2 |
| Skewness | 7 | 7 | 1 | -1 | 1 | -1 | 4 | 3 | -1 | -1 |

## TABLE XLVIII (Concluded)

## SUMMARY STATISTICS FOR UNTRANSPOSED AND NATURAL LOG TRANSPOSED
## TOTAL POLYCHLORINATED BIPHENYL DATA

| Before and After Incineration | All Sites | LN (All Sites) | 23007 | LN (23007) | 23009 | LN (23009) | 23011 | LN (23011) | 23013 | LN (23013) |
|---|---|---|---|---|---|---|---|---|---|---|
| n | 101 | 101 | 23 | 23 | 26 | 27 | 27 | 27 | 25 | 25 |
| MIN. | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| MAX. | 3.3 | 1.2 | 0.9 | -0.1 | 0.8 | -0.2 | 3.3 | 1.2 | 0.8 | -0.2 |
| Range | 3.1 | 2.8 | 0.7 | 1.5 | 0.6 | 1.4 | 3.1 | 2.8 | 0.6 | 1.4 |
| Mean | 0.3 | -1.4 | 0.3 | -1.5 | 0.3 | -1.5 | 0.6 | -1.1 | 0.2 | -1.5 |
| Median | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Std. Dev. | 0.49 | 0.59 | 0.17 | 0.40 | 0.17 | 0.42 | 0.90 | 0.93 | 0.14 | 0.35 |
| Mode | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 | 0.2 | -1.6 |
| Kurtosis | 25 | 8 | 11 | 8 | 7 | 6 | 5 | 2 | 12 | 8 |
| Skewness | 5 | 3 | 3 | 3 | 3 | 3 | 2 | 2 | 3 | 3 |

**Note:**

Includes <W and <T samples at their reported values

## TABLE XLIX

### T-TEST RESULTS FOR UNTRANSPOSED AND NATURAL LOG TRANSPOSED
### TOTAL POLYCHLORINATED BIPHENYL DATA

| Two Tailed, Homeoscadasticity | All Sites | LN (All Sites) | 23007 | LN (23007) | 23009 | LN (23009) | 23011 | LN (23011) | 23013 | LN (23013) |
|---|---|---|---|---|---|---|---|---|---|---|
| Before vs. During | 0.137 | 0.062 | 0.18 | 0.12 | 0.29 | 0.12 | 0.75 | 0.85 | 0.42 | 0.46 |
| During vs. After | **0.048** | **0.000** | 0.13 | **0.02** | 0.34 | 0.07 | 0.47 | 0.09 | 0.21 | **0.04** |
| After vs. Before | **0.030** | **0.003** | 0.11 | 0.09 | 0.24 | 0.24 | 0.12 | 0.09 | **0.04** | **0.03** |
| Before & After vs. During | **0.014** | **0.000** | **0.04** | **0.01** | 0.16 | **0.02** | 0.46 | 0.27 | 0.14 | **0.04** |
| | | | | | | | | | | |
| t-test Two Tailed, Heteroscadasticity | | | | | | | | | | |
| Before vs. During | **0.000** | **0.004** | **0.00** | **0.00** | **0.00** | **0.00** | 0.26 | 0.84 | **0.00** | 0.20 |
| During vs. After | **0.000** | **0.000** | **0.00** | **0.00** | **0.00** | **0.00** | **0.00** | **0.01** | **0.00** | **0.00** |
| After vs. Before | **0.040** | **0.004** | 0.15 | 0.12 | 0.18 | 0.17 | 0.16 | 0.11 | 0.12 | 0.10 |
| Before & After vs. During | **0.000** | **0.000** | **0.00** | **0.00** | **0.00** | **0.00** | **0.01** | 0.17 | **0.00** | **0.00** |

**Notes:**

Critical Value for 95% CI = 0.05 for two tailed

**Bolded/underlined** values indicate statistically significant differences in means

### 4.2.3 Polychlorinated Dibenzo-p-Dioxins/Dibenzofurans Air Sampling Data Preparation

While the major focus of this research was on the PCB air monitoring results, the PCDD/DF results were also of interest. The PCDD/DF results were summarized in Section 3.4, including some preliminary statistical analyses. The available 2,3,7,8-PCDD/DF I-TEQ data were analyzed further to see if any additional insight could be gained.

The first issue that was investigated was the effect of assigning values of blank, 0 and the lowest detected I-TEQ for ND values of 2,3,7,8-PCDD/DF. Next, the effect of log-transformed data on the descriptive statistics was evaluated. This data is shown below in Table L. The data in Table L appears to be log-normal distributed, based on the skewness and kurtosis values and the frequency histograms for 2,3,7,8-PCDD/DF I-TEQ, OCDD, 1,2,3,4,6,7,8-HpCDD, and OCDF that are shown below in Figures 35-38. The summary statistics for the 2,3,7,8-PCDD/DF I-TEQ data sorted by sampling site and for various treatments of ND data are shown in Table LI.

Only 16 of the 185 samples did not have at least one of the 2,3,7,8-PCDD/DF compounds detected. The most commonly detected compounds were OCDD (169/185), 1,2,3,4,6,7,8-HpCDD (140/185), OCDF (92/185), and 2,3,7,8-TeCDF (80/185). The correlations between the 2,3,7,8-PCDD/DF analytes were examined. The correlation matrix for the 2,3,7,8-PCDD/DF compounds is shown below in Table LII. Only 12 out of a possible 289 correlations were significant at $p < 0.05$ and with >40 samples. The correlations with total I-TEQ were carried out with the different treatments of ND discussed above.

# TABLE L

## SUMMARY STATISTICS FOR 2,3,7,8-POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS
## INTERNATIONAL – TOXIC EQUIVALENCY DATA

| Statistical Parameter | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cl4DF1 | Cl4DF1 | LnCl4DF1 | Cl4DD1 | Cl4DD1 | LnCl4DD1 | Cl5DF1 | Cl5DF1 | LnCl5DF1 | Cl5DF2 | Cl5DF2 | LnCl5DF2 |
| n | 80 | 185 | 80 | 1 | 185 | 1 | 13 | 185 | 13 | 22 | 185 | 22 |
| n=0 | 0 | 105 | 0 | 0 | 184 | 0 | 0 | 172 | 0 | 0 | 163 | 0 |
| n>0 | 80 | 80 | 0 | 1 | 1 | 0 | 13 | 13 | 0 | 22 | 22 | 0 |
| n blank | 105 | 0 | 105 | 184 | 0 | 184 | 172 | 0 | 172 | 163 | 0 | 163 |
| n calc. I-TEQ | 185 | 185 | 105 | 185 | 185 | 184 | 185 | 185 | 172 | 185 | 185 | 163 |
| Minimum | 1.45E-03 | 0.00E+00 | -6.54E+00 | 2.91E-01 | 0.00E+00 | -1.24E+00 | 5.81E-04 | 0.00E+00 | -7.45E+00 | 5.17E-03 | 0.00E+00 | -5.27E+00 |
| Maximum | 2.55E-01 | 2.55E-01 | -1.37E+00 | 2.91E-01 | 2.91E-01 | -1.24E+00 | 5.89E-02 | 5.89E-02 | -2.83E+00 | 8.50E-01 | 8.50E-01 | -1.62E-01 |
| Range | 2.54E-01 | 2.55E-01 | 5.17E+00 | 0.00E+00 | 2.91E-01 | 0.00E+00 | 5.83E-02 | 5.89E-02 | 4.62E+00 | 8.45E-01 | 8.50E-01 | 5.10E+00 |
| Sum | 1.29E+00 | 1.29E+00 | -3.91E+02 | 2.91E-01 | 2.91E-01 | -1.24E+00 | 1.67E-01 | 1.67E-01 | -7.09E+01 | 2.09E+00 | 2.09E+00 | -7.58E+01 |
| Median | 6.80E-03 | 0.00E+00 | -4.99E+00 | 2.91E-01 | 0.00E+00 | -1.24E+00 | 2.60E-03 | 0.00E+00 | -5.95E+00 | 2.14E-02 | 0.00E+00 | -3.84E+00 |
| Mean | 1.61E-02 | 6.96E-03 | -4.89E+00 | 2.91E-01 | 1.57E-03 | -1.24E+00 | 1.29E-02 | 9.05E-04 | -5.45E+00 | 9.52E-02 | 1.13E-02 | -3.45E+00 |
| 95% CI Upper | 5.50E-02 | 3.37E-02 | -3.89E+00 | #DIV/0! | 2.29E-02 | #DIV/0! | 3.29E-02 | 7.00E-03 | -3.92E+00 | 3.03E-01 | 8.81E-02 | -2.17E+00 |
| 95% CI Lower | -2.28E-02 | -1.98E-02 | -5.89E+00 | #DIV/0! | -1.98E-02 | #DIV/0! | -7.19E-03 | -5.19E-03 | -6.98E+00 | -1.13E-01 | -6.54E-02 | -4.73E+00 |
| Mode | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A |
| Std. Dev. | 3.89E-02 | 2.67E-02 | 1.00E+00 | #DIV/0! | 2.14E-02 | #DIV/0! | 2.01E-02 | 6.10E-03 | 1.53E+00 | 2.08E-01 | 7.68E-02 | 1.28E+00 |
| Variance | 1.52E-03 | 7.15E-04 | 1.01E+00 | #DIV/0! | 4.56E-04 | #DIV/0! | 4.03E-04 | 3.72E-05 | 2.35E+00 | 4.33E-02 | 5.89E-03 | 1.64E+00 |
| Skewness (G1) | 5 | 8 | 1 | #DIV/0! | 14 | #DIV/0! | 2 | 8 | 1 | 3 | 10 | 1 |
| Kurtosis (G2) | 29 | 66 | 2 | #DIV/0! | 185 | #DIV/0! | 2 | 73 | -1 | 10 | 95 | 2 |

## Notes:

1)   ND values treated in various manners

2)   Concentration in $pg/m^3$ I-TEQ

3)   #N/A = not applicable (no value occurred more than once)

4)   #DIV/0! = calculation cannot be performed

# TABLE L (Continued)

## SUMMARY STATISTICS FOR 2,3,7,8-POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS
## INTERNATIONAL – TOXIC EQUIVALENCY DATA

| Statistical Parameter | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cl6DF1 | Cl6DF1 | LnCl6DF1 | Cl6DF2 | Cl6DF2 | LnCl6DF2 | Cl6DF3 | Cl6DF3 | LnCl6DF3 | Cl6DF4 | Cl6DF4 | LnCl6DF4 |
| n of cases | 41 | 185 | 41 | 18 | 185 | 18 | 15 | 185 | 14 | 3 | 185 | 2 |
| n=0 | 0 | 144 | 0 | 0 | 167 | 0 | 0 | 170 | 0 | 1 | 183 | 0 |
| n>0 | 41 | 41 | 0 | 18 | 18 | 0 | 15 | 15 | 0 | 2 | 2 | 0 |
| n blank | 144 | 0 | 144 | 167 | 0 | 167 | 170 | 0 | 171 | 182 | 0 | 183 |
| n calculated | 185 | 185 | 144 | 185 | 185 | 167 | 185 | 185 | 171 | 185 | 185 | 183 |
| Minimum | 1.04E-03 | 0.00E+00 | -6.87E+00 | 1.54E-03 | 0.00E+00 | -6.48E+00 | 1.85E-03 | 0.00E+00 | -6.29E+00 | 0.00E+00 | 0.00E+00 | -4.07E+00 |
| Maximum | 1.30E-01 | 1.30E-01 | -2.04E+00 | 4.37E-02 | 4.37E-02 | -3.13E+00 | 2.20E-01 | 2.20E-01 | -1.51E+00 | 1.49E-01 | 1.49E-01 | -1.90E+00 |
| Range | 1.29E-01 | 1.30E-01 | 4.83E+00 | 4.22E-02 | 4.37E-02 | 3.35E+00 | 2.18E-01 | 2.20E-01 | 4.78E+00 | 1.49E-01 | 1.49E-01 | 2.17E+00 |
| Sum | 4.53E-01 | 4.53E-01 | -2.09E+02 | 1.31E-01 | 1.31E-01 | -9.75E+01 | 3.88E-01 | 3.88E-01 | -6.58E+01 | 1.66E-01 | 1.66E-01 | -5.98E+00 |
| Median | 5.82E-03 | 0.00E+00 | -5.15E+00 | 3.28E-03 | 0.00E+00 | -5.72E+00 | 5.69E-03 | 0.00E+00 | -5.10E+00 | 1.70E-02 | 0.00E+00 | -2.99E+00 |
| Mean | 1.10E-02 | 2.45E-03 | -5.10E+00 | 7.26E-03 | 7.07E-04 | -5.42E+00 | 2.59E-02 | 2.10E-03 | -4.70E+00 | 5.54E-02 | 8.98E-04 | -2.99E+00 |
| 95% CI Upper | 3.19E-02 | 1.32E-02 | -4.16E+00 | 1.74E-02 | 4.47E-03 | -4.52E+00 | 8.22E-02 | 1.92E-02 | -3.37E+00 | 1.37E-01 | 1.19E-02 | -1.45E+00 |
| 95% CI Lower | -9.79E-03 | -8.30E-03 | -6.04E+00 | -2.89E-03 | -3.06E-03 | -6.32E+00 | -3.05E-02 | -1.50E-02 | -6.03E+00 | -2.63E-02 | -1.01E-02 | -4.52E+00 |
| Mode | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A |
| Std. Dev. | 2.08E-02 | 1.07E-02 | 9.41E-01 | 1.02E-02 | 3.77E-03 | 8.97E-01 | 5.64E-02 | 1.71E-02 | 1.33E+00 | 8.17E-02 | 1.10E-02 | 1.54E+00 |
| Variance | 4.34E-04 | 1.15E-04 | 8.86E-01 | 1.03E-04 | 1.42E-05 | 8.04E-01 | 3.18E-03 | 2.92E-04 | 1.77E+00 | 6.67E-03 | 1.22E-04 | 2.36E+00 |
| Skewness (G1) | 5 | 10 | 1 | 3 | 9 | 1 | 3 | 10 | 1 | 2 | 13 | #DIV/0! |
| Kurtosis (G2) | 28 | 109 | 2 | 11 | 96 | 1 | 12 | 147 | 1 | #DIV/0! | 180 | #DIV/0! |

## Notes:

1) ND values treated in various manners
2) Concentration in pg/m3 I-TEQ
3) #N/A = not applicable (no value occurred more than once)
4) #DIV/0! = calculation cannot be performed

**TABLE L (Continued)**

## SUMMARY STATISTICS FOR 2,3,7,8-POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS
### INTERNATIONAL – TOXIC EQUIVALENCY DATA

| Statistical Parameter | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Cl6DD1 | Cl6DD1 | LnCl6DD1 | Cl6DD2 | Cl6DD2 | LnCl6DD2 | Cl6DD3 | Cl6DD3 | LnCl6DD3 | Cl7DF1 | Cl7DF1 | LnCl7DF1 |
| n of cases | 6 | 185 | 6 | 11 | 185 | 11 | 12 | 185 | 12 | 44 | 185 | 42 |
| n=0 | 0 | 179 | 0 | 0 | 174 | 0 | 0 | 173 | 0 | 2 | 143 | 0 |
| n>0 | 6 | 6 | 0 | 11 | 11 | 0 | 12 | 12 | 0 | 42 | 42 | 0 |
| n blank | 179 | 0 | 179 | 174 | 0 | 174 | 173 | 0 | 173 | 141 | 0 | 143 |
| n calculated | 185 | 185 | 179 | 185 | 185 | 174 | 185 | 185 | 173 | 185 | 185 | 143 |
| Minimum | 1.09E-03 | 0.00E+00 | -6.82E+00 | 1.34E-03 | 0.00E+00 | -6.62E+00 | 1.18E-03 | 0.00E+00 | -6.75E+00 | 0.00E+00 | 0.00E+00 | -8.05E+00 |
| Maximum | 1.57E-01 | 1.57E-01 | -1.85E+00 | 1.41E-01 | 1.41E-01 | -1.96E+00 | 2.12E-01 | 2.12E-01 | -1.55E+00 | 2.51E-02 | 2.51E-02 | -3.68E+00 |
| Range | 1.56E-01 | 1.57E-01 | 4.97E+00 | 1.40E-01 | 1.41E-01 | 4.66E+00 | 2.11E-01 | 2.12E-01 | 5.20E+00 | 2.51E-02 | 2.51E-02 | 4.36E+00 |
| Sum | 1.69E-01 | 1.69E-01 | -3.25E+01 | 1.75E-01 | 1.75E-01 | -6.00E+01 | 2.74E-01 | 2.74E-01 | -6.02E+01 | 8.61E-02 | 8.61E-02 | -2.83E+02 |
| Median | 3.04E-03 | 0.00E+00 | -5.81E+00 | 3.55E-03 | 0.00E+00 | -5.64E+00 | 6.05E-03 | 0.00E+00 | -5.11E+00 | 8.60E-04 | 0.00E+00 | -6.83E+00 |
| Mean | 2.82E-02 | 9.15E-04 | -5.41E+00 | 1.59E-02 | 9.46E-04 | -5.46E+00 | 2.29E-02 | 1.48E-03 | -5.02E+00 | 1.96E-03 | 4.65E-04 | -6.74E+00 |
| 95% CI Upper | 9.13E-02 | 1.25E-02 | -3.60E+00 | 5.75E-02 | 1.14E-02 | -4.19E+00 | 8.25E-02 | 1.71E-02 | -3.76E+00 | 5.79E-03 | 2.50E-03 | -5.85E+00 |
| 95% CI Lower | -3.49E-02 | -1.06E-02 | -7.23E+00 | -2.57E-02 | -9.47E-03 | -6.72E+00 | -3.68E-02 | -1.42E-02 | -6.28E+00 | -1.88E-03 | -1.57E-03 | -7.63E+00 |
| Mode | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A | #N/A | 0.00E+00 | #N/A | 6.00E-04 | 0.00E+00 | -7.42E+00 |
| Std. Dev. | 6.31E-02 | 1.16E-02 | 1.81E+00 | 4.16E-02 | 1.04E-02 | 1.26E+00 | 5.96E-02 | 1.56E-02 | 1.26E+00 | 3.84E-03 | 2.03E-03 | 8.94E-01 |
| Variance | 3.99E-03 | 1.33E-04 | 3.29E+00 | 1.73E-03 | 1.08E-04 | 1.59E+00 | 3.56E-03 | 2.44E-04 | 1.58E+00 | 1.47E-05 | 4.14E-06 | 7.99E-01 |
| Skewness (G1) | 3 | 14 | 2 | 3 | 14 | 2 | 3 | 13 | 2 | 5 | 10 | 1 |
| Kurtosis (G2) | 6 | 184 | 5 | 11 | 183 | 7 | 12 | 182 | 6 | 32 | 119 | 2 |

**Notes:**
1)   ND values treated in various manners
2)   Concentration in pg/m3 I-TEQ
3)   #N/A = not applicable (no value occurred more than once)
4)   #DIV/0! = calculation cannot be performed

# TABLE L (Continued)

## SUMMARY STATISTICS FOR 2,3,7,8-POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS
## INTERNATIONAL – TOXIC EQUIVALENCY DATA

| Statistical Parameter | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank | ND = blank | ND = 0 | ND = blank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Cl7DF2 | Cl7DF2 | LnCl7DF2 | Cl7DD1 | Cl7DD1 | LnCl7DD1 | Cl8DF1 | Cl8DF1 | LnCl8DF1 | Cl8DD1 | Cl8DD1 | LnCl8DD1 |
| n of cases | 8 | 185 | 8 | 141 | 185 | 140 | 92 | 185 | 92 | 162 | 185 | 162 |
| n=0 | 0 | 177 | 0 | 1 | 45 | 0 | 0 | 93 | 0 | 0 | 23 | 0 |
| n>0 | 8 | 8 | 0 | 140 | 140 | 0 | 92 | 92 | 0 | 162 | 162 | 0 |
| n blank | 177 | 0 | 177 | 44 | 0 | 45 | 93 | 0 | 93 | 23 | 0 | 23 |
| n calculated | 185 | 185 | 177 | 185 | 185 | 45 | 185 | 185 | 93 | 185 | 185 | 23 |
| Minimum | 6.48E-05 | 0.00E+00 | -9.64E+00 | 0.00E+00 | 0.00E+00 | -7.79E+00 | 2.01E-05 | 0.00E+00 | -1.08E+01 | 6.17E-05 | 0.00E+00 | -9.69E+00 |
| Maximum | 1.26E-02 | 1.26E-02 | -4.38E+00 | 1.73E-02 | 1.73E-02 | -4.06E+00 | 3.56E-03 | 3.56E-03 | -5.64E+00 | 3.18E-03 | 3.18E-03 | -5.75E+00 |
| Range | 1.25E-02 | 1.26E-02 | 5.27E+00 | 1.73E-02 | 1.73E-02 | 3.73E+00 | 3.54E-03 | 3.56E-03 | 5.18E+00 | 3.12E-03 | 3.18E-03 | 3.94E+00 |
| Sum | 2.08E-02 | 2.08E-02 | -5.71E+01 | 2.98E-01 | 2.98E-01 | -9.06E+02 | 1.91E-02 | 1.91E-02 | -8.45E+02 | 8.51E-02 | 8.51E-02 | -1.26E+03 |
| Median | 4.59E-04 | 0.00E+00 | -7.69E+00 | 1.42E-03 | 1.15E-03 | -6.55E+00 | 8.68E-05 | 0.00E+00 | -9.35E+00 | 3.81E-04 | 3.47E-04 | -7.87E+00 |
| Mean | 2.60E-03 | 1.12E-04 | -7.14E+00 | 2.12E-03 | 1.61E-03 | -6.47E+00 | 2.07E-04 | 1.03E-04 | -9.19E+00 | 5.25E-04 | 4.60E-04 | -7.79E+00 |
| 95% CI Upper | 6.96E-03 | 1.11E-03 | -5.47E+00 | 4.40E-03 | 3.80E-03 | -5.73E+00 | 6.91E-04 | 4.59E-04 | -8.24E+00 | 9.87E-04 | 9.26E-04 | -7.13E+00 |
| 95% CI Lower | -1.76E-03 | -8.90E-04 | -8.81E+00 | -1.67E-04 | -5.74E-04 | -7.22E+00 | -2.76E-04 | -2.52E-04 | -1.01E+01 | 6.36E-05 | -5.59E-06 | -8.45E+00 |
| Mode | #N/A | 0.00E+00 | #N/A | 1.00E-03 | 0.00E+00 | -6.91E+00 | #N/A | 0.00E+00 | #N/A | 2.68E-04 | 0.00E+00 | -8.23E+00 |
| Std. Dev. | 4.36E-03 | 1.00E-03 | 1.67E+00 | 2.28E-03 | 2.19E-03 | 7.44E-01 | 4.83E-04 | 3.55E-04 | 9.45E-01 | 4.62E-04 | 4.66E-04 | 6.60E-01 |
| Variance | 1.90E-05 | 1.00E-06 | 2.79E+00 | 5.21E-06 | 4.78E-06 | 5.54E-01 | 2.34E-07 | 1.26E-07 | 8.93E-01 | 2.13E-07 | 2.17E-07 | 4.35E-01 |
| Skewness (G1) | 2 | 11 | 0 | 4 | 4 | 1 | 5 | 7 | 1 | 3 | 3 | 1 |
| Kurtosis (G2) | 5 | 134 | -124 | 17 | 18 | 0 | 31 | 62 | 3 | 12 | 11 | 1 |

Notes:
1) ND values treated in various manners
2) Concentration in pg/m3 I-TEQ
3) #N/A = not applicable (no value occurred more than once)
4) #DIV/0! = calculation cannot be performed

218

# TABLE L (Concluded)

SUMMARY STATISTICS FOR 2,3,7,8-POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS
INTERNATIONAL – TOXIC EQUIVALENCY DATA

| Statistical Parameter | ND = blank | ND = 0 | ND = MIN. value | ND = blank |
|---|---|---|---|---|
| | 2378TOT | 2378TOT | 2378TOT | Ln2378TOT |
| n of cases | 169 | 185 | 185 | 169 |
| n=0 | 0 | 16 | 0 | 0 |
| n>0 | 169 | 169 | 185 | 2 |
| n blank | 16 | 0 | 0 | 16 |
| n calculated | 185 | 185 | 185 | 18 |
| Minimum | 1.84E-04 | 0.00E+00 | 1.84E-04 | -8.60E+00 |
| Maximum | 2.59E+00 | 2.59E+00 | 2.59E+00 | 9.52E-01 |
| Range | 2.59E+00 | 2.59E+00 | 2.59E+00 | 9.55E+00 |
| Sum | 6.80E+00 | 6.80E+00 | 6.80E+00 | -8.88E+02 |
| Median | 5.17E-03 | 4.43E-03 | 4.43E-03 | -5.26E+00 |
| Mean | 4.02E-02 | 3.68E-02 | 3.68E-02 | -5.25E+00 |
| 95% CI Upper | 2.64E-01 | 2.51E-01 | 2.51E-01 | -3.53E+00 |
| 95% CI Lower | -1.84E-01 | -1.78E-01 | -1.78E-01 | -6.97E+00 |
| Mode | #N/A | 0.00E+00 | 1.84E-04 | #N/A |
| Std. Dev. | 2.24E-01 | 2.14E-01 | 2.14E-01 | 1.72E+00 |
| Variance | 5.02E-02 | 4.59E-02 | 4.59E-02 | 2.96E+00 |
| Skewness (G1) | 10 | 10 | 10 | 0 |
| Kurtosis (G2) | 106 | 116 | 116 | 1 |

Notes:
1) ND values treated in various manners
2) Concentration in pg/m$^3$ I-TEQ
3) #N/A = not applicable (no value occurred more than once)
4) #DIV/0! = calculation cannot be performed
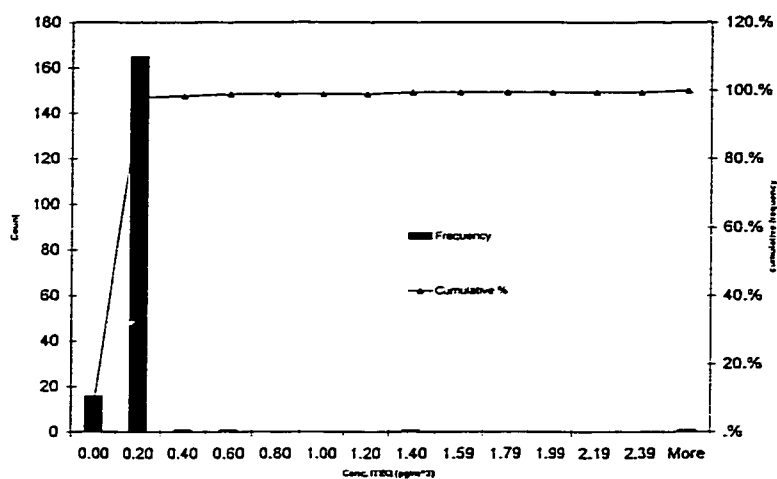
Figure 35.    Histogram frequency plot for 2,3,7,8 polychlorinated dibenzo-p-dioxins/ dibenzofurans (picograms per cubic meter, International Toxic Equivalency).
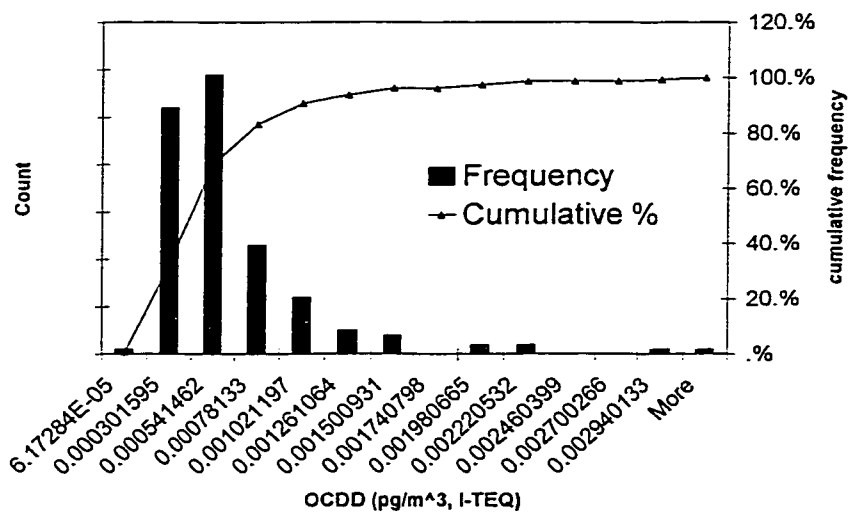


Figure 36.    Histogram frequency plot for octachlorodibenzo-p-dioxins.
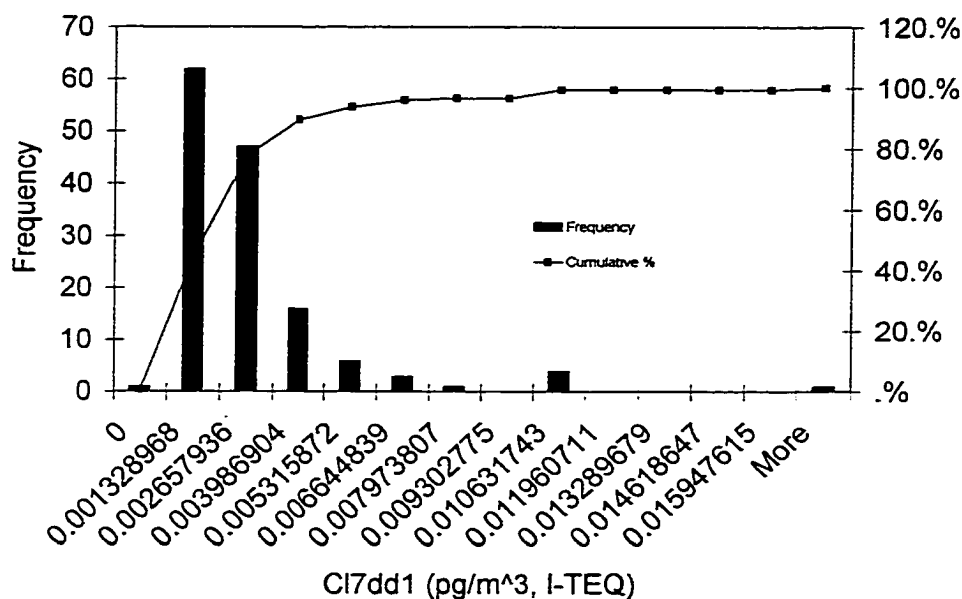
Figure 37.    Histogram frequency plot for 1,2,3,4,6,7,8-heptachloro-dibenzo-p-dioxins.
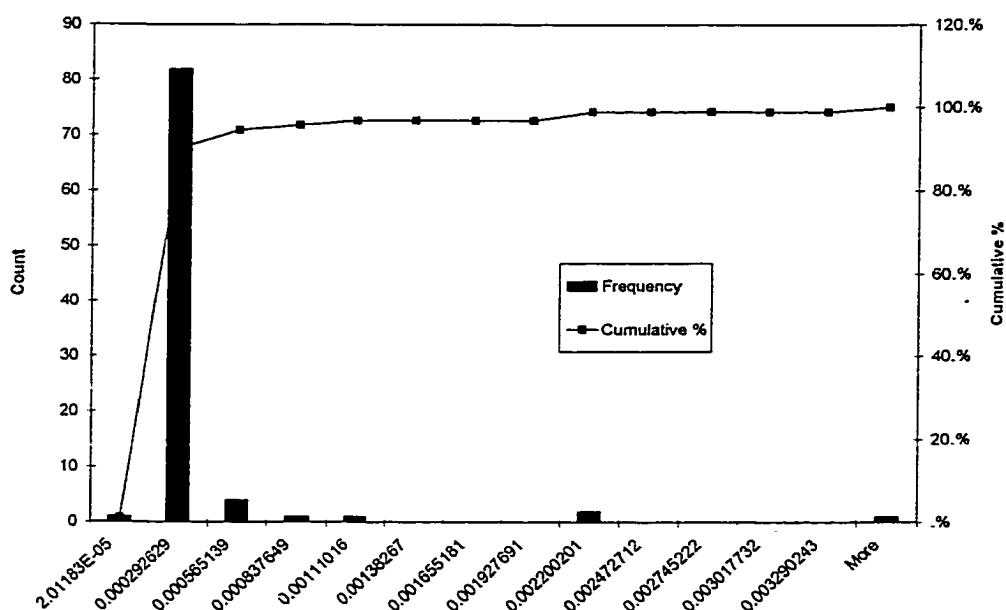


Figure 38.    Histogram frequency plot for octachlorodibenzofurans.

# TABLE LI

## SUMMARY STATISTICS FOR POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS
## INTERNATIONAL TOXIC EQUIVALENCY (PICOGRAMS PER CUBIC METER) BY SAMPLING SITE

| | 23007 | | | | 23009 | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | ND not considered | ND=2E-4 | ND=0 | ND=ND | ND not considered | ND=2E-4 | ND=0 | ND=ND |
| n of cases | 54 | 58 | 59 | 54 | 41 | 43 | 43 | 41 |
| n=0 | 0 | 0 | 5 | 0 | 0 | 0 | 2 | 0 |
| n>0 | 54 | 58 | 54 | 54 | 41 | 43 | 41 | 41 |
| n blank | 18 | 18 | 18 | 18 | 34 | 34 | 34 | 34 |
| n calculated | 72 | 76 | 77 | 72 | 75 | 77 | 77 | 75 |
| n=ND | | | | 5 | | | | 2 |
| n total | | | | 77 | | | | 77 |
| Minimum | 3.09E-04 | 2.00E-04 | 0.00E+00 | 3.09E-04 | 2.21E-04 | 2.00E-04 | 0.00E+00 | 2.21E-04 |
| Maximum | 2.59E+00 | 2.59E+00 | 2.59E+00 | 2.59E+00 | 1.38E-01 | 1.38E-01 | 1.38E-01 | 1.38E-01 |
| Range | 2.59E+00 | 2.59E+00 | 2.59E+00 | 2.59E+00 | 1.37E-01 | 1.37E-01 | 1.38E-01 | 1.37E-01 |
| Sum | 3.15E+00 | 3.15E+00 | 3.15E+00 | 3.15E+00 | 8.20E-01 | 8.20E-01 | 8.20E-01 | 8.20E-01 |
| Median | 4.25E-03 | 3.67E-03 | 3.57E-03 | 4.25E-03 | 4.86E-03 | 4.74E-03 | 4.74E-03 | 4.86E-03 |
| Mean | 5.84E-02 | 5.44E-02 | 5.34E-02 | 5.84E-02 | 2.00E-02 | 1.91E-02 | 1.91E-02 | 2.00E-02 |
| 95% CI Upper | 4.10E-01 | 3.94E-01 | 3.90E-01 | 4.10E-01 | 5.27E-02 | 5.12E-02 | 5.12E-02 | 5.27E-02 |
| 95% CI Lower | -2.93E-01 | -2.85E-01 | -2.83E-01 | -2.93E-01 | -1.26E-02 | -1.31E-02 | -1.31E-02 | -1.26E-02 |
| Mode | #N/A | 0.0002 | 0 | #N/A | #N/A | 0.0002 | 0 | #N/A |
| Std. Error | 4.78E-02 | 4.45E-02 | 4.58E-02 | 4.78E-02 | 5.10E-03 | 4.90E-03 | 5.02E-03 | 5.10E-03 |
| Std. Dev. | 0.35 | 0.34 | 0.34 | 0.35 | 0.033 | 0.032 | 0.032 | 0.033 |
| Variance | 0.12 | 0.12 | 0.11 | 0.12 | 0.0011 | 0.001 | 0.001 | 0.0011 |
| Skewness (G1) | 7 | 8 | 8 | 7 | 3 | 3 | 3 | 3 |
| Kurtosis (G2) | 54 | 58 | 59 | 54 | 7 | 7 | 7 | 7 |

TABLE LI (Concluded)

SUMMARY STATISTICS FOR POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS
INTERNATIONAL TOXIC EQUIVALENCY (PICOGRAMS PER CUBIC METER) BY SAMPLING SITE

| | | 23011 | | | | 23013 | | |
|---|---|---|---|---|---|---|---|---|
| | ND not considered | ND=2E-4 | ND=0 | ND=ND | ND not considered | ND=2E-4 | ND=0 | ND=ND |
| | 23011 | 23011 | 23011 | 23011 | 23013 | 23013 | 23013 | 23013 |
| n of cases | 39 | 43 | 43 | 39 | 35 | 40 | 40 | 35 |
| n=0 | 0 | 0 | 4 | 0 | 0 | 0 | 5 | 0 |
| n>0 | 39 | 43 | 39 | 39 | 35 | 40 | 35 | 35 |
| n blank | 34 | 34 | 34 | 34 | 37 | 37 | 37 | 37 |
| n calculated | 73 | 77 | 77 | 73 | 72 | 77 | 77 | 72 |
| n=ND | | | | 4 | | | | 5 |
| n total | | | | 77 | | | | 77 |
| Minimum | 1.84E-04 | 1.84E-04 | 0.00E+00 | 1.84E-04 | 2.24E-04 | 2.00E-04 | 0.00E+00 | 2.24E-04 |
| Maximum | 1.21E+00 | 1.21E+00 | 1.21E+00 | 1.21E+00 | 2.48E-01 | 2.48E-01 | 2.48E-01 | 2.48E-01 |
| Range | 1.21E+00 | 1.21E+00 | 1.21E+00 | 1.21E+00 | 2.48E-01 | 2.48E-01 | 2.48E-01 | 2.48E-01 |
| Sum | 2.31E+00 | 2.31E+00 | 2.31E+00 | 2.31E+00 | 5.18E-01 | 5.19E-01 | 5.18E-01 | 5.18E-01 |
| Median | 8.47E-03 | 7.34E-03 | 7.34E-03 | 8.47E-03 | 5.08E-03 | 3.90E-03 | 3.90E-03 | 5.08E-03 |
| Mean | 5.92E-02 | 5.37E-02 | 5.37E-02 | 5.92E-02 | 1.48E-02 | 1.30E-02 | 1.29E-02 | 1.48E-02 |
| 95% CI Upper | 2.71E-01 | 2.56E-01 | 2.56E-01 | 2.71E-01 | 5.71E-02 | 5.28E-02 | 5.28E-02 | 5.71E-02 |
| 95% CI Lower | -1.52E-01 | -1.48E-01 | -1.48E-01 | -1.52E-01 | -2.75E-02 | -2.68E-02 | -2.69E-02 | -2.75E-02 |
| Mode | #N/A | 0.0002 | 0 | #N/A | #N/A | 0.0002 | 0 | #N/A |
| Std. Error | 3.39E-02 | 3.08E-02 | 3.24E-02 | 3.39E-02 | 7.15E-03 | 6.29E-03 | 6.73E-03 | 7.15E-03 |
| Std. Dev. | 0.21 | 0.2 | 0.2 | 0.21 | 0.042 | 0.04 | 0.04 | 0.042 |
| Variance | 0.045 | 0.041 | 0.041 | 0.045 | 0.0018 | 0.0016 | 0.0016 | 0.0018 |
| Skewness (G1) | 5 | 5 | 5 | 5 | 5 | 6 | 6 | 5 |
| Kurtosis (G2) | 25 | 28 | 28 | 25 | 29 | 33 | 33 | 29 |

TABLE LII

## PEARSON CORRELATION MATRIX FOR OFF-SITE 2,3,7,8 POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS AMBIENT AIR DATA

| | Cl4DF1 | Cl4DD1 | Cl5DF1 | Cl5DF2 | Cl5DD1 | Cl6DF1 | Cl6DF2 | Cl6DF3 | Cl6DF4 | Cl6DD1 | Cl6DD2 | Cl6DD3 | Cl7DF1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| n detects | 80 | 1 | 13 | 22 | 3 | 41 | 18 | 15 | 2 | 6 | 11 | 12 | 44 |
| Cl4DF1 | 1.000 | | | | | | | | | | | | |
| Cl4DD1 | 0.070 | 1.000 | | | | | | | | | | | |
| Cl5DF1 | 0.620 | 0.703 | 1.000 | | | | | | | | | | |
| Cl5DF2 | 0.646 | 0.556 | 0.606 | 1.000 | | | | | | | | | |
| Cl5DD1 | 0.071 | 0.999 | 0.703 | 0.557 | 1.000 | | | | | | | | |
| Cl6DF1 | $r^2 = 0.787$ p<0.000 | 0.106 | 0.716 | 0.328 | 0.109 | 1.000 | | | | | | | |
| Cl6DF2 | 0.735 | 0.340 | 0.847 | 0.405 | 0.344 | 0.952 | 1.000 | | | | | | |
| Cl6DF3 | 0.318 | 0.942 | 0.876 | 0.602 | 0.943 | 0.420 | 0.624 | 1.000 | | | | | |
| Cl6DF4 | 0.139 | 0.994 | 0.770 | 0.551 | 0.993 | 0.205 | 0.434 | 0.970 | 1.000 | | | | |
| Cl6DD1 | 0.070 | 0.999 | 0.703 | 0.556 | 1.000 | 0.109 | 0.342 | 0.943 | 0.993 | 1.000 | | | |
| Cl6DD2 | 0.070 | 0.997 | 0.700 | 0.556 | 0.998 | 0.114 | 0.343 | 0.942 | 0.990 | 0.998 | 1.000 | | |
| Cl6DD3 | 0.089 | 0.995 | 0.719 | 0.554 | 0.996 | 0.141 | 0.369 | 0.949 | 0.992 | 0.046 | 0.998 | 1.000 | |
| Cl7DF1 | $r^2 = 0.567$ p <0.05 | 0.036 | 0.592 | 0.016 | 0.040 | 0.907 p<0.05 | 0.872 | 0.342 | 0.137 | 0.917 | 0.046 | 0.074 | 1.000 |
| Cl7DF2 | 0.298 | 0.918 | 0.885 | 0.508 | 0.919 | 0.456 | 0.660 | 0.991 | 0.955 | 0.558 | 0.917 | 0.927 | 0.414 |
| Cl7DD1 | 0.107 | 0.539 | 0.478 | 0.256 | 0.543 | 0.266 | 0.359 | 0.573 | 0.557 | 0.436 | 0.558 | 0.566 | 0.276 p<0.053 |
| Cl8DF1 | $r^2 = 0.605$ p<0.000 | 0.436 | 0.758 | 0.278 | 0.436 | 0.729 p<0.000 | 0.792 | 0.638 | 0.515 | 0.418 | 0.436 | 0.459 | 0.746 p<0.05 |
| Cl8DD1 | 0.234 | 0.400 | 0.354 | 0.295 | 0.404 | 0.184 | 0.236 | 0.417 | 0.410 | 0.881 | 0.418 | 0.426 | 0.193 |
| 2378TOT ND0 | $r^2 = 0.505$ p<0.005 | 0.881 | 0.856 | 0.843 | 0.882 | 0.419 p<0.05 | 0.590 | 0.934 | 0.898 | 0.882 | 0.881 | 0.886 | 0.227 |
| 2378TOT NDDL | $r^2 = 0.504$ p<0.000 | 0.882 | 0.856 | 0.842 | 0.882 | 0.419 p<0.000 | 0.590 | 0.934 | 0.898 | 0.881 | 0.882 | 0.886 | 0.227 |
| 2378TOT NDBLK | $r^2 = 0.505$ p<0.000 | 0.881 | 0.856 | 0.843 | 0.882 | 0.419 p<0.000 | 0.590 | 0.934 | 0.898 | 1.000 | 0.881 | 0.886 | 0.227 |

## TABLE LII (Concluded)

### PEARSON CORRELATION MATRIX FOR OFF-SITE 2,3,7,8 POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS AMBIENT AIR DATA

| | CI7DF1 | CI7DF2 | CI7DD1 | CI8DF1 | CI8DD1 | TOT2378ND0 | TOT2378NDDL | TOT2378NDBLK |
|---|---|---|---|---|---|---|---|---|
| n detected | 44 | 8 | 141 | 92 | 162 | 169 | 169 | 169 |
| CI4DF1 | | | | | | | | |
| CI4DD1 | | | | | | | | |
| CI5DF1 | | | | | | | | |
| CI5DF2 | | | | | | | | |
| CI5DD1 | | | | | | | | |
| CI6DF1 | | | | | | | | |
| CI6DF2 | | | | | | | | |
| CI6DF3 | | | | | | | | |
| CI6DF4 | | | | | | | | |
| CI6DD1 | | | | | | | | |
| CI6DD2 | | | | | | | | |
| CI6DD3 | | | | | | | | |
| CI7DF1 | 1.000 | | | | | | | |
| CI7DF2 | 0.414 | 1.000 | | | | | | |
| CI7DD1 | $r^2 = 0.276$ $p<0.053$ | 0.576 | 1.000 | | | | | |
| CI8DF1 | $r^2 = 0.746$ $p<0.05$ | 0.687 | 0.417 $p<0.000$ | 1.000 | | | | |
| CI8DD1 | 0.193 | 0.411 | $r^2 = 0.772$ $p<0.05$ | 0.497 $p<0.05$ | 1.000 | | | |
| TOT2378ND0 | 0.227 | 0.888 | $r^2 = 0.507$ $p<0.05$ | 0.564 $p<0.05$ | 0.433 $p<0.050$ | 1.000 | | |
| TOT2378NDDL | 0.227 | 0.888 | $r^2 = 0.507$ $p<0.000$ | 0.564 $p<0.05$ | 0.433 $p<0.050$ | 1.000 | 1.000 | |
| TOT2378NDBLK | 0.227 | 0.888 | $r^2 = 0.507$ $p<0.000$ | 0.564 $p<0.05$ | 0.433 $p<0.050$ | 1.000 | 1.000 | 1.000 |

**Notes:**

1) Bonferoni p values only provided for samples with both $p<0.05$ and $n>40$

2) Various treatments of ND values for TOT2378

## 4.3    Wind Analyses

Wind speed and direction may be useful as an aid in investigating possible relationships between source emissions and measurements at air monitoring stations [243].

For this project, most of the ambient air monitoring was carried out on a mid-morning to mid-morning schedule. The time for start and finish for each sample was not part of the information contained in the electronic database. Rather than manually input the start and finish for each of the 1600+ ambient air samples for PCBs, it was decided to use a 1200 hrs start (day n) to 1100 hrs finish (day n+1) as the sampling time interval for each PCB/CB air sample. In addition to the wind direction and speed data (which included minimum, maximum, and average speed), the temperature data (minimum, maximum, and average temperature) were calculated for each 24 hr sampling time period.

### 4.3.1    Wind Direction

The first step in the analysis of the wind data was to determine whether there is any association between concentration of PCBTOT (as the representative pollutant) and wind direction.

The handling of circular data, such as wind direction (with a 0-360 scale), requires different statistical analytical techniques than those used for other types of data, and those techniques are still undergoing development for application to environmental data [244-248].

A number of methods were initially identified from the literature for analyzing the data to evaluate the relationship of wind direction and PCBTOT concentration. These included:

1)   Wind roses,

2)   Linear angular rank (LAR) coefficient,

3)   Wind sector scoring,

4)   Kruskal-Wallis non-parametric test, and

5)   Trajectory modeling.

While the Kruskal-Wallis test, is more appropriate than the LAR coefficient for investigating patterns of pollutant concentrations for an area with multiple sources across wind sectors [249], it was not considered further in this research because a single source area (i.e., the CWML site) was primarily at issue.

As the research proceeded for this project, increasing concerns arose about the sensitivity of the trajectory modeling techniques and the intensive amount of computing power required. Most trajectory modeling has been used to look at effects from long-range transport, which for PCBs is typically in the 50-400 pg/m$^3$ (0.05-0.4 ng/m$^3$) range. Because the ambient air monitoring results for the Phase 3 Cleanup did not contain data for levels <0.2 ng/m$^3$ (total and di-deca homologs), the possibility of being able to see a long-range transport component was expected to be weak at best. Trajectory modeling also requires an immense amount of meteorological data and extensive computing resources. Because the information that would be produced was expected to be only marginally useful and the

hardware and software required to run the model was not readily available at UIC, the use of trajectory modeling was not pursued further in this research.

The three methods that were identified as being worth further consideration for evaluating the relationship of wind direction and PCBTOT concentration were:

1)    Wind rose (Section 4.3.1.1),

2)    Linear angular rank coefficient (Section 4.3.1.2), and

3)    Wind sector scoring (Section 4.3.1.3).

These three methods are discussed briefly below.

### 4.3.1.1 Wind Rose

Circular data can be presented graphically using a "rose diagram" [245]. For the case of wind direction data, the rose diagram is normally referred to as a "wind rose". Wind roses have been used for a long period of time by meteorologists, scientists, and planners to pictorially represent the frequencies of wind directions at a location [250]. While wind rose diagrams are useful, they provide a qualitative, not quantitative, portrayal of an association between wind direction and wind speed.

A variation of the wind rose plot, called the "pollutant rose," in which the concentration of a pollutant is plotted as a function of the predominant (or vector averaged) wind direction(s), has been used to study possible directional patterns with respect to source emissions [251]. This approach has been used to identify source impacts and in conjunction with receptor modeling in Ontario for fine and coarse particle apportionment [252].

Sommerville, et al. [243] utilized pollutant roses for several inorganic species for evaluating the impact of a biomedical waste incinerator and a municipal solid waste incinerator in urban and more rural settings. Sommerville emphasizes that pollutant roses are merely suggestive, and the presence of a relatively few unusual or "outlier" data values can be very influential in the conclusions one makes from visual examination of the data plots.

### 4.3.1.2 Linear Angular Rank Coefficient

In contrast to wind rose plots, which are qualitative in nature, statistical methods exist that may allow a more quantitative analysis of the association between concentration(s) and wind direction. The LAR coefficient, $D_n$, of Mardia [248] has been used in a limited number of studies [243] to measure the association between concentrations of "tracers" ($x_i$) and wind direction ($\Theta$, in radians). In this research, the use of (vector) average wind direction (in radians) during a sampling period was examined.

If it is assumed that a sample of air pollutant concentrations (in $ng/m^3$ etc.) and associated wind directions (as denoted by ($x_i$ and $\theta_i$)) is arranged so that the rank of $x_i$ is i (i=1,...,n) and the rank of $\theta_i$ is $r_i$, then the Linear-Angular Rank Coefficient (Equation 15) can be used:

$$D_n = a_n\left(T_c^2 + T_s^2\right) \qquad (15)$$

Where :  $n = the\ number\ of\ (x_i, \Theta_i)\ pairs,$

$$a_n = \left\{ 1 + 5\cot^2\left(\frac{\pi}{n}\right) + 4\cot^4\left(\frac{\pi}{n}\right) \right\}^{-1} \quad \text{(n even)}$$

$$a_n = \frac{2\sin^4\left(\frac{\pi}{n}\right)}{\left[1 + \cos\left(\frac{\pi}{n}\right)\right]^3} \quad \text{(n odd)}$$

$$T_c = \sum_{i=1}^{n} i\cos\left(\frac{2\pi\, r_i}{n}\right)$$

*and*

$$T_s = \sum_{i=1}^{n} i\sin\left(\frac{2\pi\, r_i}{n}\right)$$

Mardia notes that $0 \leq D_n \leq 1$ and that $D_n$ is invariant to changes in the origin of x and $\theta$. $D_n$ can be interpreted as the square of the multiple correlation coefficient ($r^2$) between the rank of $x_i$ and the sine and cosine of $\theta_i$. Therefore, values of $D_n$ near one (1) indicate association between (the ranks of) pollutant concentrations and (the ranks of) wind directions, while values near zero represent no association. This test is appropriate for areas dominated by a single major emission source of selected pollutants [243]. For this research, the concentration of PCBTOT compared to (vector) average wind direction during a sampling period is of interest.

The hypothesis to be tested is $H_o$: x and $\theta$ are independent. For large n, Mardia showed that the Test Statistic $U_n$ can be computed with Equation 16. Mardia's measure of linear-angular correlation is based upon Spearman's Correlation Coefficient.

$$U_n = 24 \frac{\left(T_c^2 + T_s^2\right)}{\left[n^2(n+1)\right]2} \sim \chi_2^2 \qquad (16)$$

and

$$D_n = \frac{U_n}{c_n}$$

$$c_n = \frac{24}{\left\{a_n * n^2(n+1)\right\}}$$

The Test Statistic $U_n$, is found to approximate the $\chi^2$ distribution with 2 degrees of freedom (DF). The null hypothesis, $H_o$, is rejected if $U_n$ is greater than the appropriate critical value (4.605 for $\chi^2$ DF=2).

There are a number of reasons why the LAR correlation test might indicate there was no association, when, in fact, there was one:

1)    if the true association was very weak;

2)    if the sample size (n) was very small;

3)    if there was a high degree of variability in the pollutant concentrations (or release rates from a source); and

4)    there was a relatively high degree of variability in the wind direction during sampling periods.

### 4.3.1.3 Source Strength Calculation (Wind Sector Scoring)

Scheff and Darrow [78, 79] made use of source strength calculations in evaluating PCB concentrations in an ambient air study in southeast Chicago. Source strength calculations can be performed using the amount of time a site is directly downwind, partially downwind, or not downwind at all of a source of interest. This is done using wind sector scoring. For example, a site that is directly downwind would be scored 1, partially downwind scored 0.5, and not downwind scored 0. This scoring is performed for each hour of the sampling period. The data are then summed and divided by the number of data points (i.e., the no. of valid wind direction data in a sampling period) to give an "average" source strength score, which will be normalized to a value of between 0 (never downwind at all) and 1 (directly downwind for all time periods during a sampling event). A correlation analysis is performed on the pollutant concentration versus the average score to determine if there is any type (linear etc.) of correlation. The wind direction "windows" used for scoring each of the air sampling stations for the Smithville project are shown below in Table LIII. The actual wind sector assignments for the scoring are provided below in Table LIV.

## TABLE LIII

HEADING AND DISTANCE INFORMATION FOR AIR SAMPLING STATIONS
FOR SMITHVILLE INCINERATION PROJECT

| Station | Center heading from site (degrees) | Angle for "seeing" site (degrees) | Center wind direction (degrees) | MIN. wind direction (degrees) | MAX. wind direction (degrees) | Est. distance (m) |
|---------|---------|---------|---------|---------|---------|---------|
| 23005 | 357 | 7 | 177 | 174 | 181 | 1400 |
| 23007 | 30 | 10 | 210 | 205 | 215 | 1100 |
| 23009 | 91 | 15 | 271 | 264 | 279 | 400 |
| 23011 | 169 | 17 | 349 | 341 | 358 | 400 |
| 23013 | 243 | 14 | 63 | 56 | 70 | 600 |

## TABLE LIV

WIND SECTOR SCORING ASSIGNMENTS FOR AIR SAMPLING STATIONS

| Sector | Middle | MIN. | MAX. | Counter=1 | Counter=0.5 | Counter=0.5 |
|--------|--------|------|------|-----------|-------------|-------------|
| N | 0 | 348.75 | 11.25 | 23011 | | |
| NNE | 22.5 | 11.25 | 33.75 | | 23013 | 23011 |
| NE | 45 | 33.75 | 56.25 | 23013 | | |
| ENE | 67.5 | 56.25 | 78.75 | 23013 | | |
| E | 90 | 78.75 | 101.25 | | 23013 | |
| ESE | 112.5 | 101.25 | 123.75 | | | |
| SE | 135 | 123.75 | 146.25 | | | |
| SSE | 157.5 | 146.25 | 168.75 | | | |
| S | 180 | 168.75 | 191.25 | | | 23007 |
| SSW | 202.5 | 191.25 | 213.75 | 23007 | | |
| SW | 225 | 213.75 | 236.25 | 23007 | | |
| WSW | 247.5 | 236.25 | 258.75 | | 23007 | 23009 |
| W | 270 | 258.75 | 281.25 | 23009 | | |
| WNW | 292.5 | 281.25 | 303.75 | | | 23009 |
| NW | 315 | 303.75 | 326.25 | | 23011 | |
| NNW | 337.5 | 326.25 | 348.75 | 23011 | | |

## 4.3.1.4 <u>Evaluation of Wind Analysis Methodologies</u>

It was not known *a priori* which of the three methods would be most suitable for analyzing the data. Therefore, a small subset of the meteorological data (the month of February, 1991) was analyzed manually by each of the three methods for comparison purposes before selecting the method that would be used for the rest of the data.

The highest PCBTOT concentration observed at any of the air sampling stations was 5 ng/m$^3$ at 23011 for the Feb. 23, 1991 sampling date, which corresponds to the Feb. 22-23 time period for sampling. Table LV contains the wind data for the Feb. 23, 1991 samples. Example calculations for this data using the three different methods are described in the sections below.

**TABLE LV**

SMITHVILLE WIND DATA FOR FEBRUARY 22-23, 1991

| YR (1991) | Month | Day | Sample day | Hr | Hour (°C) | Wind direction (degrees) | Temperature (°C) | Wind speed (km/hr) | Wind speed (m/s) |
|---|---|---|---|---|---|---|---|---|---|
| 91 | 2 | 22 | 23 | 12 | 1 | 288 | 2.0 | 29.0 | 8.1 |
| 91 | 2 | 22 | 23 | 13 | 2 | 286 | 2.2 | 33.0 | 9.2 |
| 91 | 2 | 22 | 23 | 14 | 3 | 285 | 2.7 | 29.0 | 8.1 |
| 91 | 2 | 22 | 23 | 15 | 4 | 277 | 2.1 | 24.0 | 6.7 |
| 91 | 2 | 22 | 23 | 16 | 5 | 306 | 0.0 | 30.0 | 8.3 |
| 91 | 2 | 22 | 23 | 17 | 6 | 300 | 0.5 | 33.0 | 9.2 |
| 91 | 2 | 22 | 23 | 18 | 7 | 302 | -1.0 | 31.0 | 8.6 |
| 91 | 2 | 22 | 23 | 19 | 8 | 309 | -2.6 | 33.0 | 9.2 |
| 91 | 2 | 22 | 23 | 20 | 9 | 306 | -4.0 | 28.0 | 7.8 |
| 91 | 2 | 22 | 23 | 21 | 10 | 309 | -5.2 | 31.0 | 8.6 |
| 91 | 2 | 22 | 23 | 22 | 11 | 311 | -5.9 | 29.0 | 8.1 |
| 91 | 2 | 22 | 23 | 23 | 12 | 317 | -6.5 | 28.0 | 7.8 |
| 91 | 2 | 22 | 23 | 24 | 13 | 325 | -7.2 | 32.0 | 8.9 |
| 91 | 2 | 23 | 23 | 1 | 14 | 326 | -7.7 | 28.0 | 7.8 |
| 91 | 2 | 23 | 23 | 2 | 15 | 342 | -8.8 | 24.0 | 6.7 |
| 91 | 2 | 23 | 23 | 3 | 16 | 1 | -9.7 | 24.0 | 6.7 |
| 91 | 2 | 23 | 23 | 4 | 17 | 359 | -10.6 | 22.0 | 6.1 |
| 91 | 2 | 23 | 23 | 5 | 18 | 0 | -11.0 | 19.0 | 5.3 |
| 91 | 2 | 23 | 23 | 6 | 19 | 358 | -11.4 | 17.0 | 4.7 |
| 91 | 2 | 23 | 23 | 7 | 20 | 347 | -11.8 | 19.0 | 5.3 |
| 91 | 2 | 23 | 23 | 8 | 21 | 347 | -11.8 | 16.0 | 4.4 |
| 91 | 2 | 23 | 23 | 9 | 22 | 359 | -11.7 | 15.0 | 4.2 |
| 91 | 2 | 23 | 23 | 10 | 23 | 34 | -11.3 | 13.0 | 3.6 |
| 91 | 2 | 23 | 23 | 11 | 24 | 32 | -11.0 | 11.0 | 3.1 |

#### 4.3.1.4.1 **Wind Rose**

The WRPlotview[tm] (Lakes Environmental, Waterloo, Canada) software interface to WRPLOT (USEPA, RTP, North Carolina) can be used to produce wind rose diagrams. However, the underlying WRPLOT software has some restrictions, namely that it can only address different start and end times for data in a **single calendar** day. In order to produce the wind rose for sampling periods that take place across two calendar days (such as was the case for PCB/CB, VOC, and Inorganics for the Smithville project), "adjustments" must be made in time and date to trick the software into thinking it is a 24 hour (or shorter) time period in the same calendar day. While this can be done on a manual basis for a few sampling periods, as shown below, it is very difficult to develop a reliable, automated method to produce the changes for all sampling periods. There is an even greater restriction in that the WRPLOT software apparently cannot handle sampling periods >24 hrs, which means it cannot be used for the PCDD/DF sampling, with typical sampling periods of 48 hrs or more.

The wind rose produced for the Feb. 22-23, 1991 sampling period is shown in Figure 39 below. The sector assignments for the wind rose are shown in Table LVI below. A visual review of this wind rose indicates that the average wind direction is somewhere between NW and N.
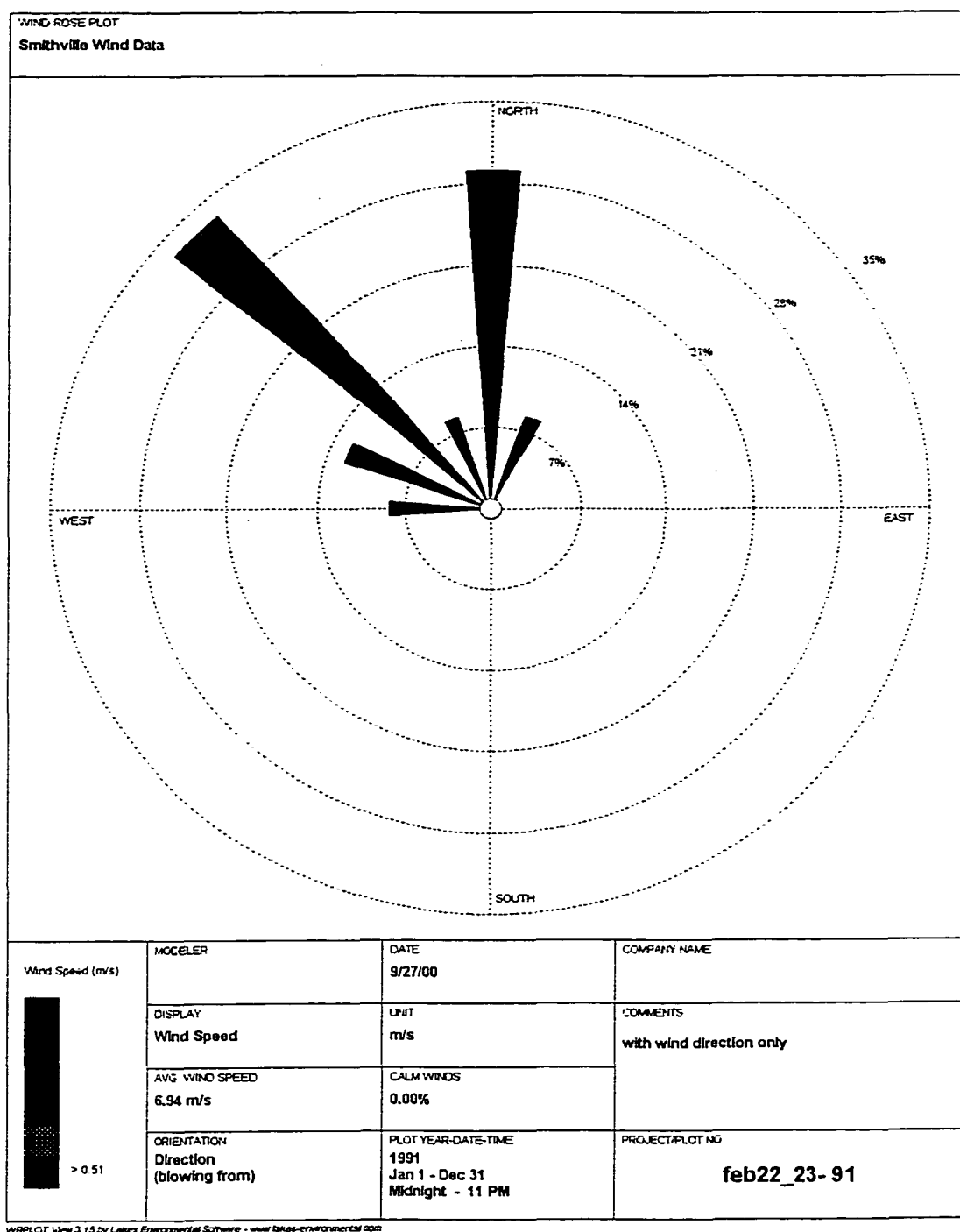
Figure 39.    Wind rose plot for February 22-23, 1991 sampling period.

**TABLE LVI**

## AVERAGE WIND DIRECTION CALCULATIONS FOR FEBRUARY 22-23, 1991

| YR (1991) | Month | Sample Day | hr °C | Wind direction (degrees) | Wind Sector | Θ (radians) | Sin (Θ) | Cos (Θ) |
|---|---|---|---|---|---|---|---|---|
| 91 | 2 | 23 | 1 | 288 | WNW | 5.026548 | -0.95106 | 0.309017 |
| 91 | 2 | 23 | 2 | 286 | WNW | 4.991642 | -0.96126 | 0.2756374 |
| 91 | 2 | 23 | 3 | 285 | WNW | 4.974188 | -0.96593 | 0.258819 |
| 91 | 2 | 23 | 4 | 277 | W | 4.834562 | -0.99255 | 0.1218693 |
| 91 | 2 | 23 | 5 | 306 | NW | 5.340708 | -0.80902 | 0.5877853 |
| 91 | 2 | 23 | 6 | 300 | WNW | 5.235988 | -0.86603 | 0.5 |
| 91 | 2 | 23 | 7 | 302 | WNW | 5.270894 | -0.84805 | 0.5299193 |
| 91 | 2 | 23 | 8 | 309 | NW | 5.393067 | -0.77715 | 0.6293204 |
| 91 | 2 | 23 | 9 | 306 | NW | 5.340708 | -0.80902 | 0.5877853 |
| 91 | 2 | 23 | 10 | 309 | NW | 5.393067 | -0.77715 | 0.6293204 |
| 91 | 2 | 23 | 11 | 311 | NW | 5.427974 | -0.75471 | 0.656059 |
| 91 | 2 | 23 | 12 | 317 | NW | 5.532694 | -0.682 | 0.7313537 |
| 91 | 2 | 23 | 13 | 325 | NW | 5.67232 | -0.57358 | 0.819152 |
| 91 | 2 | 23 | 14 | 326 | NW | 5.689773 | -0.55919 | 0.8290376 |
| 91 | 2 | 23 | 15 | 342 | NNW | 5.969026 | -0.30902 | 0.9510565 |
| 91 | 2 | 23 | 16 | 1 | N | 0.017453 | 0.017452 | 0.9998477 |
| 91 | 2 | 23 | 17 | 359 | N | 6.265732 | -0.01745 | 0.9998477 |
| 91 | 2 | 23 | 18 | 0 | N | 0 | 0 | 1 |
| 91 | 2 | 23 | 19 | 358 | N | 6.248279 | -0.0349 | 0.9993908 |
| 91 | 2 | 23 | 20 | 347 | NNW | 6.056293 | -0.22495 | 0.9743701 |
| 91 | 2 | 23 | 21 | 347 | NNW | 6.056293 | -0.22495 | 0.9743701 |
| 91 | 2 | 23 | 22 | 359 | N | 6.265732 | -0.01745 | 0.9998477 |
| 91 | 2 | 23 | 23 | 34 | NE | 0.593412 | 0.559193 | 0.8290376 |
| 91 | 2 | 23 | 24 | 32 | NNE | 0.558505 | 0.529919 | 0.8480481 |
| | | | | N | 5 | Sums | -11.0488 | 17.040892 |
| | | | | NNE | 1 | Y=sum(sin(Θ))/n | -0.46037 | |
| | | | | NE | 1 | X=sum(cos(Θ))/n | | 0.7100372 |
| | | | | ENE | 0 | r^2=X^2+Y^2 | 0.716091 | |
| | | | | E | 0 | r=sqrt(r^2) | 0.846222 | |
| | | | | ESE | 0 | ave_cos=x/r | 0.839068 | |
| | | | | SE | 0 | Θaverage=arcos(x/r) | 0.575229 | radians |
| | | | | SSE | 0 | Quadrant=1 or 4 | 32.95822 | degrees |
| | | | | S | 0 | ave_sin=y/r | -0.51759 | |
| | | | | SSW | 0 | Θaverage =arcsin | -0.54403 | radians |
| | | | | SW | 0 | Quadrant=3 or 4 | -31.1705 | degrees |
| | | | | WSW | 0 | + cos, - sin, ∴quadrant=4 | 327.0418 | degrees |
| | | | | W | 1 | *Vector ave. wind direction for sampling period* | | |
| | | | | WNW | 5 | | | |
| | | | | NW | 8 | | | |
| | | | | NNW | 3 | | | |
| | | | | Sum | 24 | | | |

### 4.3.1.4.2     <u>Calculation of Average Wind Direction for Linear Angular Rank Coefficient</u>

In order to effectively use the LAR Coefficient, the (vector) average wind direction for a sampling period must be determined. The calculation of average values for circular value data, such as wind direction, is discussed in detail in Zar [245]. Briefly, the wind direction angle (in degrees) for each hour is converted to $\Theta$ (the value in radians), and the value of the sine and cosine are calculated. The sine and cosine values are then summed and divided by the number of hourly data points (n=24 in this case) to give a value for X and Y in the unit circle; the radius, $R$ (hypotenuse), is then calculated using the Pythagorean theorem. The value of Y/R is then the value for sine of the average angle (in radians) and X/R is the value of cosine for the average angle (in radians). Depending upon the signs (+/-) of Y/R and X/R, the quadrant is determined, which then allows the average angle (in degrees) to be determined. For the Feb. 22-23, 1991 data, the vector average wind angle is calculated to be approximately 327° (see Table LVI). This average wind direction is not very helpful as an indicator of whether or not one of the air sampling stations is possibly impacted by being downwind of the Smithville Site because none of the stations are downwind at this heading. Even if an average wind direction is in the "window" that one or more of the sampling stations see, the site there may in fact be only a minimal amount of time downwind of the Site. If the wind direction does not change significantly during a sampling period, then it may be acceptable to use the average wind direction. However, an average wind direction over a 24-hour period in which there is a "large" wind change can provide data that is not helpful and may even be misleading. Normally, the standard deviation of the average wind direction is used to determine if there is a "large" wind direction variation [194]. The

methodology for calculating the standard deviation of wind direction has been described by USEPA in the document "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV" [253]. Unfortunately, the standard deviation information for hourly averaged wind direction data provided by MOE was not available.

The February, 1991 PCBTOT and vector average wind direction for air samples taken at station 23009 (Witmer) were analyzed using the LAR correlation method. The data used are shown below in Table LVII. The calculations for $D_n$ and $U_n$ are shown in Table LVIII. These calculations gave a value for $D_n$ of 0.125, which is quite small, and $U_n$=2.15, which is not significant because the critical value for $\chi^2$ (with 2 DF) is 4.605. These results do not show an association between wind direction and concentration. It is worth noting here that this computation could not be easily performed for each sample automatically.

## TABLE LVII

### FEBRUARY, 1991 23009 DATA FOR LINEAR ANGULAR RANK CALCULATIONS

| YR (1991) | Month | Day | PCBTOT | Angle_rev | Ave_theta _radians | PCBTOT_ ranks1 (I) | Ave_theta_ radians_ ranks (ri) | n | 2*PI*ri/n | Cos ( ) | I *cos() | Sin ( ) | I*sin () |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 91 | 2 | 23 | 3.4 | 327 | 5.71 | 1 | 1 | 18 | 0.349 | 0.94 | 0.94 | 0.342 | 0.342 |
| 91 | 2 | 17 | 2.6 | 227 | 3.96 | 2 | 9 | 18 | 3.14 | -1 | -2 | 1.2251E-16 | 2.4503E-16 |
| 91 | 2 | 25 | 1.9 | 11 | 0.20 | 3 | 17 | 18 | 5.93 | 0.94 | 2.82 | -0.342 | -1.03 |
| 91 | 2 | 15 | 1.0 | 291 | 5.07 | 4.5 | 2 | 18 | 0.698 | 0.766 | 3.45 | 0.643 | 2.89 |
| 91 | 2 | 24 | 1.0 | 72 | 1.26 | 4.5 | 14 | 18 | 4.89 | 0.174 | 0.781 | -0.985 | -4.43 |
| 91 | 2 | 27 | 0.7 | 252 | 4.40 | 6 | 4 | 18 | 1.4 | 0.174 | 1.04 | 0.985 | 5.9 |
| 91 | 2 | 14 | 0.4 | 50 | 0.88 | 7 | 16 | 18 | 5.59 | 0.766 | 5.36 | -0.643 | -4.5 |
| 91 | 2 | 1 | 0.2 | 249 | 4.3 | 13 | 6 | 18 | 2.09 | -0.5 | -6.5 | 0.866 | 11.26 |
| 91 | 2 | 5 | 0.2 | 215 | 3.75 | 13 | 12 | 18 | 4.19 | -0.5 | -6.5 | -0.866 | -11.26 |
| 91 | 2 | 7 | 0.2 | 9 | 0.15 | 13 | 18 | 18 | 6.28 | 1 | 13 | -2.45E-16 | -3.185E-15 |
| 91 | 2 | 8 | 0.2 | 281 | 4.90 | 13 | 3 | 18 | 1.05 | 0.5 | 6.5 | 0.866 | 11.26 |
| 91 | 2 | 9 | 0.2 | 228 | 3.97 | 13 | 7 | 18 | 2.44 | -0.766 | -9.96 | 0.643 | 8.36 |
| 91 | 2 | 10 | 0.2 | 252 | 4.39 | 13 | 5 | 18 | 1.75 | -0.174 | -2.26 | 0.985 | 12.8 |
| 91 | 2 | 13 | 0.2 | 222 | 3.87 | 13 | 10 | 18 | 3.49 | -0.94 | -12.22 | -0.342 | -4.45 |
| 91 | 2 | 18 | 0.2 | 59 | 1.02 | 13 | 15 | 18 | 5.24 | 0.5 | 6.5 | -0.866 | -11.26 |
| 91 | 2 | 19 | 0.2 | 123 | 2.14 | 13 | 13 | 18 | 4.54 | -0.174 | -2.26 | -0.985 | -12.8 |
| 91 | 2 | 20 | 0.2 | 228 | 3.96 | 13 | 8 | 18 | 2.79 | -0.94 | -12.22 | 0.342 | 4.45 |
| 91 | 2 | 21 | 0.2 | 219 | 3.84 | 13 | 11 | 18 | 3.84 | -0.766 | -9.96 | -0.643 | -8.36 |

# TABLE LVIII

## CALCULATIONS OF LINEAR RANK CORRELATION COEFFICIENT AND TEST STATISTIC
## FOR FEBRUARY, 1991 23009 TOTAL POLYCHLORINATED BIPHENYL DATA

| $T_c$ = sum (I $*$cos $(2\pi r_i/n)$) | $T_c$ = -23.472429 | $T_s$ = sum(I$*$sin$(2\pi r_i/n)$) | $T_s$ = -0.8137977 |
|---|---|---|---|
| $a_n = \{1+5\cot^2(\pi/n) + 4\cot^4(\pi/n)\}^{-1}$ For n even (here n=18) | $\pi/n$ = 0.17453293 | $\cot(\pi/n)$ = $1/\tan(\pi/n)$= 5.67128182 | $\cot^2(\pi/n)$ = 32.1634375 |
| | $5\cot^2(\pi/n)$ = 160.817187 | $1+5\cot^2(\pi/n)$ = 161.817187 | $\cot^4(\pi/n)$ = 1034.48671 |
| | | | $4\cot^4(\pi/n)$ = 4137.94684 |
| | $\{1+5\cot^2(\pi/n) + 4\cot^4(\pi/n)\}^{=}$ 4299.76403 | | |
| | $a_n$ = 0.00023257 | | |
| $U_n = 24*(T_c^2 +T_s^2)/\{n^2(n+1)\}$ | $T_c^2$ = 550.954915 | $T_s^2$ = 0.662266 | $(T_c^2 +T_s^2)$ = 551.617182 |
| | $\{n^2(n+1)\}$ = 6156 | | |
| $c_n = 24/a_n\, n^2(n+1)$ | $c_n$ = 16.7632126 | | |
| | $U_n$ = 2.15055432 | $\chi_2^2$ = 4.605 below critical value so accept $H_o$,: there is no relationship | |
| $D_n = U_n/c_n$ | $D_n$ = 0.12829011 | | |

#### 4.3.1.4.3 Calculation for Wind Sector Scoring

For the Feb. 22-23, 1991 sampling period, the wind sector counts shown in Table LIX were assigned as shown in Table LIV. Table LX contains the calculated wind sector scores for each of the air sampling stations. As can be seen from this methodology, it becomes very clear that only 23011 was downwind from the site for any significant period of time (fully or partially downwind for 16 out of 24 hours) with a score for the period of 0.5 (which is equivalent to being downwind of the site for 12 out of 24 hours. As was pointed out above, 23011 also had the highest concentration of PCBTOT (5.0 ng/m$^3$) for this date.

The differences in scores for calendar day n and calendar day n +1 vs. the sampling day score were examined for the February, 1991 data for each of air sampling stations. These results indicated that there were differences in the score calculated for each of these time periods. An example plot for the 23009 data is shown in Figure 40. Therefore, the score value that will be used going forward in this work will be the one calculated based upon the sampling day, not calendar day.

**TABLE LIX**

ADDITIONAL WIND SECTOR SCORE CALCULATION FOR FEBRUARY 22-23, 1991

| YR (1991) | Month | Sample Day | hr °C | Wind Direction (degrees) | $\Theta$ (radians) | Windsect | Data_cnt | Count007 | Count009 | Count011 | Count013 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 91 | 2 | 23 | 1 | 288 | 5.026548 | WNW | 1 | 0 | 0.5 | 0 | 0 |
| 91 | 2 | 23 | 2 | 286 | 4.991642 | WNW | 1 | 0 | 0.5 | 0 | 0 |
| 91 | 2 | 23 | 3 | 285 | 4.974188 | WNW | 1 | 0 | 0.5 | 0 | 0 |
| 91 | 2 | 23 | 4 | 277 | 4.834562 | W | 1 | 0 | 1 | 0 | 0 |
| 91 | 2 | 23 | 5 | 306 | 5.340708 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 6 | 300 | 5.235988 | WNW | 1 | 0 | 0.5 | 0 | 0 |
| 91 | 2 | 23 | 7 | 302 | 5.270894 | WNW | 1 | 0 | 0.5 | 0 | 0 |
| 91 | 2 | 23 | 8 | 309 | 5.393067 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 9 | 306 | 5.340708 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 10 | 309 | 5.393067 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 11 | 311 | 5.427974 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 12 | 317 | 5.532694 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 13 | 325 | 5.67232 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 14 | 326 | 5.689773 | NW | 1 | 0 | 0 | 0.5 | 0 |
| 91 | 2 | 23 | 15 | 342 | 5.969026 | NNW | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 16 | 1 | 0.017453 | N | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 17 | 359 | 6.265732 | N | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 18 | 0 | 0 | N | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 19 | 358 | 6.248279 | N | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 20 | 347 | 6.056293 | NNW | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 21 | 347 | 6.056293 | NNW | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 22 | 359 | 6.265732 | N | 1 | 0 | 0 | 1 | 0 |
| 91 | 2 | 23 | 23 | 34 | 0.593412 | NE | 1 | 0 | 0 | 0 | 0.5 |
| 91 | 2 | 23 | 24 | 32 | 0.558505 | NNE | 1 | 0 | 0 | 0 | 0.5 |

**TABLE LX**

CALCULATION OF WIND SECTOR SCORES FOR FEBRUARY 22-23 SAMPLING

| | Data counter | 23007 | 23009 | 23011 | 23013 |
|---|---|---|---|---|---|
| Sum of counts | 24 | 0 | 3.5 | 12 | 1 |
| Score(s) | | 0 | 0.15 | 0.5 | 0.04 |

Scatter plots for score value vs. average angle for Site ID 23007, 23009, 23011, and 23013, and are shown in Figures 41 to 44. There does not appear to be a strong correlation for any of the stations. In most of these plots, the maximum score occurs for average wind directions that are close to the angle for "seeing" the site.

The correlation of score vs. PCBTOT concentration was examined for the February, 1991 data for each of the four sampling sites. The plots and simple linear regression equations with slope, intercept, and $r^2$ values for all Sites and Site ID 23011 are shown in Figures 45 and 46, respectively.
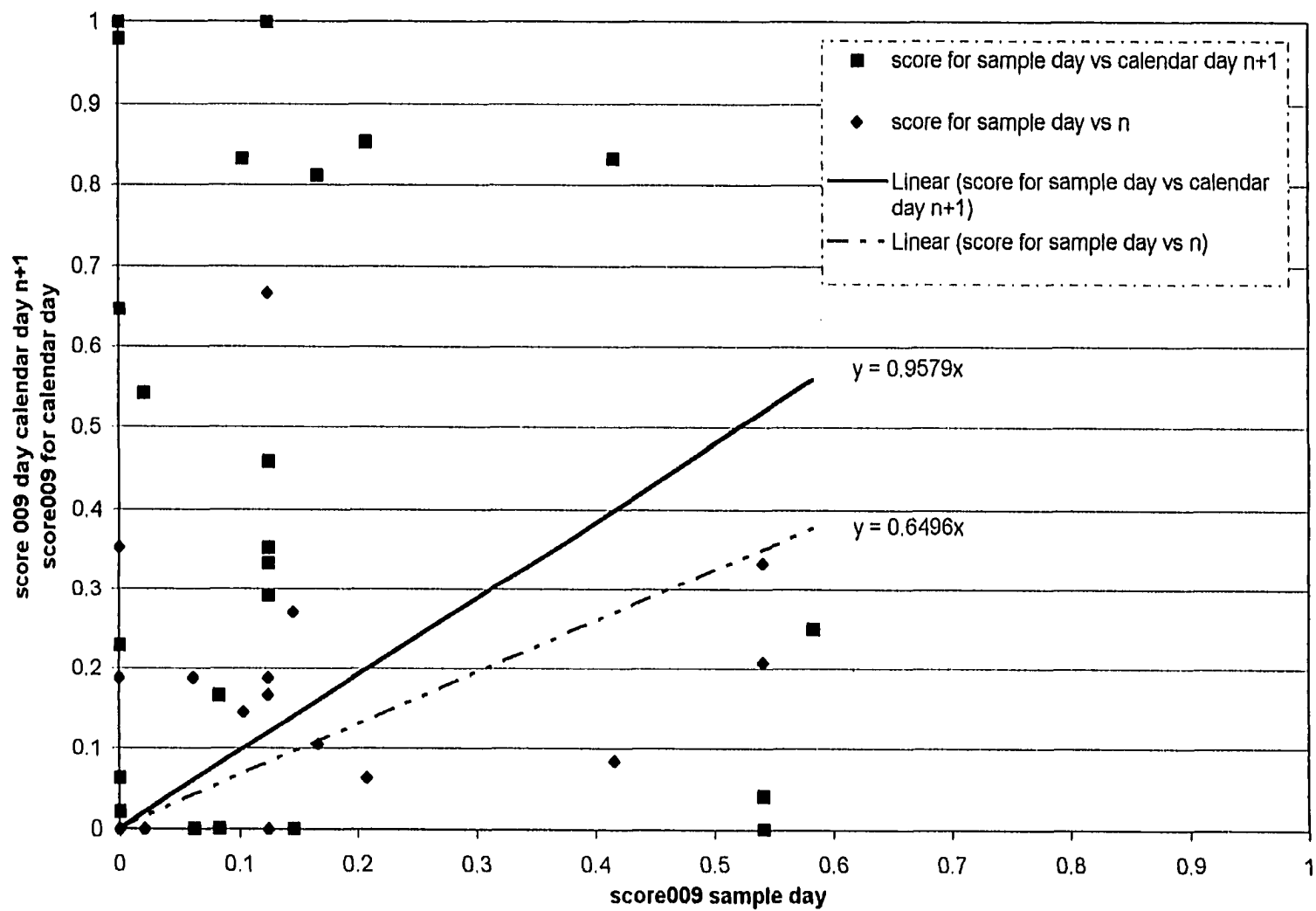
Figure 40.    23009 scores for calendar days N, N+1 and sampling period February 22-23, 1991.
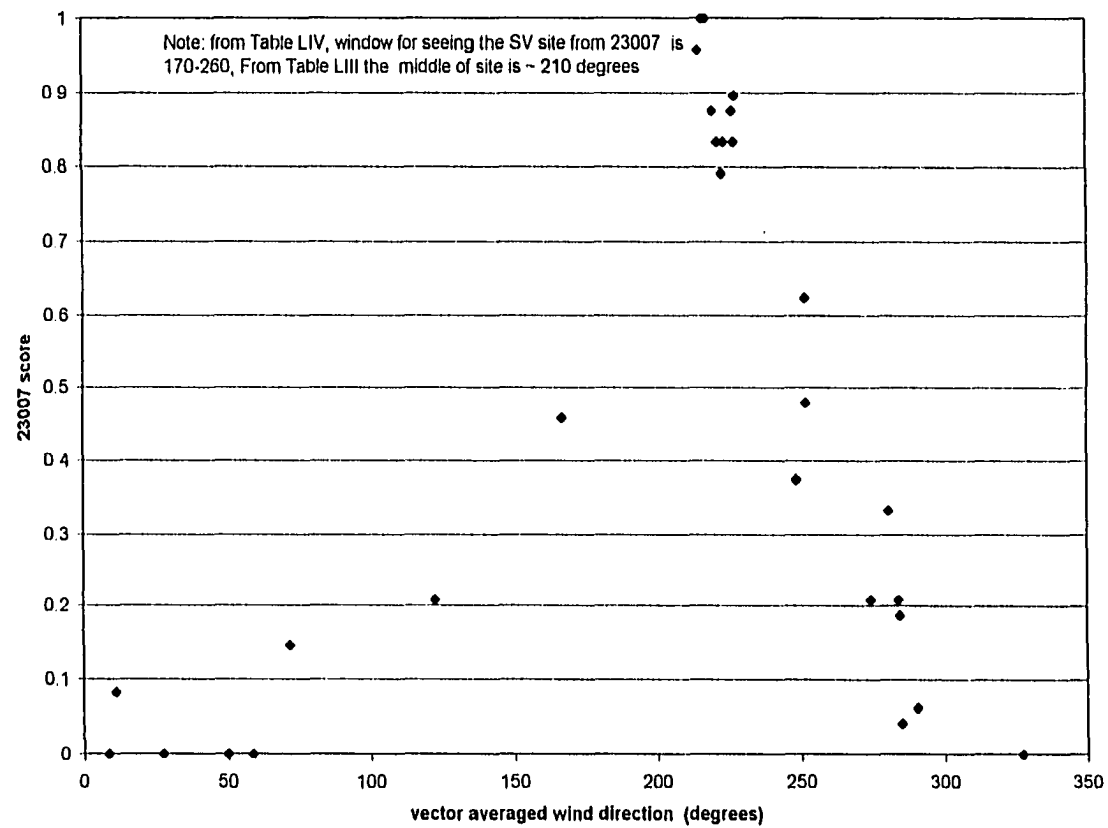
Figure 41. Score versus average angle for sample period for 23007 February, 1991 data.
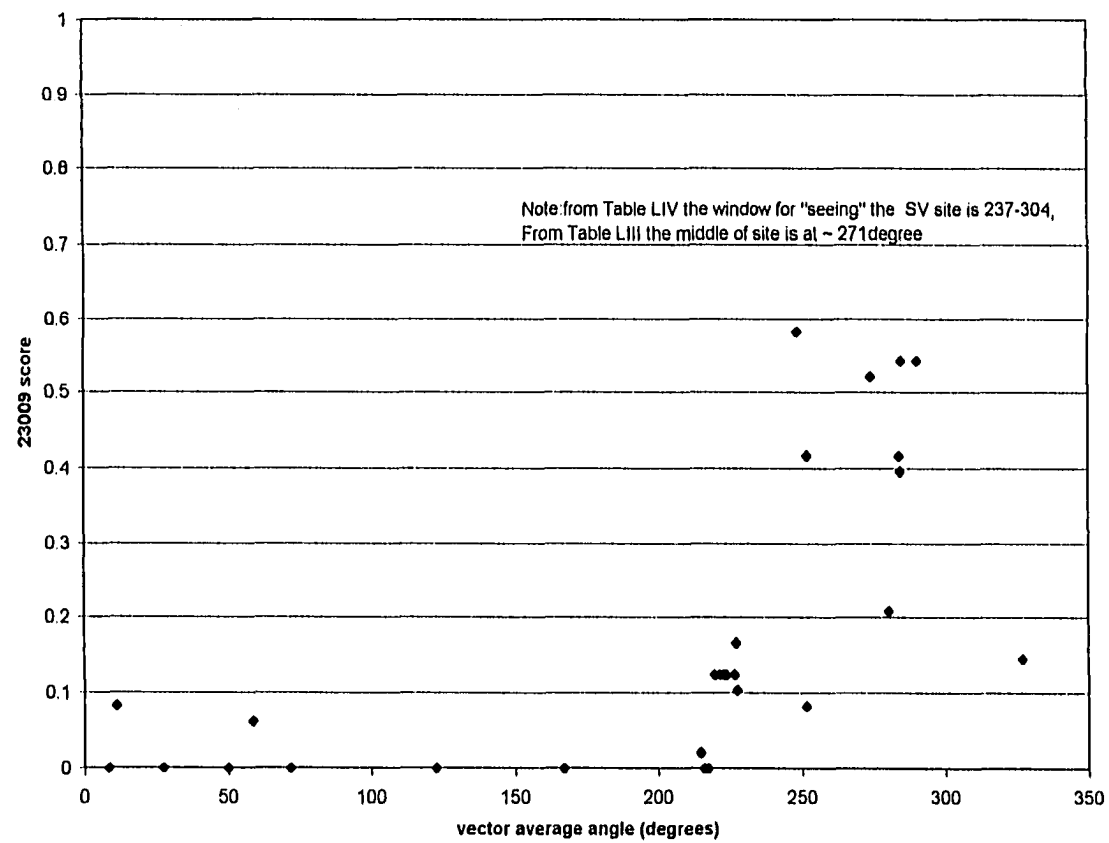
Figure 42.    Score versus average angle for sample period for 23009 February, 1991 data.

Note from Table LIV the angles for "seeing" the
SV site are 304-34 degrees   From Table LIII
the center wind direction is ~ 349 degrees
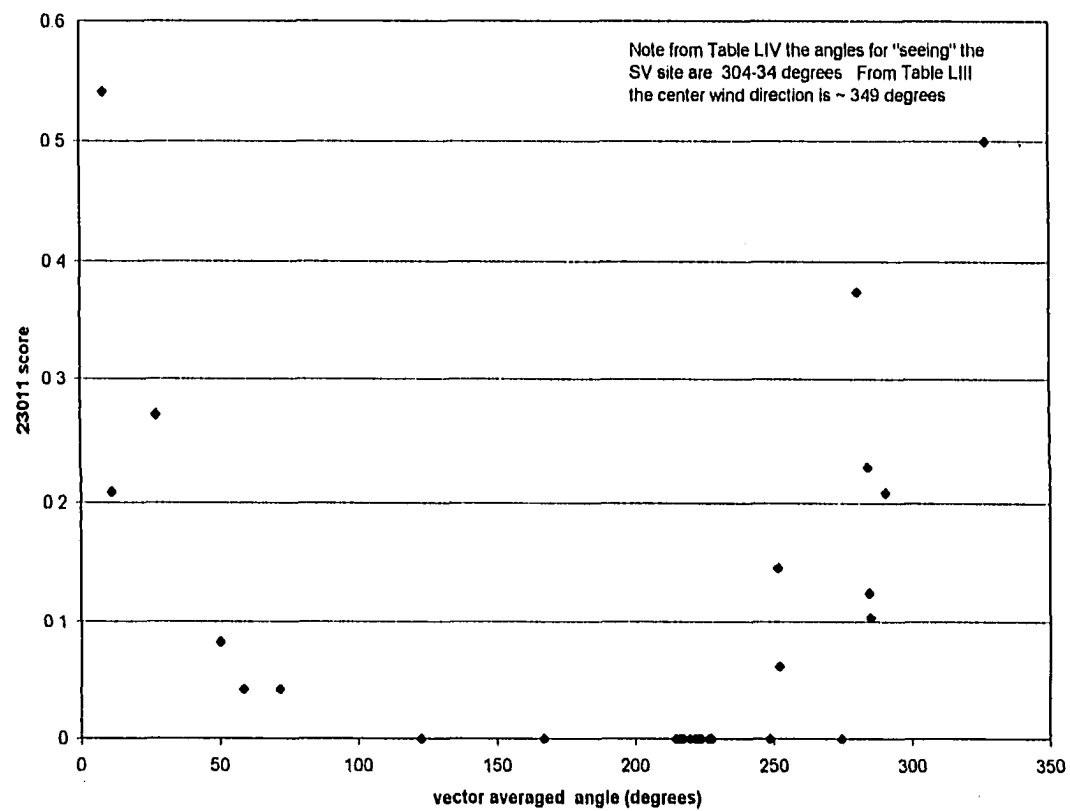
Figure 43.    Score versus average angle for sample period for 23011 February, 1991 data.

Note: From Table LIV the window for "seeing" the SV site is 11-101.
From Table LIII the centered wind direction is ~ 63 degrees.
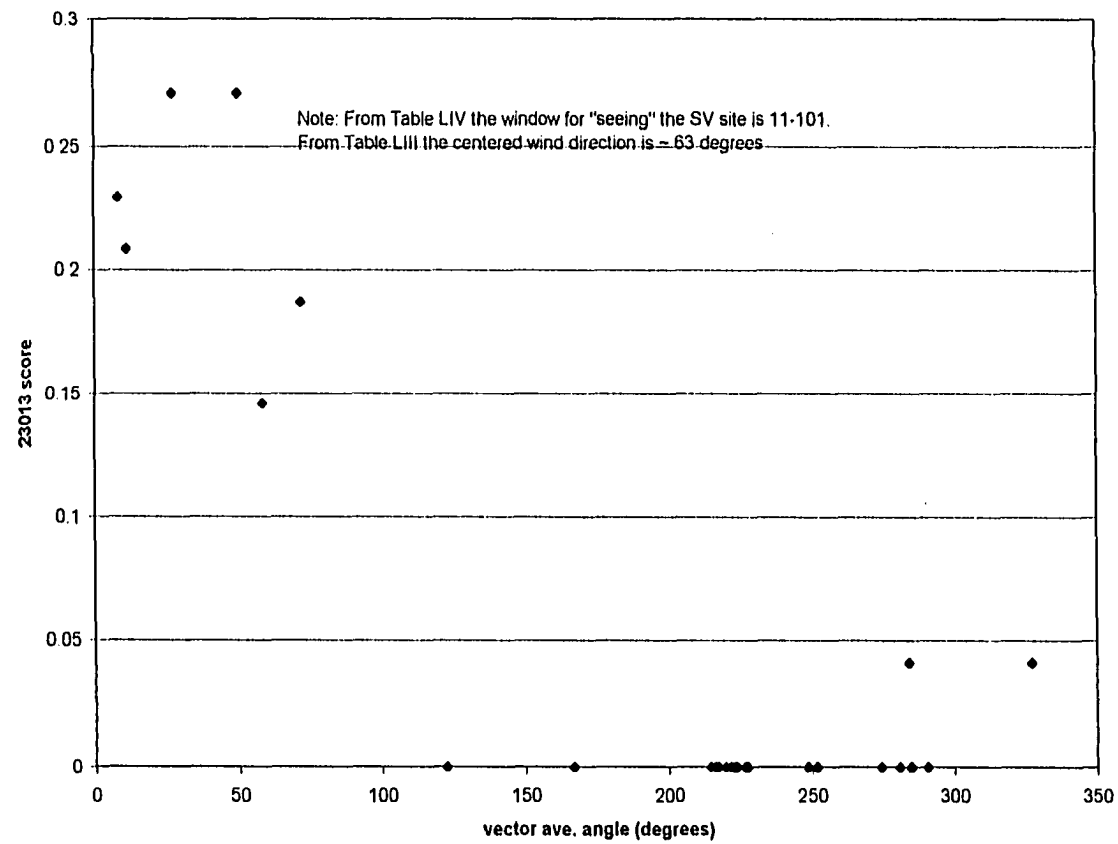
Figure 44.     Score versus average angle for sample period for 23013 February, 1991 data.
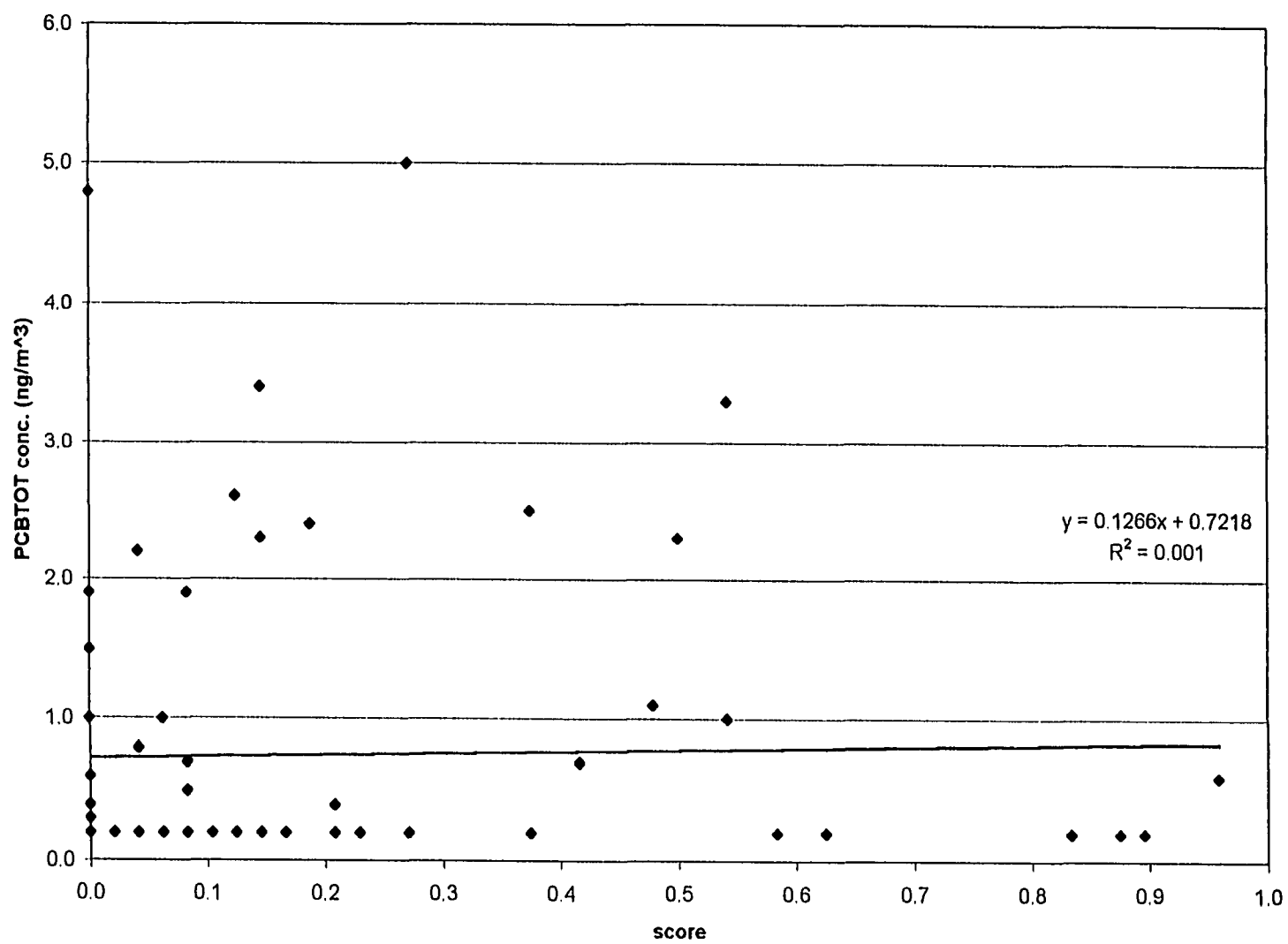
Figure 45. Total polychlorinated biphenyls versus score for February, 1991 data, all site combined.
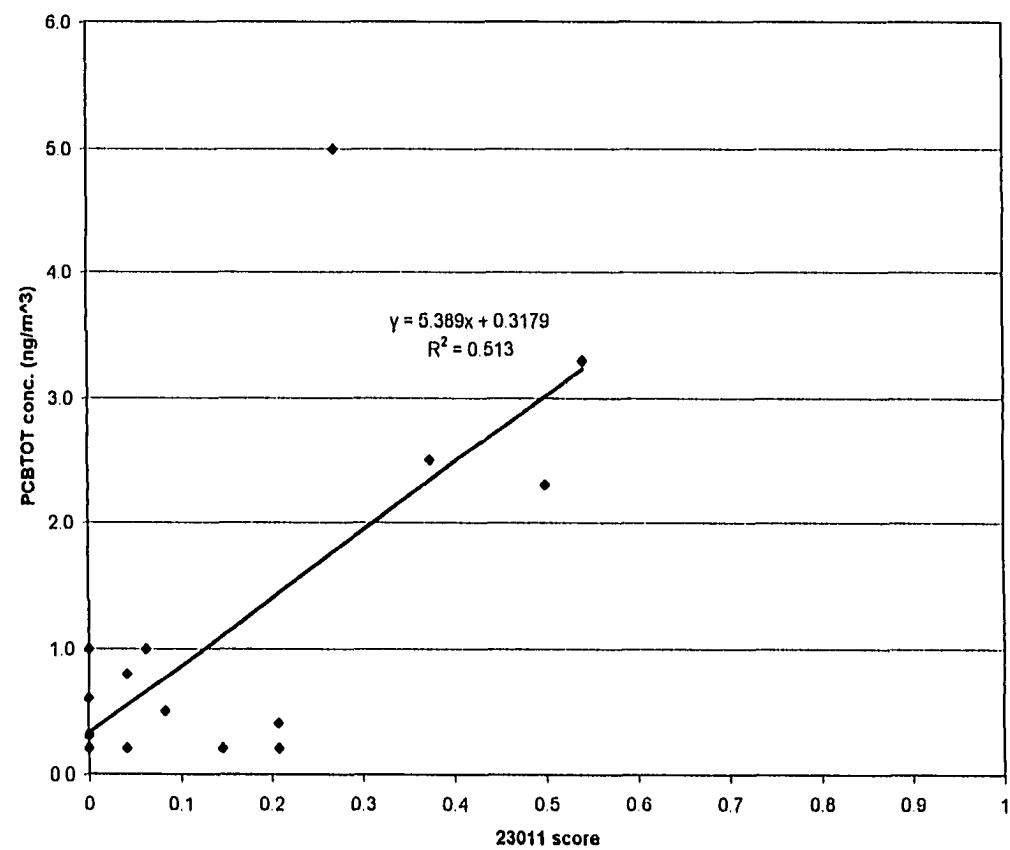
Figure 46. Score versus total polychlorinated biphenyls for 23011 February, 1991 data (n=20).

#### 4.3.1.4.4      Selection of Wind Direction Analysis Method

In Subsections 4.3.1.2 and 4.3.1.3 (above), three methods of analyzing wind direction and PCBTOT concentration were tested on a limited subset of the Smithville monitoring data to determine which method to use for the full data set. On the basis of this experience, it was decided to use wind sector scoring going forward in the research.

The reasons for this decision included:

1)      the ease of automation for this method;

2)      this method can produce data amenable to simple linear regression and multiple variable regression statistical analyses; and

3)      this method produces data that is more indicative of influence from the Site based on wind direction data only.

In addition to the score for each site for a sampling period, the meteorological data also included the minimum, maximum and average wind speed, and the minimum, maximum and average air temperature.

The main reasons for not using the wind rose method were:

1)      this method gives qualitative data only;

2)      this method was not easy to automate, and wind data sets would need to be manually produced for each of the approximately 400 hundred sampling days;

3)      400 separate wind rose plots were not amenable to quantitative statistical analysis method(s); and

4)      periods of >24 hours could not be handled by the program as it existed.

The main reasons for not using the LAR correlation method were:

1) The use of the LAR correlation method for sampling periods of longer than 12 hours has not been reported and/or validated.

2) The LAR correlation method is best used under relatively constant wind conditions, or at least conditions in which the wind variation has been quantified for the sampling period. In this case, we did not have any way of describing the wind variation for a sampling period.

3) The LAR method is not easy to automate.

## 4.3.2  Wind Speed Data

In Subsection 4.3.1 above, discussions focused on data analysis of PCBTOT concentration and wind direction. Wind speed can also have an impact. In general, concentrations would be expected to be higher for lower wind speeds, assuming all other factors (wind direction, emission rate, mixing height, etc.) are the same, due to lower mixing (or dilution). For purposes of data analysis, it is often easier to group the data into wind speed categories.

One of the more commonly recognized wind speed groupings is that suggested by Pasquill for the so-called Pasquill-Gilford stability class [194]. There are 5 categories of wind speed in this classification, as shown below in Table LXI. Wind rose plots can provide additional information on wind speed during a sampling period. The same Feb. 22-23, 1991 data shown in Figure 39 is plotted in Figure 47 with the wind speeds categorized according to

Table LXI. Wania, et al. [102] used 4 slightly different wind speed groupings (shown in Table LXII) for their analysis of the relationships between ambient air PCB concentrations and temperature.

## TABLE LXI

WIND SPEED (METERS PER SECOND) CATEGORIES
FOR PASQUILL-GILFORD STABILITY CLASSES [194]

| 10 m wind speed | | | |
|---|---|---|---|
| MIN. (m/s) | MAX. (m/s) | MIN. (km/hr) | MAX. (km/hr) |
| 0 | 2 | 0 | 7.2 |
| 2 | 3 | 7.2 | 10.8 |
| 3 | 5 | 10.8 | 18 |
| 5 | 6 | 18 | 21.6 |
| 6 | | 21.6 | |
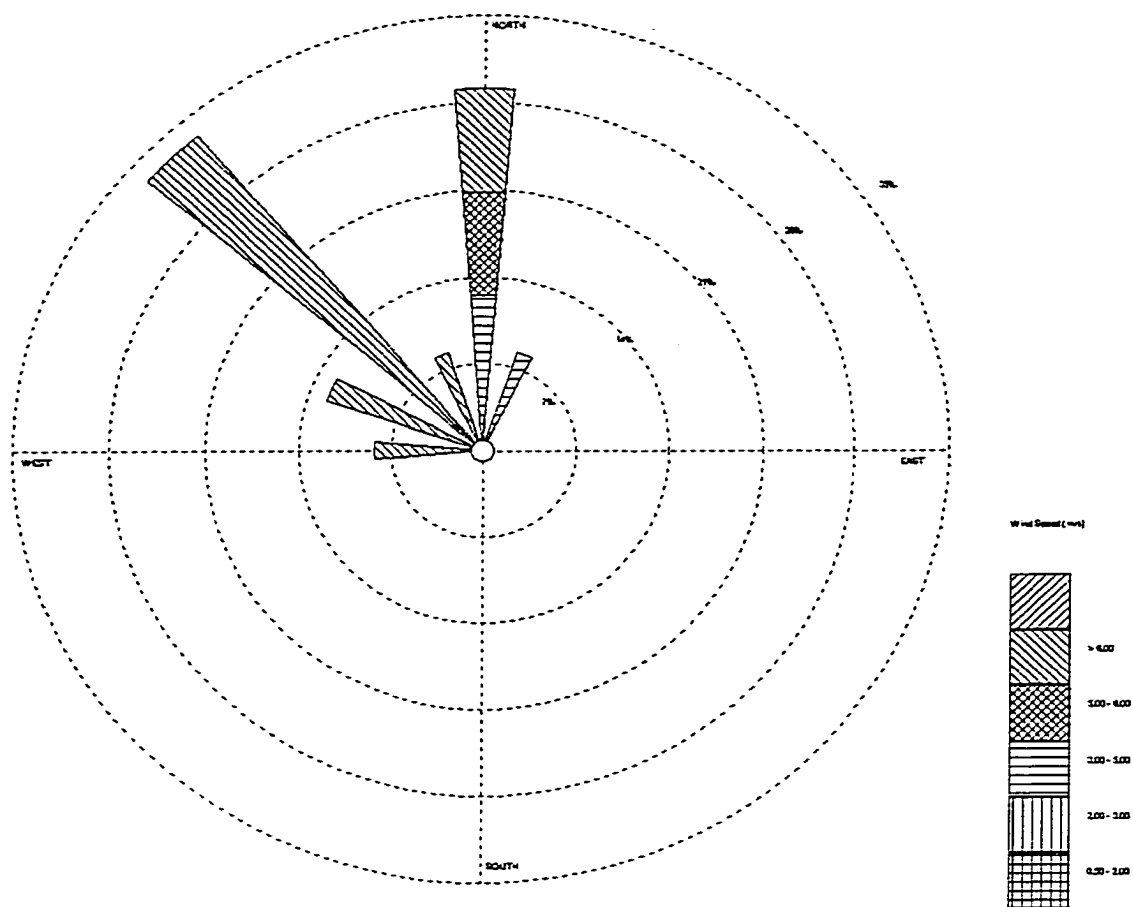
Figure 47.    Wind rose for February 22-23, 1991 data with wind speed classified according to Pasquill.

**TABLE LXII**

WIND SPEED CATEGORIES USED BY WANIA ET ALII [102]

| Wind speed | | | |
|---|---|---|---|
| MIN. (m/s) | MAX. (m/s) | MIN. (km/hr) | MAX. (km/hr) |
| 0 | 3 | 0 | 10.4 |
| 3 | 6 | 10.4 | 21.6 |
| 6 | 9 | 21.6 | 32.4 |
| 9 | | 32.4 | |

**Note:**

Wind speed is believed to be average wind speed during sampling period

The wind rose for the Feb. 22-23, 1991 data is shown below in Figure 48 using Wania's suggested wind speed categories. While there are probably other wind speed categorizations that have been used, these two were considered to be adequate for this research.

The Feb. 22-23, 1991 wind speed and temperature data in Table LXIV were statistically analyzed. Some selected statistics (mean, MIN., MAX., std. dev.) are shown below in Table LXIII.
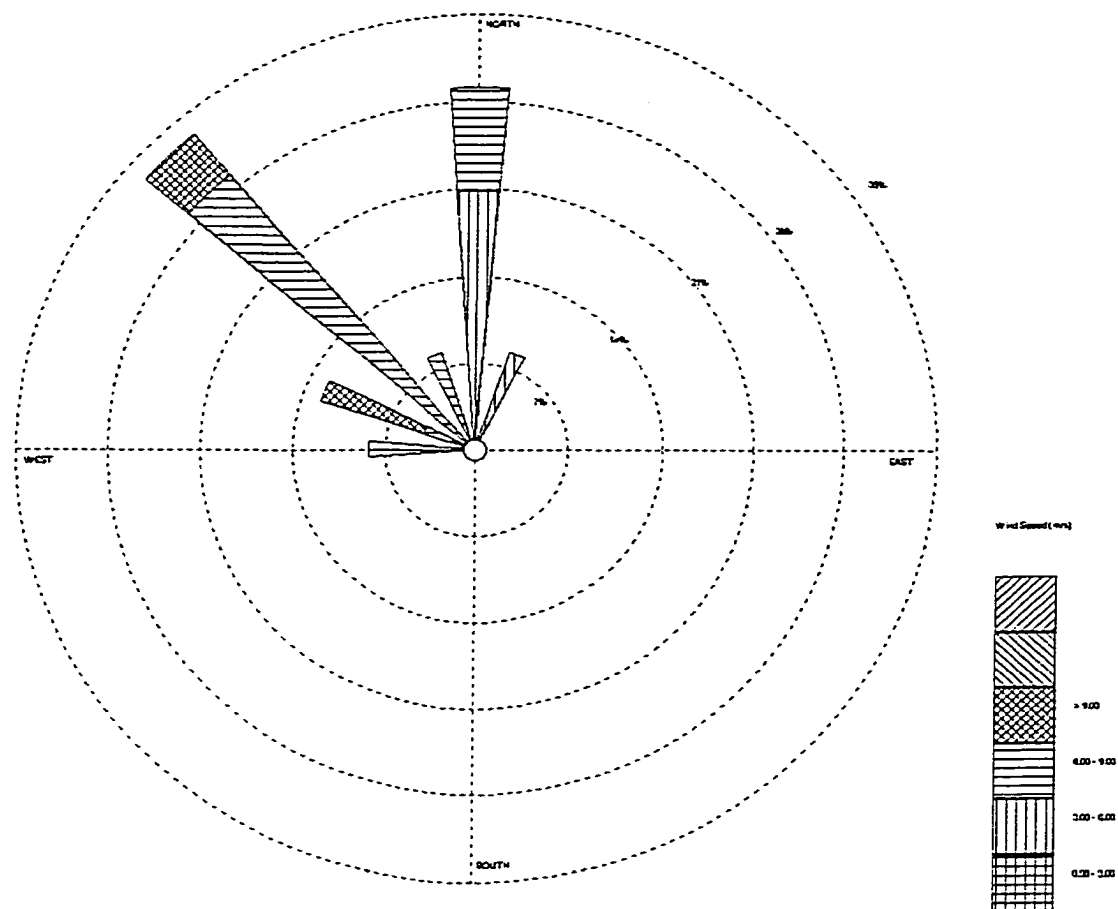
Figure 48.    Wind rose for February 22-23, 1991 sampling period, wind speeds classified based on values in Wania, et alii [102].

# TABLE LXIII

SELECTED STATISTICS FOR FEBRUARY 22-23, 1991
WIND SPEED AND TEMPERATURE DATA

|  | Wind Speed (km/hr) | Wind Speed (m/s) | Temperature ($^{o}$C) |
|---|---|---|---|
| sum | 598.0 | 166.1 | -139.7 |
| n | 24.0 | 24.0 | 24.0 |
| average | 24.9 | 6.9 | -5.8 |
| MIN. | 11.0 | 3.1 | -11.8 |
| MAX. | 33.0 | 9.2 | 2.7 |
| std. dev. | 6.86 | 1.91 | 5.30 |

**4.4      Wind Sector Score and Total Polychlorinated Biphenyl Concentrations**

Wind sector scoring was used to examine if there is any relationship between the observed PCB air concentrations and wind direction during a sampling period. The wind sector scores for all samples were calculated from the site meteorological data using a program written in SAS$^{tm}$.

**4.4.1   Summary of Wind Sector Score Results**

The summary statistics for the wind sector scores are shown in Table LXIV. The data (for all dates) are shown for all sites and for each of the four off-site sampling locations. The mean wind sector score for all sites is 0.172, which can be considered as roughly equivalent to a maximum of 17% of the time directly downwind or 34% of the time partially downwind (or a combination of the two). For all of the wind sector score data, 0 is the mode value.

There are differences in the mean values of the wind sector scores between the sampling locations. Qualitatively, it appears that the wind sector score for Site ID 23013 is different (and much lower) than for the other sites. However, only 23007, with a mean of 0.335, has a 95% confidence interval (CI) that does not include 0. In other words, the mean values for the other Sites are not significantly different from 0. For all of the wind sector score data, 0 is the mode value. The data appear to be log-normally distributed. The interpretation of the data distribution form is based upon a visual review of the frequency distribution plot and the fact that the median values are different from (and less than) the mean score.

In Table LXV, the mean wind sector scores were compared using Student's t-test [228]. The mean wind sector scores for the sampling sites are different from each other, except for 23011 vs. 23009, based on the one-sided t-test results at the $\alpha = 0.1$ and 0.05 level.

Histogram frequency plots are shown for the wind sector score and PCBTOT for the combined data and by Site ID in Figure 49-53. Both the PCBTOT and wind sector score data are distributed similarly (log-normal).

## TABLE LXIV

SUMMARY STATISTICS FOR WIND SECTOR SCORE, OFF-SITE DATA COMBINED AND BY SAMPLING SITE

| Site | n | Mean Score | Std. Dev. | 95% CI | Median | Mode | MIN. | MAX. | Range | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|---|---|---|
| All Sites | 1584 | 0.1720 | 0.240 | | 0.063 | 0 | 0 | 1.0 | 1.0 | 1.63 | 1.965 |
| 23007 | 396 | 0.335 | 0.322 | | 0.271 | 0 | 0 | 1 | 1 | 0.565 | -1.040 |
| 23009 | 391 | 0.144 | 0.190 | | 0.063 | 0 | 0 | 0.917 | 0.917 | 1.671 | 2.535 |
| 23011 | 397 | 0.139 | 0.200 | | 0.042 | 0 | 0 | 1 | 1 | 1.85 | 3.394 |
| 23013 | 400 | 0.072 | 0.108 | | 0 | 0 | 0 | 0.5 | 0.5 | 1.629 | 2.054 |

## TABLE LXV

T-TEST STATISTICS FOR WIND SECTOR SCORES AT SAMPLING LOCATIONS

| | 23007 vs. 23009 | 23007 vs. 23011 | 23007 vs. 23013 | 23009 vs. 23011 | 23009 vs. 23013 | 23013 vs. 23011 |
|---|---|---|---|---|---|---|
| n (lowest) | 391 | 396 | 396 | 391 | 391 | 397 |
| t critical 0.90 (one sided) D.F. = 200 | 1.286 | 1.286 | 1.286 | 1.286 | 1.286 | 1.286 |
| t (critical) 0.95 (one side) D.F. = 200 | 1.653 | 1.653 | 1.653 | 1.653 | 1.653 | 1.653 |
| t (calculated) | 10.15 | 10.30 | 15.42 | 0.0139 | 6.53 | 5.88 |
| Accept or reject $H_o$, There is no difference in means | Reject | Reject | Reject | Accept | Reject | Reject |

**Note:**
D.F. = degrees of freedom
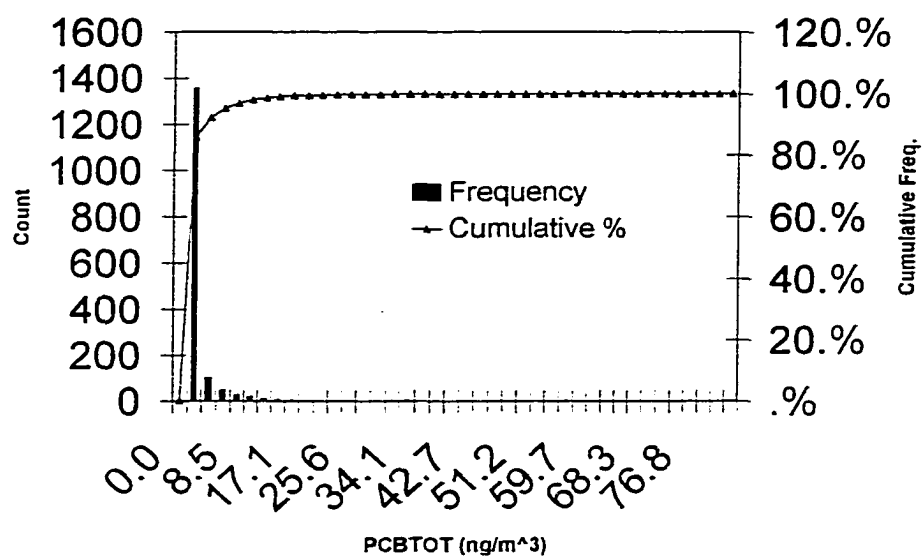
a) PCBTOT Data (ng/m³)
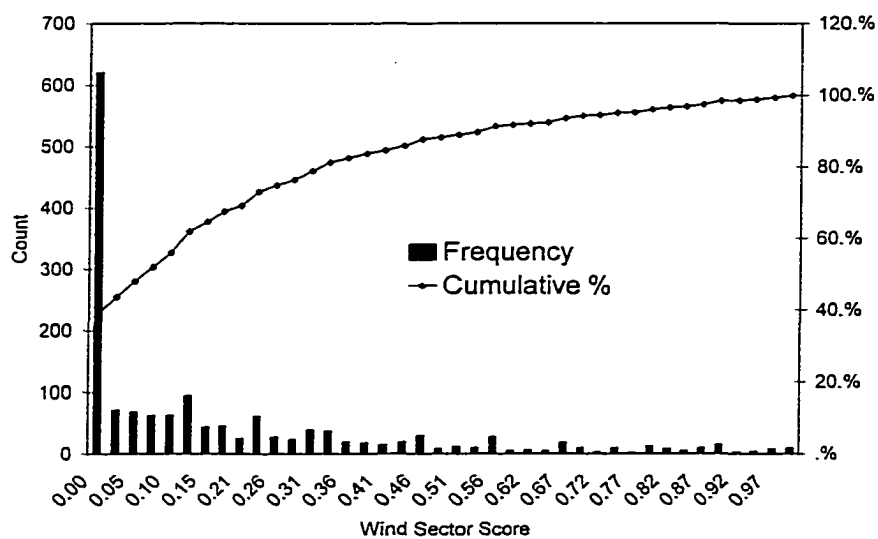


b) Wind Sector Score

Figure 49.    Histogram plot for air sampling data, all sites, all dates:    a) total polychlorinated biphenyl data, and b) wind sector score.
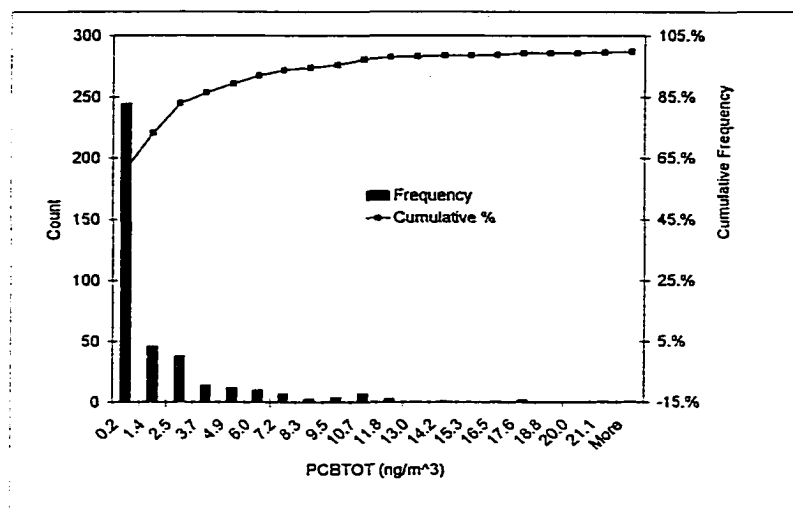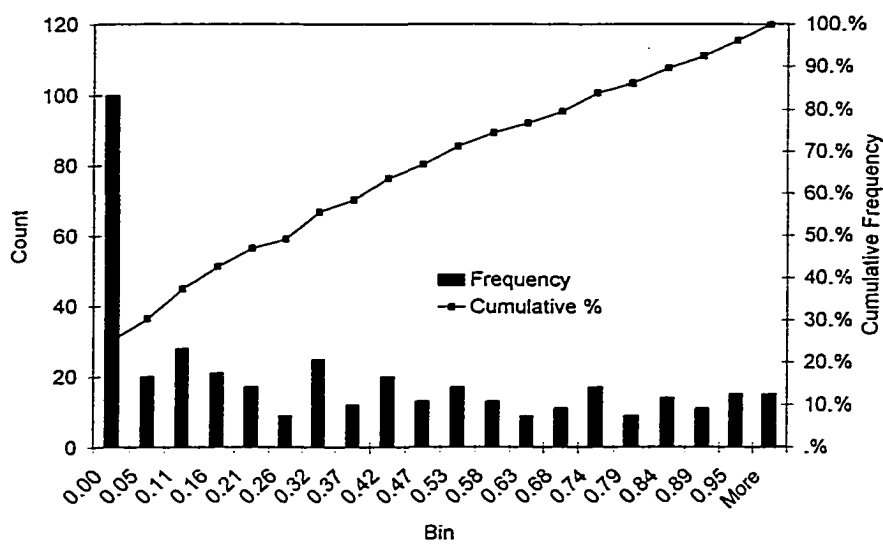
a) PCBTOT Data (ng/m³)



b) Wind Sector Score

Figure 50.    Histogram plot for 23007 air sampling data:  a) total polychlorinated biphenyl data, and b) wind sector score.
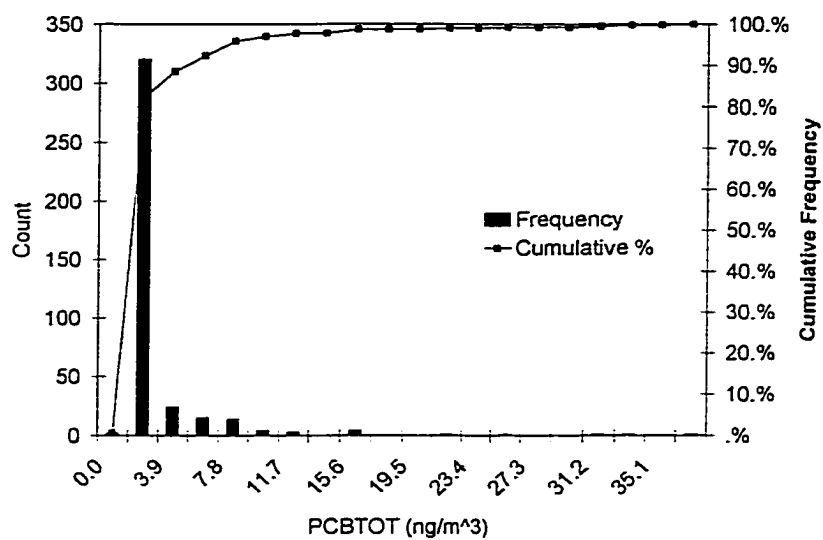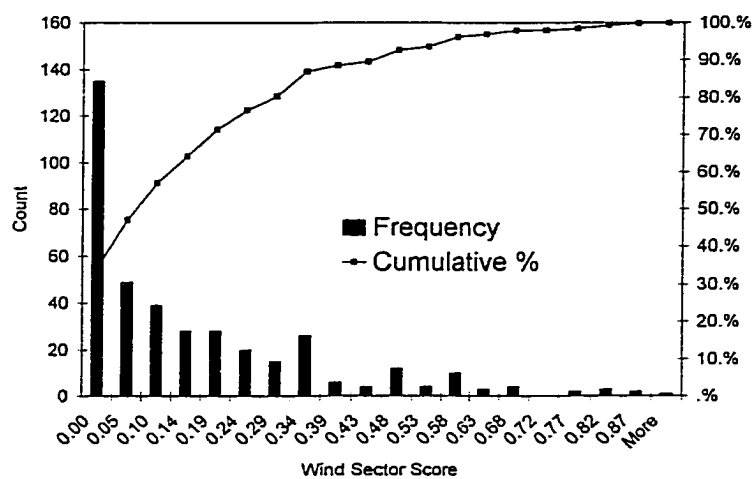
a) PCBTOT data



b) Wind Sector Score

Figure 51.    Histogram plot for 23009 air sampling data:  a) total polychlorinated biphenyl data, and b) wind sector score.
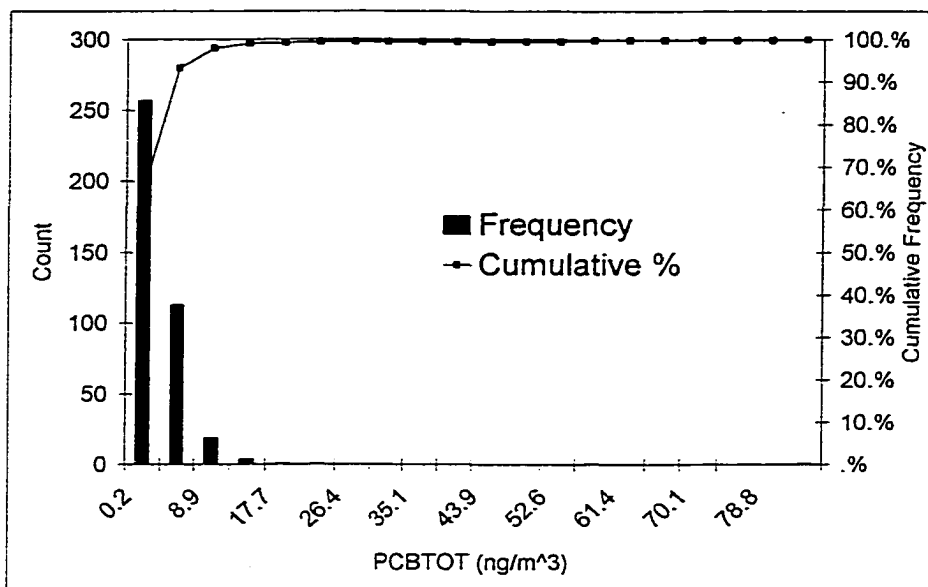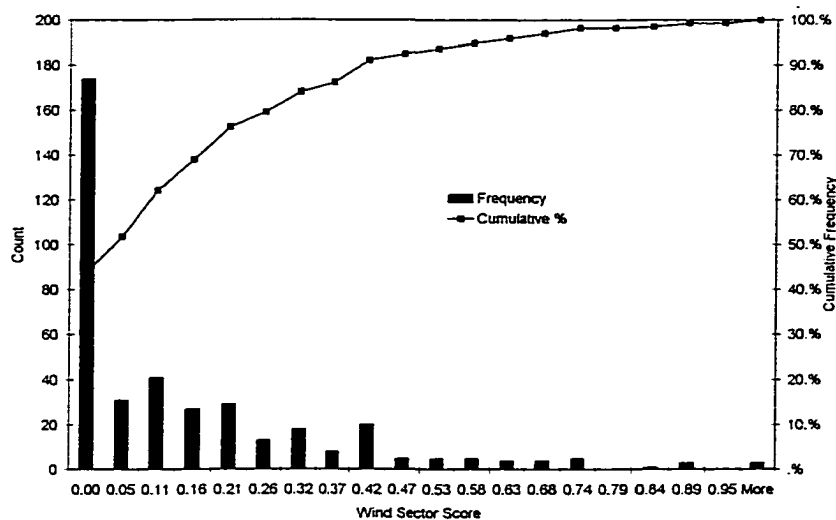
a) PCBTOT Data (ng/m³)



b) Wind Sector Score

Figure 52.    Histogram plot for 23011 air sampling data:   a) total polychlorinated biphenyl data, and b) wind sector score.
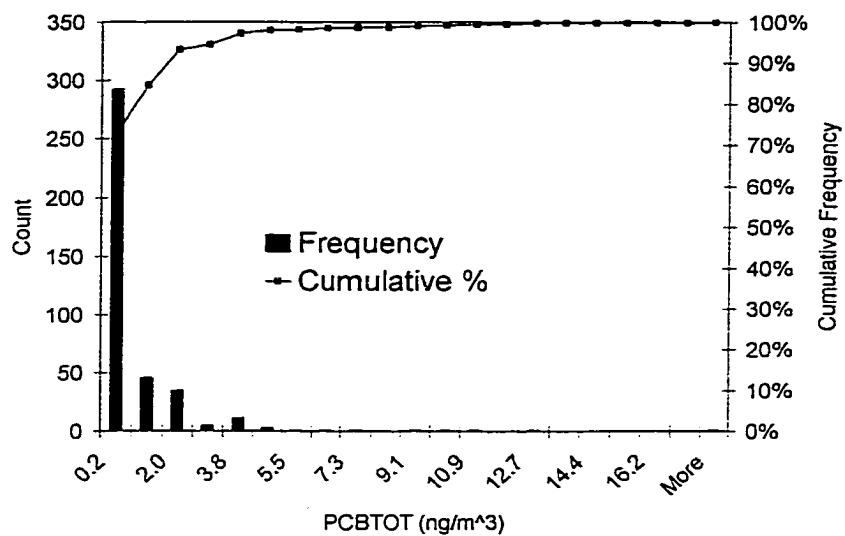
a) PCBTOT Data (ng/m$^3$)
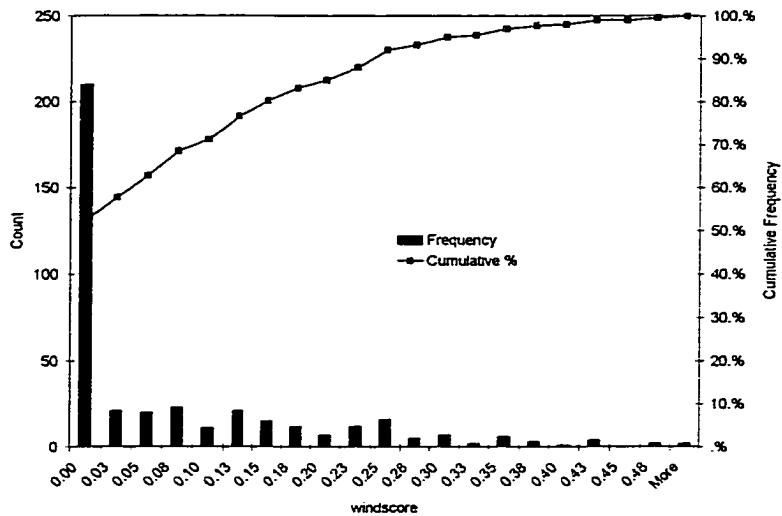


b) Wind Sector Score

Figure 53.    Histogram plot for 23013 air sampling data:  a) total polychlorinated biphenyl data, and b) wind sector score.

### 4.4.2  Polychlorinated Biphenyl Concentration Correlation With Wind Sector Scores

The summary statistics for the PCBTOT data (all sites, and sorted by Site ID) are shown in Table LXVI. The summary statistics were also determined for various treatments of <W and <T values and detects only:

- Table LXVII shows the data summary statistics with data flagged as <W set equal to 0 (PCBTOT_1).

- Table LXVIII shows the data summary statistics for <W and <T values set equal to 0 (PCTOT_2).

- Table LXIX shows the summary statistics for the detected values only (PCBTOT_2>0).

The use of PCBTOT is a more conservative (i.e., biased high) approach. Based on the review of the data in Tables LXVI-LXIX, it was decided to use the PCBTOT data for data analysis going forward in this research.

A review of the PCBTOT data sorted by Site ID (in Table LXVI) indicates that the mean and maximum values for 23013 are different from the rest of the sites. It is notable that the 23013 location also had the lowest mean wind sector score.

The correlation between wind sector score and PCB concentration was examined further by simple linear regression using a least squares fit [234]; [254]; [240].

## TABLE LXVI

SUMMARY STATISTICS FOR TOTAL POLYCHLORINATED BIPHENYL DATA,
ALL DATA COMBINED AND SORTED BY SITE

| Site | n | Mean | Std. Dev. | Median | Mode | MIN. | MAX. | Range | Skewness | Kurtosis |
|------|---|------|-----------|--------|------|------|------|-------|----------|----------|
| All Sites | 1584 | 1.32 | 3.79 | 0.20 | 0.20 | 0.0 | 83.2 | 83.2 | 11 | 178 |
| 23007 | 396 | 1.58 | 3.09 | 0.2 | 0.2 | 0.2 | 22.3 | 22.1 | 3 | 14 |
| 23009 | 391 | 1.60 | 3.98 | 0.2 | 0.2 | 0.00 | 37.0 | 37.0 | 5 | 36 |
| 23011 | 397 | 1.42 | 5.40 | 0.2 | 0.2 | 0.2 | 83.2 | 83.0 | 12 | 158 |
| 23013 | 400 | 0.69 | 1.56 | 0.2 | 0.2 | 0.2 | 18 | 17.8 | 6 | 53 |

## TABLE LXVII

SUMMARY STATISTICS FOR TOTAL POLYCHLORINATED BIPHENYLS_1 (APPROXIMATELY EQUAL TO OR LESS
THAN THE DETECTION LIMIT FOR TOTAL POLYCHLORINATED BIPHENYL DATA EQUAL TO ZERO)

| Site | n | Mean | Std. Dev. | Median | Mode | MIN. | MAX. | Range | Skewness | Kurtosis |
|------|---|------|-----------|--------|------|------|------|-------|----------|----------|
| All Sites | 1584 | 1.18 | 3.82 | 0 | 0 | 0 | 83.2 | 83.2 | 10 | 172 |
| 23007 | 396 | 1.44 | 3.14 | 0 | 0 | 0 | 22.3 | 22.3 | 3 | 13 |
| 23009 | 391 | 1.48 | 4.02 | 0 | 0 | 0 | 37.0 | 37.0 | 5 | 35 |
| 23011 | 397 | 1.29 | 5.43 | 0 | 0 | 0 | 83.2 | 83.2 | 12 | 156 |
| 23013 | 400 | 0.54 | 1.60 | 0 | 0 | 0 | 18 | 18 | 6 | 49 |

# TABLE LXVIII

SUMMARY STATISTICS FOR TOTAL POLYCHLORINATED BIPHENYL_2
(APPROXIMATELY EQUAL TO OR LESS THAN DETECTION AND QUANTITATION LIMIT
FOR TOTAL POLYCHLORINATED BIPHENYL DATA EQUAL TO ZERO)

| Site | n | Mean | Std. Dev. | Median | Mode | MIN. | MAX. | Range | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|---|---|
| All Sites | 1584 | 1.11 | 3.84 | 0 | 0 | 0 | 83.2 | 83.2 | 10 | 170 |
| 23007 | 396 | 1.39 | 3.15 | 0 | 0 | 0 | 22.3 | 22.3 | 3 | 13 |
| 23009 | 391 | 1.39 | 4.05 | 0 | 0 | 0 | 37.0 | 37.0 | 5 | 35 |
| 23011 | 397 | 1.21 | 5.45 | 0 | 0 | 0 | 83.2 | 83.2 | 12 | 155 |
| 23013 | 400 | 0.47 | 1.61 | 0 | 0 | 0 | 18.0 | 18.0 | 6 | 49 |

# TABLE LXIX

SUMMARY STATISTICS FOR DETECTED TOTAL POLYCHLORINATED BIPHENYL VALUES
(TOTAL POLYCHLORINATED BIPHENYL_2 GREATER THAN ZERO)

| Site | n | Mean | Std. Dev. | Median | Mode | MIN. | MAX. | range | Skewness | Kurtosis |
|---|---|---|---|---|---|---|---|---|---|---|
| All Sites | 366 | 4.82 | 6.785 | 2.85 | 1.20 | 0.2 | 83.2 | 83 | 6 | 59 |
| 23007 | 118 | 4.672 | 4.25 | 3.05 | 1.3 | 0.2 | 22.3 | 22.1 | 2 | 4 |
| 23009 | 99 | 5.51 | 6.51 | 3.2 | 1.1 | 1.2 | 37 | 35.9 | 3 | 10 |
| 23011 | 87 | 5.52 | 10.6 | 3.0 | 1.1 | 0.2 | 82.3 | 82.1 | 6 | 39 |
| 23013 | 62 | 3.03 | 3.0 | 1.9 | 1.2 | 1.0 | 18.0 | 17.0 | 3 | 11 |

#### 4.4.2.1 Analysis for Combined Data

The linear regression results for PCB (total) concentrations as a function of wind sector score (all dates, all sites) are summarized in Table LXX. A scatter plot of the data is shown in Figure 54. A visual review of the scatter plot and of the SAS™ regression analysis reports shows a very small positive correlation. However, the correlation was not statistically significant.

### TABLE LXX

LINEAR REGRESSION RESULTS FOR TOTAL POLYCHLORINATED BIPHENYLS
VERSUS WIND SECTOR SCORE

| | n | M | b | $r^2$ | r |
|---|---|---|---|---|---|
| PCBTOT | 1584 | -2.75 | 0.850 | 0.0302 | 0.174 |
| PCBTOT_1 (<W = 0) | 1584 | -2.78 | 0.70 | 0.0303 | 0.174 |
| PCBTOT_2 (<W & <T = 0) | 1584 | -2.82 | 0.63 | 0.0308 | 0.176 |
| PCBTOT_2 > 0 (DETECTED VALUES ONLY) | 366 | -3.16 | 3.98 | 0.0174 | 0.132 |

**Notes:**

Parameters for equation $y = M*x + b$, where y = PCBTOT concentration (ng/m3) (conc.), x = wind sector score, m =slope, b =intercept, r = correlation coefficient
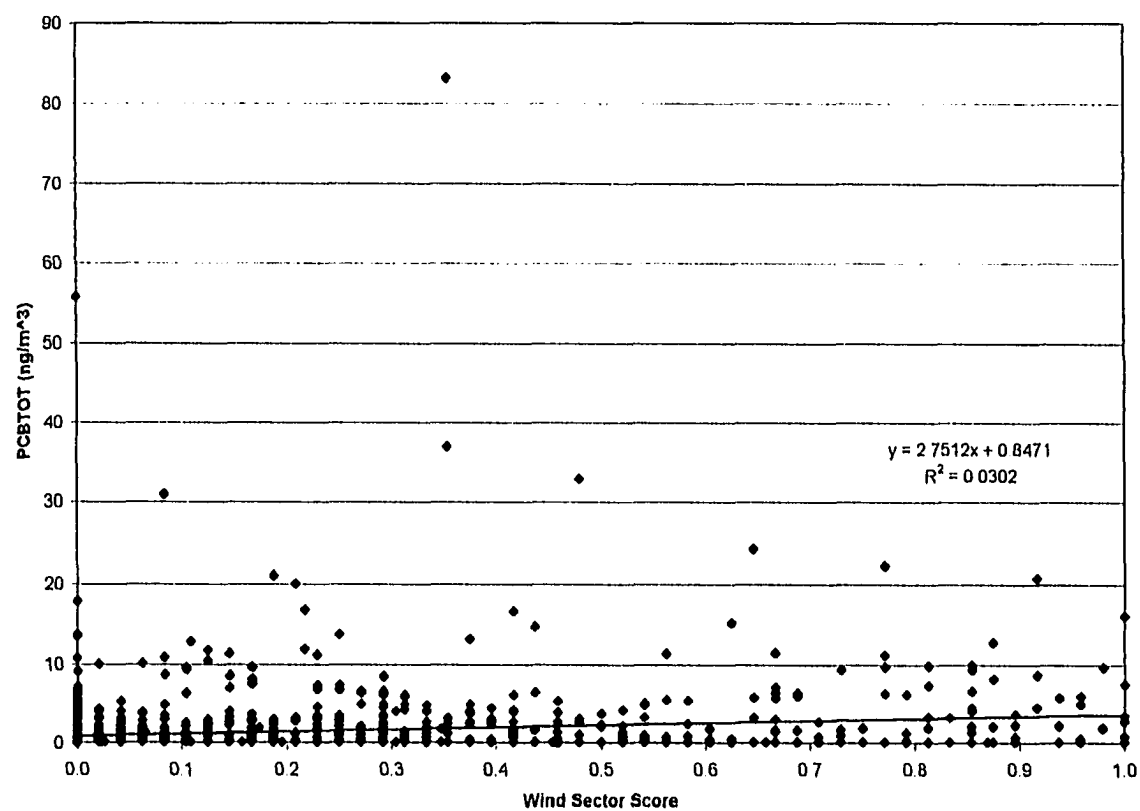
Figure 54.    Scatter plot of total polychlorinated biphenyl concentrations versus wind sector score for all sites, all dates.

#### 4.4.2.2 Analysis for Data Sorted by Sampling Site

The linear regression data for PCBTOT concentration as a function of the Wind

Sector Score, sorted by Site ID, are summarized in Table LXXI. Once again, there does not

appear to be any significant correlation between the PCB concentration and Wind Sector

Score.

### TABLE LXXI

TOTAL POLYCHLORINATED BIPHENYLS VERSUS
WIND SECTOR SCORES BY SITE IDENTIFICATION

|          | n    | M     | b    | $r^2$  | r    |
|----------|------|-------|------|-------|------|
| All data | 1584 | 2.746 | 0.85 | 0.030 | 0.17 |
| 23007    | 396  | 2.04  | 0.90 | 0.045 | 0.21 |
| 23009    | 391  | 4.98  | 0.88 | 0.052 | 0.24 |
| 23011    | 397  | 3.14  | 0.99 | 0.014 | 0.12 |
| 23013    | 400  | 1.95  | 0.55 | 0.019 | 0.14 |

**Notes:**

Parameters for equation $y = M*x + b$, where $y$ = PCBTOT conc., $x$ = wind sector score, $M$ = slope, $b$ = intercept, $r$ = correlation coefficient

#### 4.4.2.3 Analysis by Month

In Sections 4.4.2.1 and 4.4.2.2 above, the PCBTOT data for all dates combined does

not appear to show any correlation with the Wind Sector Score. However, when the data is

grouped by month (Table LXXII) and the linear regression analysis for PCBTOT vs. Wind

Sector Score is run again, seasonal trends can be seen. For example, January, 1991 (n=105)

gave a slope of −0.025, with an $r^2$ of 0.0302. August, 1991 data (N=154) gave a slope of

7.756 and an $r^2$ = 0.251. The interpretation is that this is indicative of a seasonal effect, most

likely due to a temperature effect because SVOCs, such as PCBs, have been found to exhibit

seasonal concentration fluctuations in other studies in the Great Lakes air shed. A scatter

plot of this August, 1991 data, with the calculated regression line, is shown in Figure 55.

## TABLE LXXII

### LINEAR REGRESSION OF TOTAL POLYCHLORINATED BIPHENYLS VERSUS WIND SECTOR SCORE, ALL SITES, BY MONTH

|  | n | M | b | $r^2$ | r | Mean ave. wind speed (m/s) | Mean ave. temp. (°C) |
|---|---|---|---|---|---|---|---|
| All Months | 1584 | 2.75 | 0.85 | 0.030 | 0.174 | 3.33 | 10.3 |
| 1 | 105 | -0.025 | 0.33 | 0.0 | 0.0141 | 4.68 | -1.4 |
| 2 | 114 | 0.137 | 0.534 | 0.001 | 0.036 | 4.48 | -2.3 |
| 3 | 139 | 1.953 | 1.5 | 0.027 | 0.164 | 4.05 | 0.6 |
| 4 | 144 | 1.062 | 0.406 | 0.024 | 0.156 | 3.33 | 7.3 |
| 5 | 155 | -0.073 | 0.935 | 0.0 | 0.01 | 2.62 | 16.1 |
| 6 | 131 | 8.485 | 1.63 | **0.062** | 0.248 | 3 | 19.2 |
| 7 | 150 | 3.249 | 0.54 | **0.024** | 0.156 | 2.95 | 20.9 |
| 8 | 154 | 7.75 | 0.964 | **0.251** | 0.501 | 2.63 | 20.3 |
| 9 | 138 | 3.02 | 0.47 | **0.156** | 0.395 | 2.66 | 16.7 |
| 10 | 165 | 1.176 | 0.17 | 0.3 | 0.548 | 3.52 | 10.8 |
| 11 | 109 | 0.306 | 0.283 | 0.029 | 0.169 | 3.5 | 2.9 |
| 12 | 80 | 0.82 | 0.139 | 0.074 | 0.271 | 3.3 | -1.0 |

**Notes:**

Parameters for equation $y = m*x + b$, where $y$ = PCBTOT conc., $x$ = wind sector score, M= slope, b = intercept, r = correlation coefficient

**Bold** signifies statistically significant values
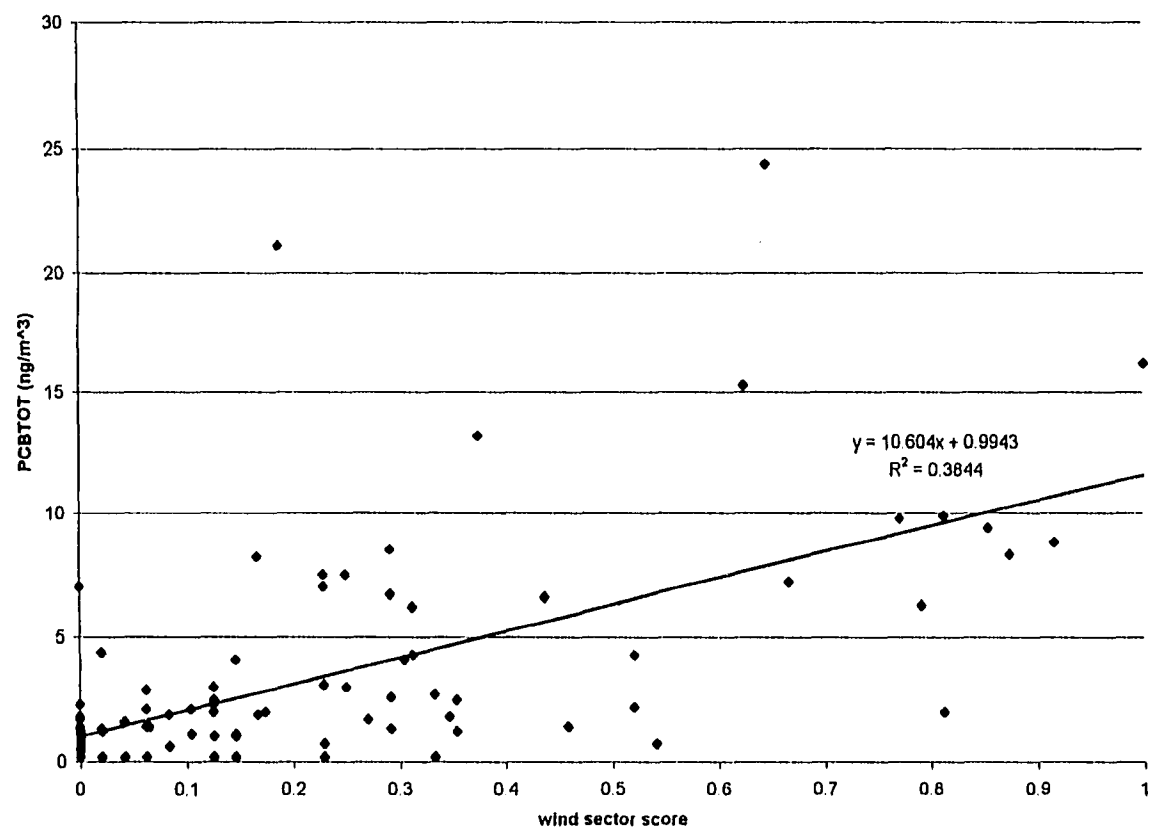
Figure 55.    Scatter plot of total polychlorinated biphenyl concentration versus wind sector score for all sites, month=8, yr=91.

In the plot of PCBTOT data by date (Figure 22), it can be seen that the range and maximum PCBTOT concentrations observed in 1992 are not nearly as great as was seen in 1991. Therefore, the PCBTOT data was also regressed by month for the whole project, and by month and year, to see if the monthly effect seen in Table LXXII occurred in both years. These linear regression data are summarized in Tables LXXIII through LXXVII. The purpose of this analysis was to see if the correlation was dominated by any one year. The data show that the significant correlations only occurred for 1991.

**TABLE LXXIII**

LINEAR REGRESSION RESULTS FOR TOTAL POLYCHLORINATED BIPHENYLS
VERSUS WIND SECTOR SCORE, ALL SITES, BY YEAR AND MONTH

| | n | M | b | $r^2$ | r | Mean ave. wind speed (m/s) | Mean ave. temp (°C) |
|---|---|---|---|---|---|---|---|
| All Months | 1584 | 2.75 | 0.85 | 0.030 | 0.17 | 3.3 | 10.3 |
| yr = 1991 | 1087 | 3.79 | 1.093 | 0.043 | 0.21 | 3.3 | 11.5 |
| 1 | 26 | -0.25 | 0.51 | 0.01 | 0.1 | 5 | -7.6 |
| 2 | 75 | 0.127 | 0.72 | 0.001 | 0.03 | 4.7 | -1.9 |
| 3 | 99 | 2.53 | 1.9 | 0.04 | 0.2 | 4.1 | 0.9 |
| 4 | 104 | 1.54 | 0.4 | 0.044 | 0.21 | 3.4 | 7.8 |
| 5 | 119 | 0.132 | 1.04 | 0.0 | 0.01 | 2.2 | 16.6 |
| 6 | 91 | 13.86 | 1.93 | **0.11** | 0.33 | 3.1 | 20.3 |
| 7 | 111 | 5.66 | 3.18 | 0.037 | 0.19 | 2.9 | 21.5 |
| 8 | 110 | 10.6 | 1 | **0.38** | 0.62 | 2.7 | 21.1 |
| 9 | 110 | 3.8 | 0.52 | **0.2** | 0.45 | 2.5 | 16.2 |
| 10 | 124 | 1.39 | 119 | **0.36** | 0.6 | 3.7 | 11.7 |
| 11 | 82 | 0.35 | 0.32 | 0.03 | 0.17 | 3.7 | 2.8 |
| 12 | 36 | 1.79 | 0.063 | 0.162 | 0.4 | 3.3 | -1.4 |
| yr = 1992 | 457 | -0.19 | 0.39 | 0.004 | 0.06 | 3.2 | 8 |
| 1 | 39 | -0.172 | 0.36 | 0.01 | 0.1 | 4.7 | -3 |
| 2 | 39 | 3.05E-17 | 0.2 | - | -- | 4 | -3.19 |
| 3 | 40 | -0.75 | 0.65 | 0.02 | 0.14 | 4 | -0.3 |
| 4 | 40 | -0.68 | 0.51 | 0.024 | 0.15 | 3.1 | 5.9 |
| 5 | 36 | -0.473 | 0.53 | 0.025 | 0.16 | 4.0 | 14.6 |
| 6 | 40 | 0.1 118 | 0.26 | 0.008 | 0.09 | 2.8 | 16.8 |
| 7 | 39 | -0.146 | 0.65 | 0.002 | 0.04 | 3.1 | 19.3 |
| 8 | 44 | -0.344 | 0.64 | -- | -- | 2.6 | 18.2 |
| 9 | 28 | 0.0011 | 0.221 | 0 | 0 | 3.3 | 18.4 |
| 10 | 41 | 3.65E-17 | 0.2 | - | -- | 3.1 | 8.3 |
| 11 | 27 | 3.77E-17 | 0.2 | - | -- | 3 | 3.1 |
| 12 | 44 | 4.82E-17 | 0.2 | -- | -- | 3.3 | -0.7 |
| yr=1993, month=1 | 40 | 0.22 | 0.21 | 0.029 | 0.17 | 4.5 | 4.2 |

**Notes:**

Parameters for equation $y = M*x + b$, where $y$= PCBTOT conc., $x$ = revised (corrected) wind sector score (score_rev), $M$ = slope, $b$ = intercept, $r$ = correlation coefficient

**TABLE LXXIV**

LINEAR REGRESSION RESULTS FOR TOTAL POLYCHLORINATED BIPHENYLS
VERSUS WIND SECTOR SCORE, SITE IDENTIFICATION 23007, BY MONTH

| | n | M | b | $r^2$ | r | Mean wind speed (m/s) | Mean ave. temp. (°C) |
|---|---|---|---|---|---|---|---|
| All Months | 396 | 2.04 | 0.9 | 0.045 | 0.21 | 3.3 | 10.3 |
| 1 | 25 | -0.0645 | 0.273 | 0.014 | 0.12 | 4.7 | -1.4 |
| 2 | 29 | -0.227 | 0.46 | 0.025 | 0.16 | 4.5 | -2.3 |
| 3 | 34 | 0.644 | 1.28 | 0.008 | 0.09 | 4.1 | 0.6 |
| 4 | 36 | 0.641 | 0.78 | 0.005 | 0.07 | 3.2 | 7.3 |
| 5 | 39 | -3.061 | 3.07 | 0.08 | 0.28 | 2.2 | 16.1 |
| 6 | 34 | 4.622 | 1.64 | **0.102** | 0.32 | 3 | 19.2 |
| 7 | 38 | 4.89 | 1.06 | **0.147** | 0.38 | 3 | 20.9 |
| 8 | 37 | 5.9 | 1.26 | **0.264** | 0.51 | 2.6 | 20.3 |
| 9 | 34 | 2.25 | 0.34 | **0.165** | 0.41 | 2.7 | 16.7 |
| 10 | 42 | 1.67 | -0.047 | **0.338** | 0.58 | 3.5 | 10.8 |
| 11 | 27 | 0.41 | 0.197 | **0.154** | 0.39 | 3.5 | 2.9 |
| 12 | 20 | 1.38 | -0.0013 | 0.081 | 0.28 | 3.3 | -1 |

**Notes:** Parameters for equation $y = M*x + b$, where $y =$ PCBTOT conc., $x =$ score_rev, $M =$ slope, $b =$ intercept, $r =$ correlation coefficient

**TABLE LXXV**

LINEAR REGRESSION RESULTS FOR TOTAL POLYCHLORINATED BIPHENYLS
VERSUS WIND SECTOR SCORE, SITE IDENTIFICATION 23009, BY MONTH

| | n | M | b | $r^2$ | r | Mean wind speed (m/s) | Mean ave. temp. (°C) |
|---|---|---|---|---|---|---|---|
| All Months | 391 | 4.98 | 0.88 | 0.056 | 0.24 | 3.4 | 10.2 |
| 1 | 27 | 0.107 | 0.227 | 0.027 | 0.17 | 4.7 | -1.5 |
| 2 | 28 | -0.14 | 0.567 | 0.001 | 0.03 | 4.5 | -1.9 |
| 3 | 35 | 5.263 | 1.569 | **0.167** | 0.41 | 4 | 0.5 |
| 4 | 36 | 1.65 | 0.296 | **0.145** | 0.38 | 3.3 | 7.4 |
| 5 | 39 | 3.58 | 0.291 | **0.31** | 0.56 | 2.6 | 16.2 |
| 6 | 32 | 41.3 | -0.429 | **0.507** | 0.71 | 3.1 | 19.3 |
| 7 | 36 | 22.91 | 3.145 | **0.137** | 0.37 | 2.9 | 20.9 |
| 8 | 37 | 23.46 | -0.78 | **0.613** | 0.78 | 2.7 | 20.3 |
| 9 | 33 | 6.55 | 0.689 | **0.307** | 0.55 | 2.7 | 16.6 |
| 10 | 41 | 0.293 | 0.24 | 0.023 | 0.15 | 3.5 | 10.8 |
| 11 | 27 | -0.096 | 0.38 | 0.003 | 0.05 | 3.6 | 3 |
| 12 | 20 | 6.51E-17 | 0.2 | -- | -- | 3.3 | -1 |

**Notes:** Parameters for equation $y = M*x + b$, where $y =$ PCBTOT conc., $x =$ score_rev, $M =$ slope, $b =$ intercept, $r =$ correlation coefficient

**TABLE LXXVI**

LINEAR REGRESSION RESULTS FOR TOTAL POLYCHLORINATED BIPHENYLS
VERSUS WIND SECTOR SCORE, SITE IDENTIFICATION 23011, BY MONTH

| | n | M | b | r² | r | Mean wind speed (m/s) | Mean ave. temp. (°C) |
|---|---|---|---|---|---|---|---|
| All Months | 397 | 3.134 | 0.99 | 0.014 | 0.12 | 3.3 | 10.2 |
| 1 | | 1.15 | 0.33 | 0.058 | 0.24 | 4.7 | -1.3 |
| 2 | 28 | 3.76 | 0.285 | 0.324 | 0.57 | 4.3 | -2.4 |
| 3 | 35 | 1.085 | 1.71 | 0.0124 | 0.11 | 4.0 | 0.5 |
| 4 | 36 | 0.37 | 0.462 | 0.009 | 0.1 | 3.3 | 7.1 |
| 5 | 38 | -0.132 | 0.452 | 0.002 | 0.04 | 2.7 | 15.9 |
| 6 | 31 | 14.4 | 2.5 | 0.048 | 0.22 | 2.9 | 19.2 |
| 7 | 38 | 2.03 | 3.24 | 0.002 | 0.04 | 3 | 21 |
| 8 | 40 | 5.55 | 1.42 | **0.07** | 0.26 | 2.6 | 20.1 |
| 9 | 35 | 1.18 | 0.57 | **0.029** | 0.17 | 2.5 | 16.7 |
| 10 | 41 | 0.67 | 0.216 | **0.302** | 0.55 | 3.5 | 10.8 |
| 11 | 28 | 1.79 | 0.15 | **0.316** | 0.56 | 3.3 | 2.9 |
| 12 | 20 | 7.62E-17 | 0.2 | - | - | 3.3 | -1 |

**Notes:** Parameters for equation $y = M*x + b$, where $y =$ PCBTOT conc., $x =$ score_rev, $M =$ slope, $b =$ intercept, $r =$ correlation coefficient

**TABLE LXXVII**

LINEAR REGRESSION RESULTS FOR TOTAL POLYCHLORINATED BIPHENYLS
VERSUS WIND SECTOR SCORE, SITE IDENTIFICATION 23013, BY MONTH

| | n | M | b | r² | r | Mean wind speed (m/s) | Mean ave. temp. (°C) |
|---|---|---|---|---|---|---|---|
| All Months | 400 | 1.95 | 0.55 | 0.019 | | 3.4 | 10.4 |
| 1 | 26 | -0.032 | 0.38 | 0 | | 4.7 | -1.5 |
| 2 | 29 | -0.5 | 0.59 | 0.002 | | 4.6 | -2.5 |
| 3 | 34 | -2.89 | 1.77 | 0.016 | | 4.1 | 0.6 |
| 4 | 36 | -0.06 | 0.31 | 0.0011 | | 3.3 | 7.4 |
| 5 | 39 | 0.187 | 0.47 | 0.0 | | 2.6 | 16.2 |
| 6 | 34 | 9.41 | 0.36 | **0.13** | | 3.0 | 19.1 |
| 7 | 38 | 4.67 | 0.9 | **0.1** | | 3 | 20.9 |
| 8 | 40 | 3.26 | 0.63 | **0.115** | | 2.6 | 20.4 |
| 9 | 36 | 2.7 | 0.29 | **0.134** | | 2.7 | 16.7 |
| 10 | 41 | 0.61 | 0.25 | 0.03 | | 3.5 | 10.1 |
| 11 | 27 | -0.75 | 0.35 | 0.025 | | 3.6 | 3 |
| 12 | 20 | 5.40E-17 | 0.2 | - | | 3.3 | -1 |

**Notes:** Parameters for equation $y = M*x + b$, where $y =$ PCBTOT conc., $x =$ score_rev, $M =$ slope, $b =$ intercept, $r =$ correlation coefficient

**4.4.3 Summary Statistics for Average Temperature and Wind Speed**

In Section 4.4.2 above, it was shown that there was an increase in the correlation coefficient for PCBTOT vs. Wind Sector Score for the warmer months, especially July, August, and September. This increase was much larger in 1991 than in 1992. It was suspected that this increase was at least in part due to a temperature effect. The mean values for PCBTOT, average wind speed, and average temperature, by month and by month and year, respectively, are shown in Table LXXVIII and LXXIX.

**TABLE LXXVIII**

MEAN VALUES FOR TOTAL POLYCHLORINATED BIPHENYLS,
WIND SECTOR SCORE, AVERAGE WIND SPEED, AND
AVERAGE TEMPERATURE, ALL SITES, BY MONTH

| | n | Mean PCBTOT Concentration (ng/m$^3$) | Mean Wind Sector Score | Mean ave. wind speed (m/s) | Mean ave. temp. (°C) |
|---|---|---|---|---|---|
| All Months | 1584 | 1.3 | 0.17 | 3.33 | 10.295 |
| 1 | 105 | 0.3 | 0.15 | 4.68 | -1.4 |
| 2 | 114 | 0.6 | 0.18 | 4.48 | -2.34 |
| 3 | 139 | 1.8 | 0.16 | 4.05 | 0.55 |
| 4 | 144 | 0.6 | 0.16 | 3.33 | 7.29 |
| 5 | 155 | 0.9 | 0.16 | 2.62 | 16.12 |
| 6 | 131 | 3.1 | 0.18 | 3 | 19.18 |
| 7 | 150 | 3.3 | 0.18 | 2.95 | 20.92 |
| 8 | 154 | 2.3 | 0.19 | 2.63 | 20.3 |
| 9 | 138 | 1 | 0.17 | 2.66 | 16.7 |
| 10 | 165 | 0.4 | 0.19 | 3.52 | 10.83 |
| 11 | 109 | 0.3 | 0.18 | 3.5 | 2.87 |
| 12 | 80 | 0.3 | 0.17 | 3.3 | -0.99 |

**TABLE LXXIX**

MEAN VALUES FOR TOTAL POLYCHLORINATED BIPHENYLS,
WIND SECTOR SCORE, AVERAGE WIND SPEED, AND
AVERAGE TEMPERATURE, ALL SITES, BY YEAR AND MONTH

| | n | PCBTOT | Mean Wind Sector Score | Mean ave. wind speed (m/s) | Mean ave. temp. (°C) |
|---|---|---|---|---|---|
| All Months | 1584 | 1.32 | 0.17 | 3.3 | 10.3 |
| yr =1991 | 1087 | 1.76 | 0.18 | 33. | 11.5 |
| 1 | 26 | 0.47 | 0.19 | 5 | -7.6 |
| 2 | 75 | 0.75 | 0.19 | 4.7 | -1.9 |
| 3 | 99 | 2.33 | 0.17 | 4.1 | 0.9 |
| 4 | 104 | 0.65 | 0.16 | 3.4 | 7.8 |
| 5 | 119 | 1.07 | 0.16 | 2.2 | 16.6 |
| 6 | 91 | 4.4 | 0.18 | 3.1 | 20.3 |
| 7 | 111 | 4.17 | 0.18 | 2.9 | 21.5 |
| 8 | 110 | 3 | 0.19 | 2.7 | 21.1 |
| 9 | 110 | 1.18 | 0.17 | 2.5 | 16.2 |
| 10 | 124 | 0.45 | 0.19 | 3.7 | 11.7 |
| 11 | 82 | 0.38 | 0.19 | 3.7 | 2.8 |
| 12 | 36 | 0.36 | 0.17 | 3.3 | -1.4 |
| yr=1992 | 457 | 0.36 | 0.17 | 3.4 | 8 |
| 1 | 39 | 0.33 | 0.16 | 4.7 | -3 |
| 2 | 39 | 0.2 | 0.17 | 4 | -3.2 |
| 3 | 40 | 0.55 | 0.14 | 4 | -0.3 |
| 4 | 40 | 0.4 | 0.17 | 3.1 | 5.9 |
| 5 | 36 | 0.45 | 0.17 | 4 | 14.6 |
| 6 | 40 | 0.28 | 0.18 | 2.8 | 16.8 |
| 7 | 39 | 0.62 | 0.18 | 3.1 | 19.3 |
| 8 | 44 | 0.58 | 0.18 | 2.6 | 18.2 |
| 9 | 28 | 0.22 | 0.15 | 3.3 | 18.4 |
| 10 | 41 | 0.2 | 0.17 | 3.1 | 8.3 |
| 11 | 27 | 0.2 | 0.15 | 3 | 3.1 |
| 12 | 44 | 0.2 | 0.16 | 3.3 | -0.7 |
| yr=1993, month=1 | 40 | 0.235 | 0.11 | 4.5 | 4.2 |

A few general comments can be made from the data in Tables LXXVIII and LXXIX. The mean wind sector scores are in the 0.15 to 0.2 range for all months. Mean wind speeds are generally lower for the warmer months. In general, the highest mean PCBTOT concentrations occurred in the warmest months.

## 4.5    Polychlorinated Biphenyl Concentrations and Temperature

In Section 4.4, it was shown that the correlation ($r^2$) between wind sector score and PCBTOT concentration increased for the summer months. It was suspected that this increase was, at least partially, temperature related. In this Section 4.5, the effect of temperature on PCB concentrations (for homologs and total) is investigated further.

### 4.5.1    Combined Data and Sorted by Site Identification

When the PCBTOT concentration and average temperature for samples from all sites are plotted on the same graph (Figure 56), there appears to be a temperature relationship, with the highest PCB concentrations generally occurring during the sampling periods with the highest average temperature. However, the correlation cannot be directly examined. While the actual range of PCBTOT concentrations observed differed between sites, the temperature effect was present at all sites, as can be seen in the plots of PCBTOT and average temperature by sampling date for the four sampling sites (Figures 57-60). It is noted that the PCBTOT concentration range was much greater in 1991 (0.2-83 $ng/m^3$) than in 1992 (0.2-6 $ng/m^3$), even though the temperatures observed were only slightly lower in 1992.

Possible explanations for the differences in PCBTOT concentrations between years are proposed in other areas of this thesis.
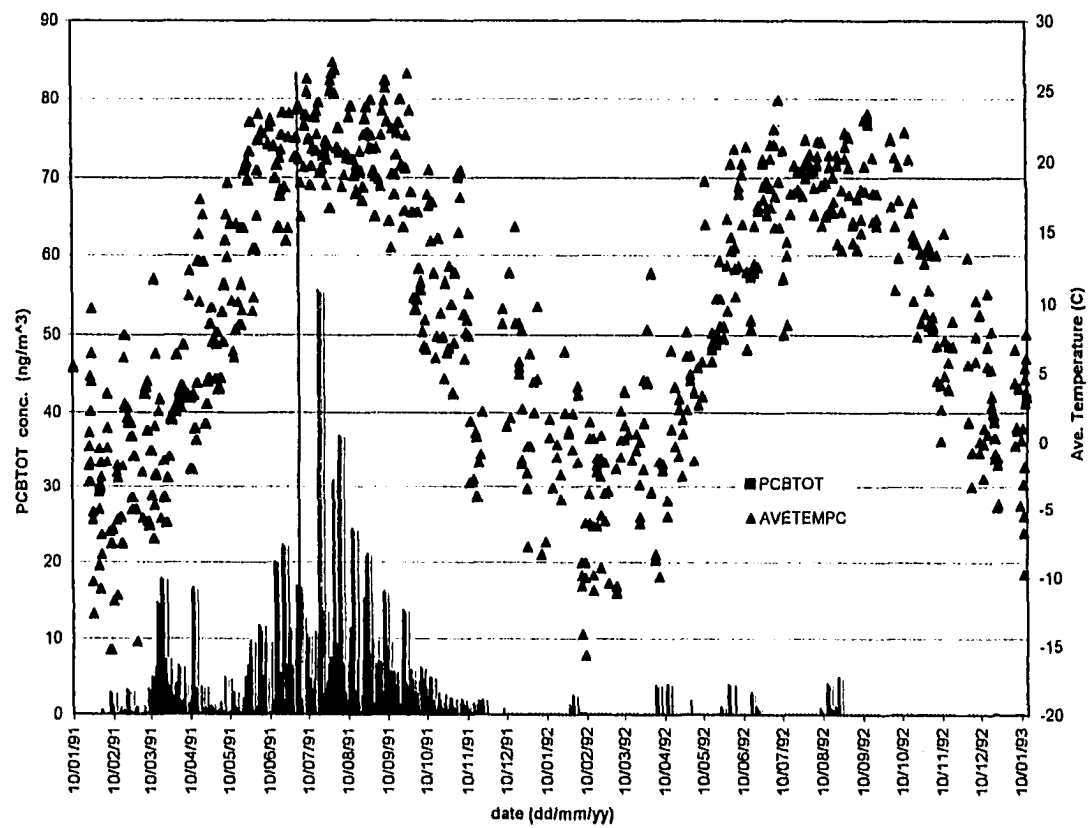
Figure 56.   Total polychlorinated biphenyl concentrations and average temperature by date, all sites.
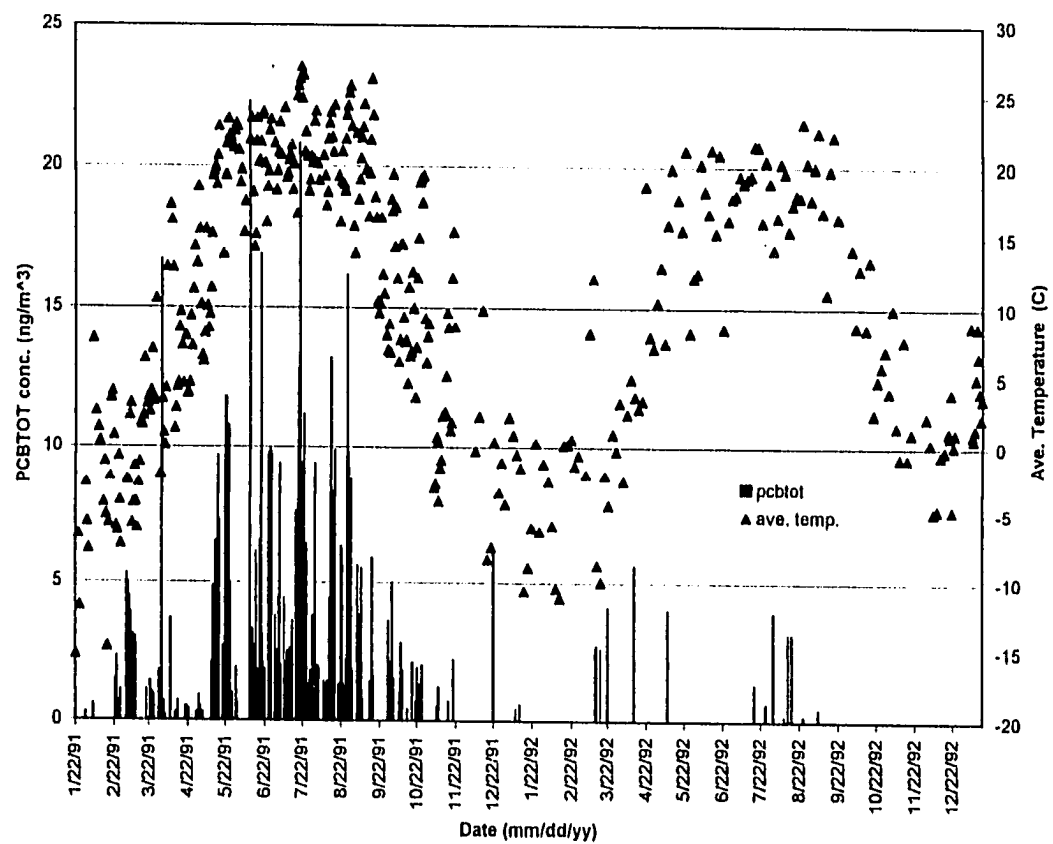
Figure 57.  Total polychlorinated biphenyl concentrations and average temperature by date, site identification number 23007.
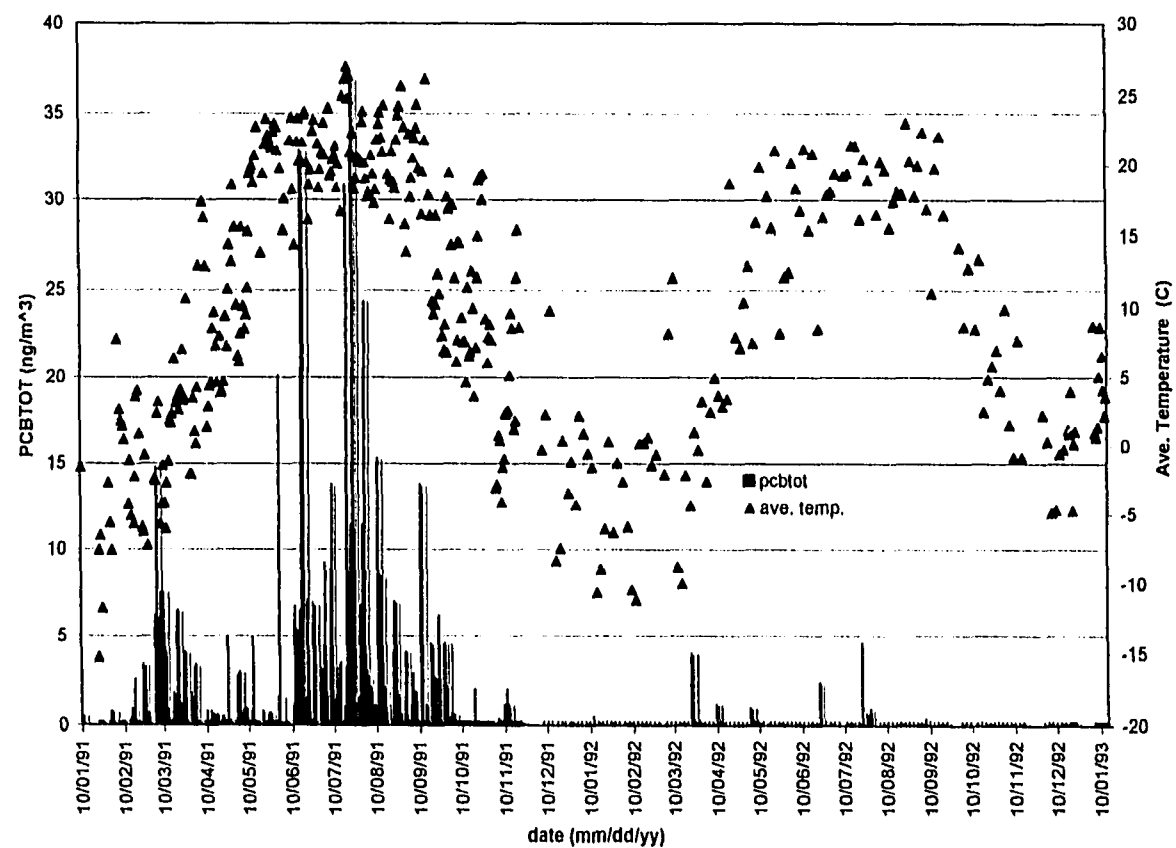
Figure 58.    Total polychlorinated biphenyl concentrations and average temperature by date, site identification number 23009.
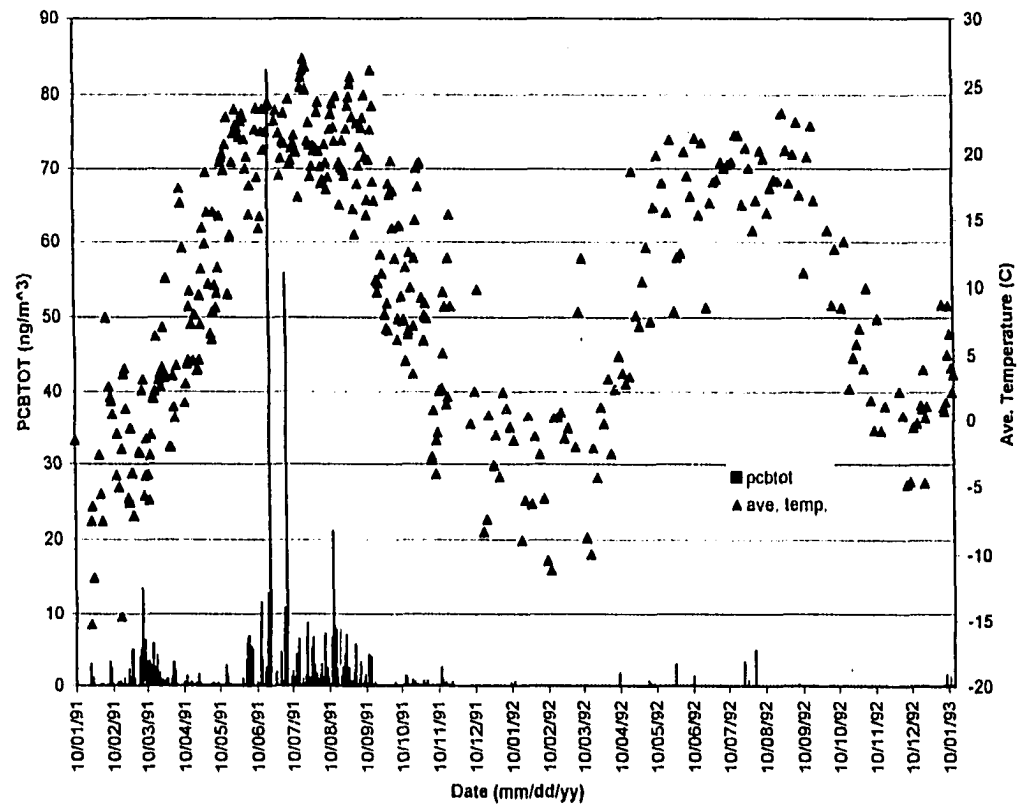
Figure 59.    Total polychlorinated biphenyl concentrations and average temperature by date, site identification number 23011.
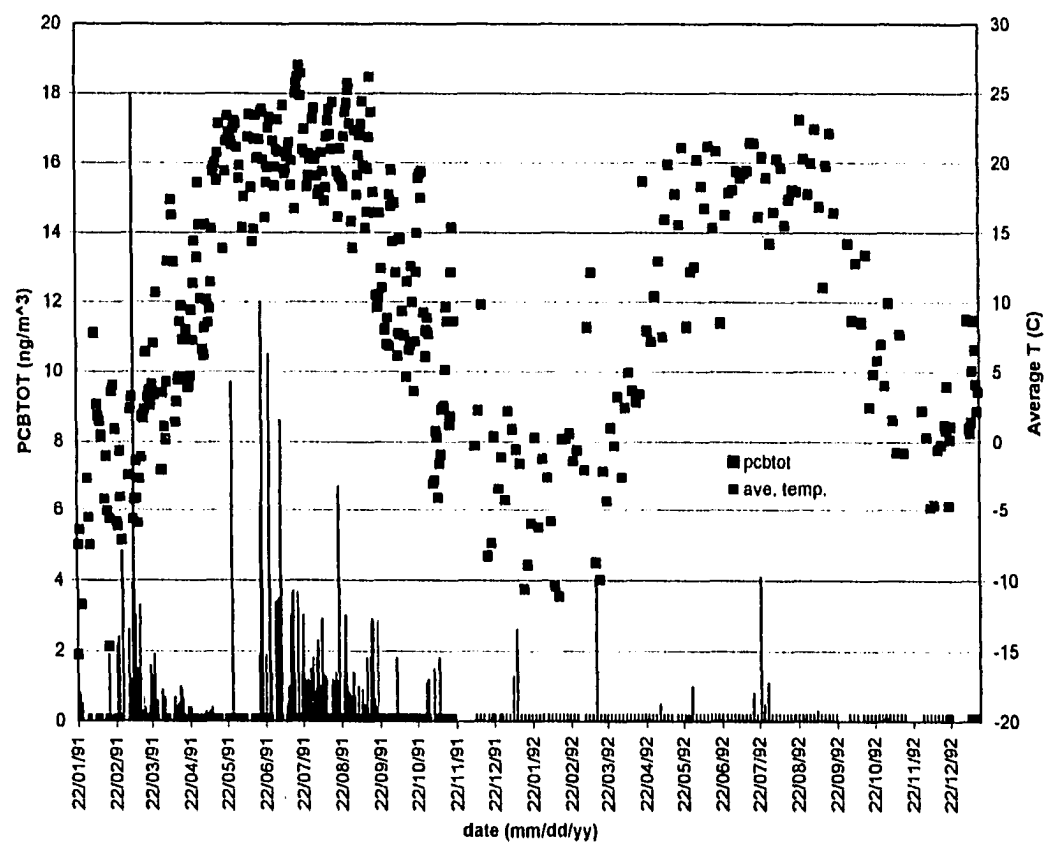
Figure 60.    Total polychlorinated biphenyl concentrations and average temperature by date, site identification number 23013.

### 4.5.2 Total Polychlorinated Biphenyls and Temperature

The monthly mean PCBTOT and average temperature values are plotted by **month** in Figure 61. The monthly mean PCBTOT and average temperature values are plotted by **year** and **month** in Figure 62. The monthly mean for March, 1991 does not fall on the same line as the other months at the same temperature. The reason for this difference is not known.

Both Figures 61 and 62 would appear to confirm the temperature relationship that was postulated based on Figures 56-60. When the monthly mean PCBTOT and monthly mean temperature, grouped by month=1, 2, 3 etc., are plotted against each other (Figure 63), there is a non-linear relationship. In Figure 64, the mean PCBTOT and mean average temperature in °C are plotted against each other by year and month during the project. Both Figures 63 and 64 show a strong temperature effect, even though the concentrations observed in 1992 were much less than in 1991. The relationship appears to be strongly curvilinear, with elevated mean PCBTOT occurring when mean average temperature $>15°C$. From Figures 56 to 60 and Figure 62, we note that for March, 1991, the PCBTOT concentrations are elevated by more than would seem to be explained by temperature alone.
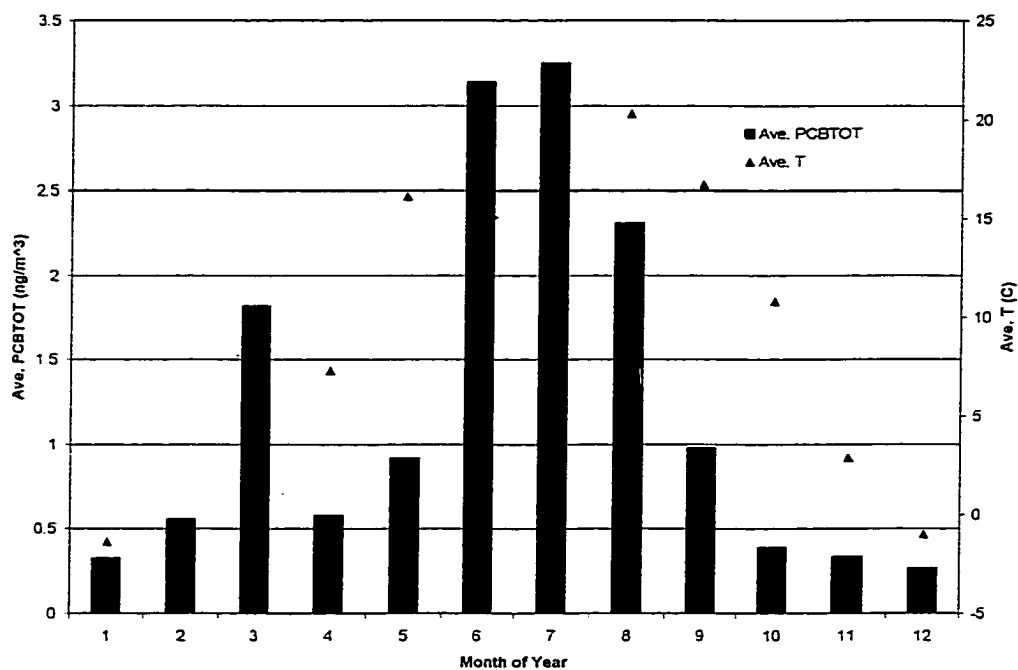
Figure 61. Combined monthly mean total polychlorinated biphenyl concentrations and mean average temperatures for air samples, all data, by month.
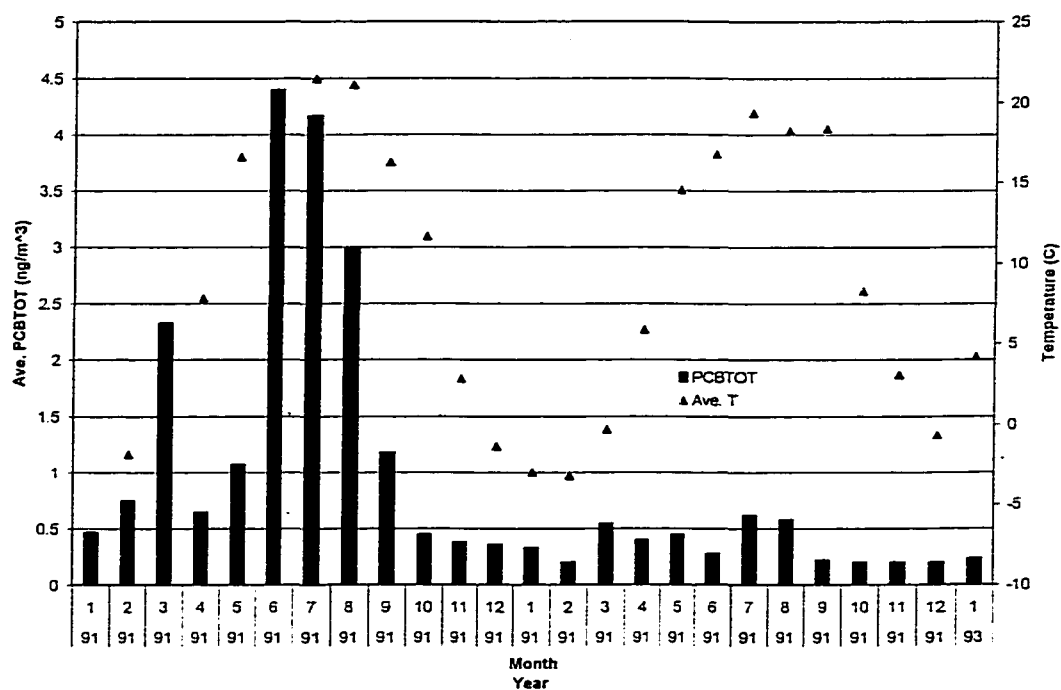
Figure 62.    Monthly mean total polychlorinated biphenyl concentrations and mean average temperatures for all data, by year, month.
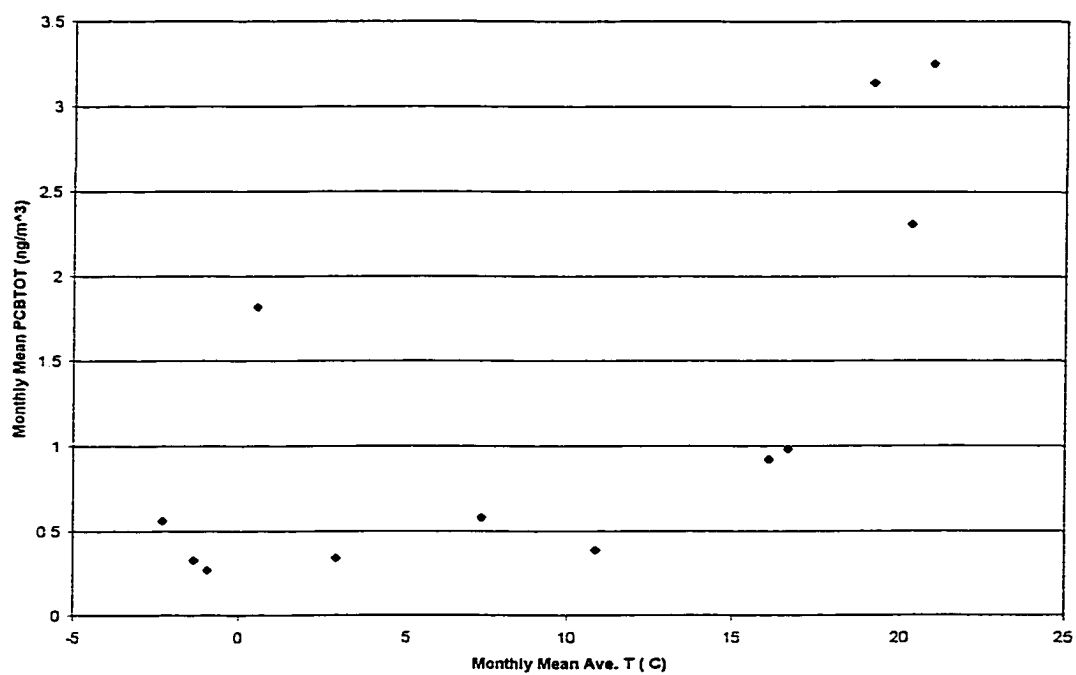
Figure 63.    Combined monthly mean total polychlorinated biphenyl concentrations versus average temperature by month, all sites by month (i.e., 12 data points).
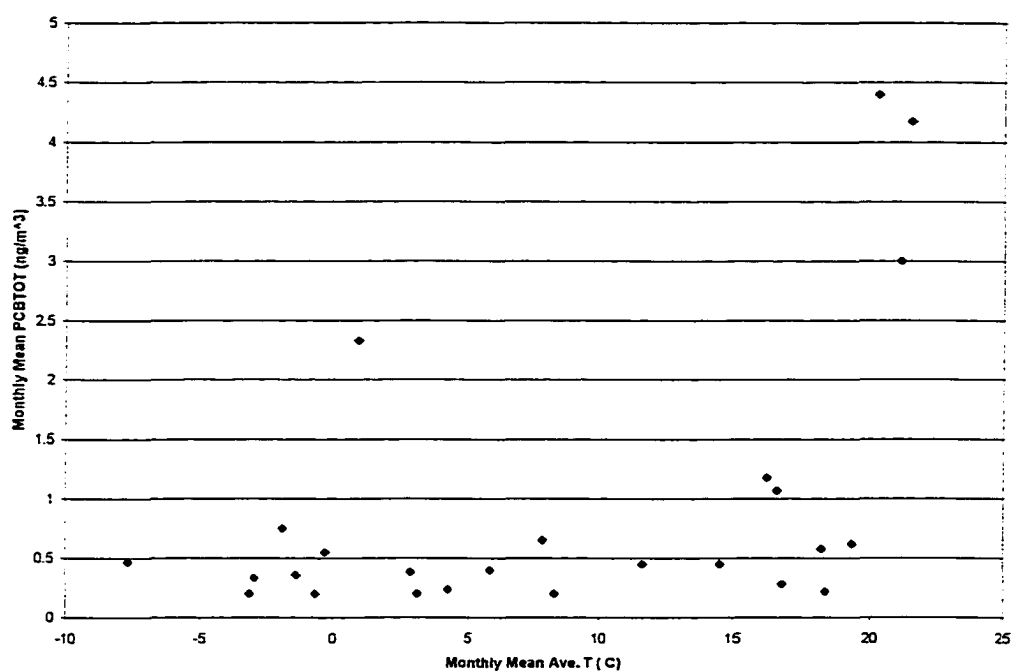
Figure 64.   Monthly mean total polychlorinated biphenyl concentrations versus average temperature by month, all sites each month (i.e., 25 data points) during project.

### 4.5.3   Clausius-Clapeyron Relationships for Polychlorinated Biphenyls

Wania, et al. [102] have reviewed the general issues regarding temperature dependence of atmospheric concentrations of SVOCs, such as PCBs. Previously published work by Hoff [57, 105, 198] and others have shown PCB concentration-temperature relationships in the Great Lakes area [72, 74, 84, 103, 255-257], in the UK [68-71, 258-260], in Scandinavia [64, 261-263], in Germany [264], and in the Baltic Sea Region [265].

Most of these studies used filter and sorbent cartridges to collect and analyze the "particle" and "gas" phase separately. At elevated ambient temperatures, increased PCB concentrations were observed in these studies, especially in the "gas phase." This observation has been interpreted as an indication that volatilization from the earth's surface (or other sources) is an important factor in the environmental fate and transport of these chemicals. However, almost all of the previously published data covers rural/urban background sites, with concentrations much lower than seen here, and did not discuss temperature relationships near specific point sources and/or at higher concentration ranges.

The body of research outlined above (and work by other researchers) has, in the 1990's, led to a recognition that the temperature dependent behavior of SVOCs is consistent with the liquid-vapor equilibrium described by the Clausius-Clapeyron (CC) Equation [40, 105, 258, 266] as shown in equation (3) below:

$$LnP_{vap} = -\frac{\Delta H_{VAP}}{RT} + b \qquad (3)$$

This can be interpreted as the regression of the natural logarithm of vapor pressure on 1/T (in K), yielding the slope M and the intercept b, where $M = -\Delta H_{vap}/R$, which can be rearranged to $\Delta H_{vap} = -M*R$. If poor linearity is observed for the vapor pressure plot, it suggests that: i) the compound being observed is not in the vapor phase; or ii) that its behavior is not being governed by temperature dependent volatilization; or iii) that equilibrium does not exist; or iv) other atmospheric deposition processes are important; or v) a combination of these factors in addition to temperature are controlling gas phase (and total) concentrations [68, 267].

### 4.5.3.1 Clausius-Clapeyron Relationship for Smithville Data

The concentration data from the Smithville project for the di-deca-PCBs (*detects only*, and *all data* {includes detects and <W and <T values at the reported limit}) and PCBTOT were converted to $P_{vap}$, and the Ln $P_{vap}$ values were evaluated using the CC relationship. Table LXXX shows the results for the linear regression analysis (using least square fit) of the *detects only* data for all sites. Table LXXXI shows the results for the following, by homolog:

1)  *all data* for 1991, 1992 and 1993,

2)  *detects only* for 1991, 1992 and 1993,

3)  *all data* for 1991,

4)  *detects only* for 1991,

5)  *all data* for 1992,

6)  *detects only* for 1992,

7)    *all data* for 1993, and

8)    *detects only* for 1993.

The PCBDI, PCBTRI and PCBTET, PCBHEX and PCBOCT homologs were only observed in the 1991 sampling year, when the ambient air concentrations of PCB were generally higher. In 1992, only the PCBPNT and PCBHEX homologs and PCBTOT were reported above the <W and <T limits more than 1 time. No PCB homologs were reported above the <W or <T limits for the January 1993 post incineration sampling.

An example CC plot for the PCBDI homolog data in Table LXXX is shown in Figure 65. The CC plot for the PCBDI homolog data in Table LXXXI is shown in Figure 66. Table LXXXII shows the results from a linear regression analysis of the *detects only* data for the ave. temp of <0°C. There are no slopes statistically different from 0 for the ave. temp. of <0°C *detects only* data. Table LXXXIII shows the results from a linear regression analysis of the *detects only* data for the ave. temp. of ≥0°C. The value of 0 was chosen based upon previous work of Hoff and Halsall [105]. The slopes for PCBDI, PCBTRI, PCBTET and PCBTOT are statistically different from 0 for this data. Table LXXXIV and Table LXXXV show the results for linear regression analyses on the *all data* set for the ave. temp. of <0°C and ≥0°C respectively. There are no slopes statistically different from 0 for the ave. temp. of <0°C *all data* set; however, as seen above, the slopes for a number of homologs (PCBDI, PCBTRI, PCBPNT, PCBHEX, PCBHEPT, PCBOT and PCBTOT) are statistically different from 0 for the ave. temp. of ≥0°C.

Using all of the data (including <W and <T values) is conservative and drastically reduces the magnitude of the slope; however, the statistical significance (whether or not the slope is or is not equal to zero) was usually not affected for the data. Thus, the conclusions reached using the two data sets are generally the same; there is a temperature effect, but the magnitude of the effect (the slopes) calculated are different. It is suspected that there are many different factors represented in the full data set besides just temperature, such as wind sector score and Site ID, site operations, etc. It appears that the data for detects *only* are the best ones for evaluating the magnitude of the temperature dependence, which can then be compared with literature values. Therefore, the *detects only* data set was used for additional investigations, as outlined below.

It is recognized that using the *detect only* data results in smaller data set than the 1584 samples that were actually taken during the project. It is also recognized that it is more appropriate to analyze the temperature dependence of individual congeners rather than homologs or PCBTOT; however, as was explained earlier, the congener-specific results were not available for this work.

# TABLE LXXX

## LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS
## ONE OVER TEMPERATURE, DETECTS ONLY

| Homolog | n | M | t | p | 95% CI | b | $r^2$ |
|---------|-----|--------|------|---------|--------|--------|-------|
| PCBDI | 103 | **-6.07** | 4.3 | <0.0001 | 2.801 | 3.057 | 0.146 |
| PCBTRI | 125 | **-3.813** | 5.34 | <0.0001 | 1.417 | -4.277 | 0.188 |
| PCBTET | 125 | **-4.099** | 5.74 | <0.0001 | 1.418 | -4.496 | 0.211 |
| PCBPNT | 137 | -0.469 | 0.74 | -0.4596 | 1.227 | -16.43 | 0.004 |
| PCBHEX | 7 | -1.181 | 0.69 | 0.519 | 4.172 | -13.78 | 0.087 |
| PCBHEPT | 4 | -3.971 | 2.36 | 0.1424 | 5.346 | -3.8 | 0.754 |
| PCBOCT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 312 | **-1.389** | 3.35 | 0.0009 | 0.822 | -12.61 | 0.035 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0

## TABLE LXXXI

### LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER TEMPERATURE, ALL DATA AND DETECTS ONLY, COMBINED AND BY YEAR

| Homolog | case | YR | n | M | std. error | t | p | 95% C.I. | b | r^2 |
|---|---|---|---|---|---|---|---|---|---|---|
| PCBDI | all data | 91,92,93 | 1584 | -1.84E+00 | 1.24E-01 | 14.91 | <0.0001 | 0.243 | 13.263 | 0.1232 |
| | detects only | 91,92,93 | 103 | -6.07E+00 | 1.41E+00 | 4.3 | 0.0001 | 2.801 | 3.057 | 0.155 |
| | all data | 91 | 1087 | -2.28E+00 | 1.75E-01 | 13.02 | <0.0001 | 0.343 | -11.67 | 0.135 |
| | detects only | 91 | 103 | -6.07E+00 | 1.41E+00 | 4.3 | <0.0001 | 2.735 | 3.06 | 0.155 |
| | all data | 92 | 457 | -2.76E-01 | 1.80E-02 | 15.22 | <0.0001 | 0.035 | -19 | 0.337 |
| | detects only | 92 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 93 | 40 | -2.78E-01 | 1.80E-04 | 1534 | <0.0001 | 0.000 | -19 | 0.99 |
| | detects only | 93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTRI | all data | 91,92,93 | 1584 | -2.013 | 0.155 | 12.99 | <0.0001 | 0.304 | 12.747 | 0.0964 |
| | detects only | 91,92,93 | 125 | -3.8131 | 0.7144 | 5.34 | 0.0001 | 1.417 | -4.27714 | 0.188 |
| | all data | 91 | 1087 | -2.44E+00 | 2.20E-01 | 11.13 | <0.0001 | 0.432 | -11.2 | 0.103 |
| | detects only | 91 | 124 | -3.78E+00 | 7.10E-01 | 5.31 | <0.0001 | 1.409 | -4.35 | 0.188 |
| | all data | 92 | 457 | -3.10E-01 | 5.00E-02 | 6.3 | <0.0001 | 0.098 | 19.02 | 0.08 |
| | detects only | 92 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 93 | 40 | -2.78E-01 | 1.80E-04 | 1535 | <0.0001 | 0.000 | -19.2 | 0.99 |
| | detects only | 93 | 0 | | | | | 0.000 | | |
| PCBTET | all data | 91,92,93 | 1584 | 0.226 | 0.1505 | 1.5 | 0.1329 | 0.295 | -20.72 | 0.0014 |
| | detects only | 91,92,93 | 125 | -4.0992 | 0.7145 | 5.74 | 0.0001 | 1.418 | -4.496 | 0.211 |
| | all data | 91 | 1087 | 0.673 | 0.2 | 3.32 | 0.009 | 0.392 | -22.2 | 0.01 |
| | detects only | 91 | 124 | -4.075 | 0.71 | 5.72 | <0.0001 | 1.409 | 4.421 | 0.211 |
| | all data | 92 | 457 | 0.059 | 0.16 | 0.38 | 0.7 | 0.317 | -20.4 | 0.003 |
| | detects only | 92 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 93 | 40 | 0.66 | 0.94 | 0.7 | 0.5 | 1.900 | -22.6 | 0.013 |
| | detects only | 93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

# TABLE LXXXI (Continued)

## LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS
## ONE OVER TEMPERATURE, ALL DATA AND DETECTS ONLY, COMBINED AND BY YEAR

| Homolog | case | YR | n | M | std. error | t | p | 95% C.I. | b | r^2 |
|---|---|---|---|---|---|---|---|---|---|---|
| PCBPNT | all data | 91,92,93 | 1584 | **-1.87** | 0.144 | 13.01 | <0.0001 | 0.283 | -13.43 | 0.0967 |
| | detects only | 91,92,93 | 137 | -0.4689 | 0.6323 | 0.74 | -0.4596 | 1.227 | -16.43 | 0.004 |
| | all data | 91 | 1087 | **-2.08** | 0.2 | 10.64 | <0.0001 | 0.392 | -12.6 | 0.095 |
| | detects only | 91 | 126 | 0.486 | 0.62 | 0.78 | 0.434 | 1.203 | -16.35 | 0.005 |
| | all data | 92 | 457 | **-0.707** | 0.15 | 4.74 | <0.0001 | 0.294 | -17.75 | 0.05 |
| | detects only | 92 | 11 | 2.346 | 4.15 | 0.56 | 0.58 | 9.246 | -26.52 | 0.034 |
| | all data | 93 | 40 | 0.66 | 0.94 | 0.7 | 0.58 | 1.900 | -22.7 | 0.013 |
| | detects only | 93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEX | all data | 91,92,93 | 1584 | **-0.167** | 0.039 | 4.24 | <0.0001 | 0.077 | -19.84 | 0.0113 |
| | detects only | 91,92,93 | 7 | -1.181 | 1.705 | 0.69 | 0.519 | 4.172 | -13.78 | 0.087 |
| | all data | 91 | 1087 | -0.083 | 0.06 | 1.46 | 0.145 | 0.118 | -20.1 | 0.002 |
| | detects only | 91 | 7 | -1.181 | 1.71 | 0.69 | 0.52 | 4.184 | -13.8 | 0.09 |
| | all data | 92 | 457 | **-0.28** | 0.00019 | 1423 | <0.0001 | 0.000 | -19.45 | 0.99 |
| | detects only | 92 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 93 | 40 | **-0.278** | 0.00018 | 1534 | <0.0001 | 0.000 | -19.5 | 0.999 |
| | detects only | 93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | all data | 91,92,93 | 1584 | **-0.267** | 0.0298 | 8.98 | <0.0001 | 0.058 | -19.58 | 0.0485 |
| | detects only | 91,92,93 | 4 | -3.971 | 1.68 | 2.36 | 0.1424 | 5.346 | -3.8 | 0.75354 |
| | all data | 91 | 1087 | **-0.229** | 0.022 | 10.62 | <0.0001 | 0.043 | -19.73 | -0.094 |
| | detects only | 91 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 92 | 457 | **-0.384** | 0.09 | 4.22 | <0.0001 | 0.175 | -19.16 | 0.04 |
| | detects only | 92 | 3 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 93 | 40 | **-2.78** | 0.00018 | 1534 | <0.0001 | 0.000 | -19.6 | 0.999 |
| | detects only | 93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

# TABLE LXXXI (Concluded)

## LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS
## ONE OVER TEMPERATURE, ALL DATA AND DETECTS ONLY, COMBINED AND BY YEAR

| Homolog | case | YR | n | M | std. error | t | p | 95% C.I. | b | r^2 |
|---|---|---|---|---|---|---|---|---|---|---|
| PCBOCT | all data | 91,92,93 | 1584 | **-0.274** | 0.009 | 29.73 | <0.0001 | 0.018 | -19.66 | 0.3588 |
| | detects only | 91,92,93 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 91 | 1087 | **-0.269** | 0.0135 | 20 | <0.0001 | 0.026 | -19.7 | 0.27 |
| | detects only | 91 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 92 | 457 | **-0.28** | -0.0002 | 1423 | <0.0001 | 0.000 | -19.63 | 0.999 |
| | detects only | 92 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | all data | 93 | 40 | **-0.278** | 0.00018 | 1534 | <0.0001 | 0.000 | -19.6 | 0.99 |
| | detects only | 93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | all data | 91,92,93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | all data | 91,92,93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | all data | 91,92,93 | 1584 | **-1.535** | 0.119 | 12.87 | <0.0001 | 0.233 | -12.62 | 0.095 |
| | detects only | 91,92,93 | 313 | **-1.389** | 0.415 | 3.35 | 0.0009 | 0.822 | -12.61 | thing |
| | all data | 91 | 1087 | **-3.789** | 0.71 | 5.31 | <0.0001 | 1.393 | -4.35 | 0.188 |
| | detects only | 91 | 291 | **-1.55** | 0.43 | 3.6 | 0.0004 | 0.853 | -12.02 | 0.043 |
| | all data | 92 | 457 | **-0.33** | 0.093 | 3.6 | 0.0004 | 0.180 | -17.11 | 0.028 |
| | detects only | 92 | 22 | 2.66 | 1.49 | 1.79 | 0.089 | 3.090 | -27.3 | 0.138 |
| | all data | 93 | 40 | 0.14 | 0.43 | 0.34 | 0.73 | 0.869 | -18.9 | 0.0003 |
| | detects only | 93 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject $H_0$, Slope Is Equal To 0
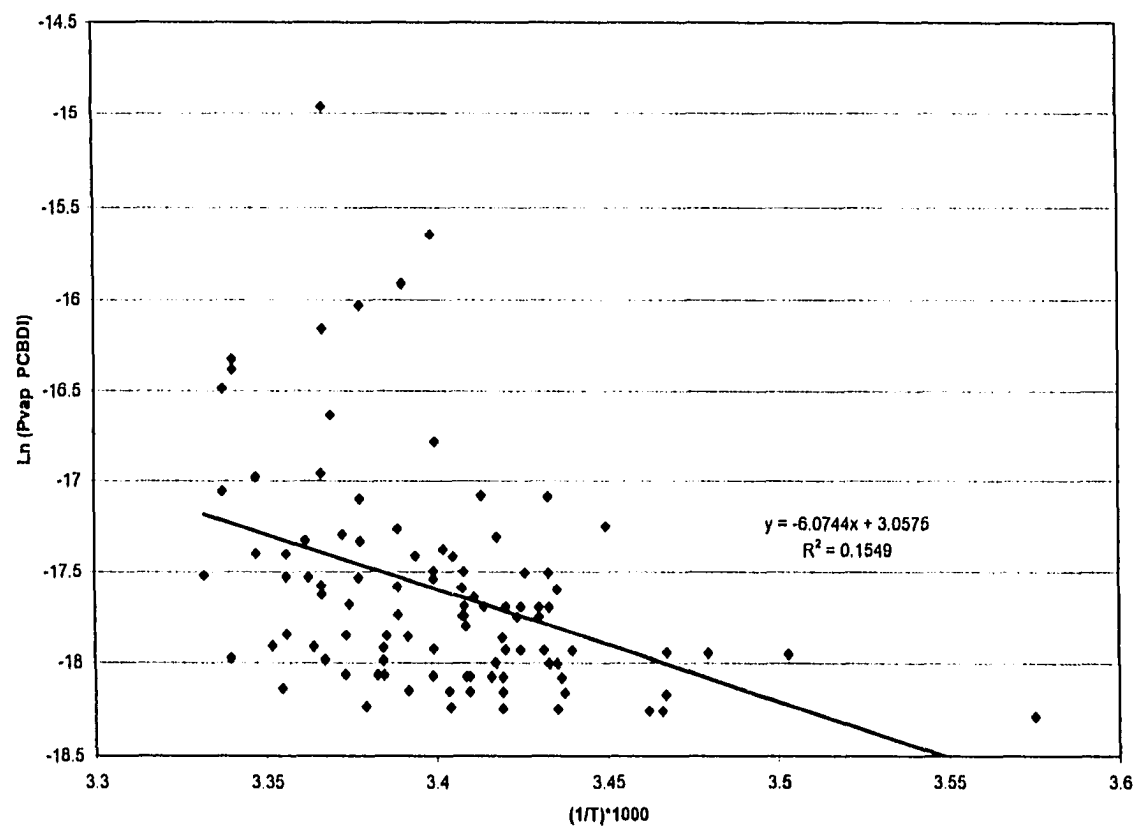
Figure 65.    Clausius-Clapeyron plot for natural log of vapor pressure (dichlorobiphenyl detects only) versus 1000*(1/T), all sites.
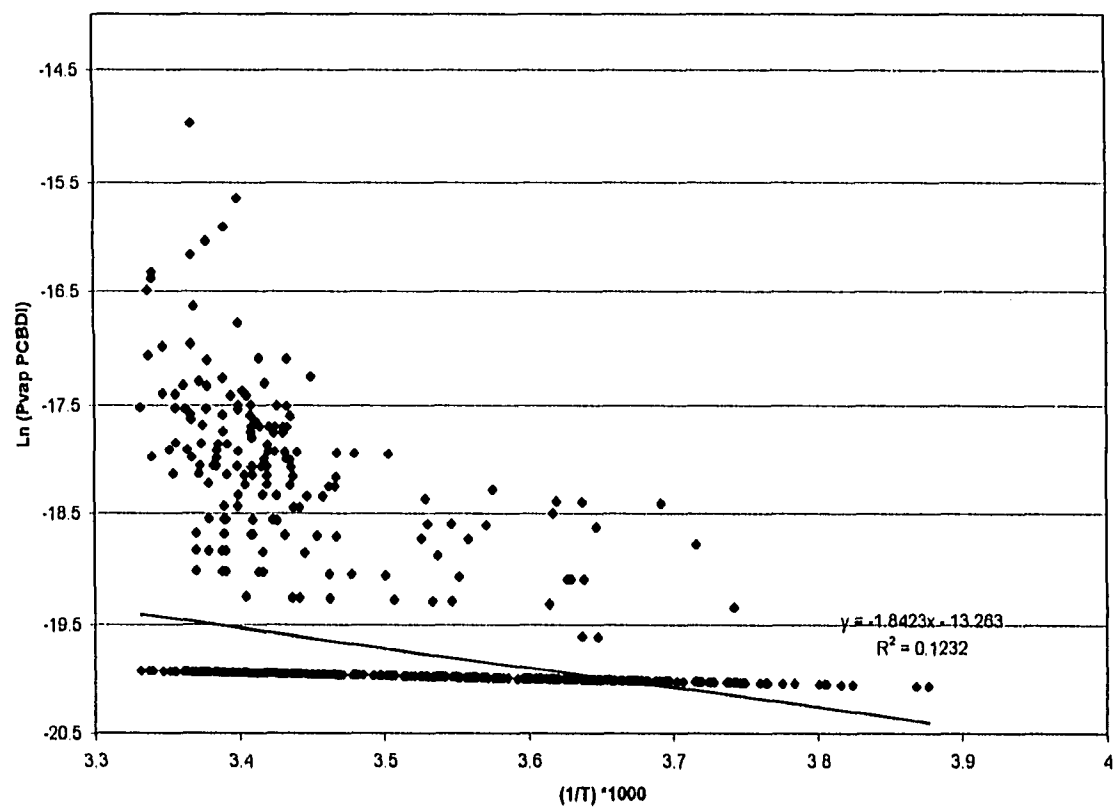
Figure 66.     Clausius-Clapeyron plot for natural log of vapor pressure (dichlorobiphenyl all data) versus 1000*(1/T), all sites.

**TABLE LXXXII**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, TEMPERATURE IS LESS THAN ZERO

| Homolog | n | M | t | p | 95% CI | b | $r^2$ |
|---------|-----|--------|------|-------|--------|--------|-------|
| PCBDI | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTRI | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTET | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBPNT | 9 | -2.907 | 1.1 | 0.3 | 5.972 | -7.5 | 0.148 |
| PCBHEX | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 44 | -0.289 | 0.11 | 0.915 | 5.357 | -16.61 | 0.0 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE LXXXIII**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, TEMPERATURE IS GREATER THAN ZERO

| Homolog | n | M | t | p | 95% CI | b | $r^2$ |
|---------|---|---|---|---|--------|---|-------|
| PCBDI | 103 | **6.07E+00** | 4.3 | <0.0001 | 2.79744 | 3.06 | 0.155 |
| PCBTRI | 123 | **-4.185** | 5.09 | <0.0001 | 1.62688 | -3.01 | 0.176 |
| PCBTET | 123 | **-4.473** | 5.44 | <0.0001 | 1.62688 | 5.77 | 0.197 |
| PCBPNT | 128 | -1.355 | 1.06 | 0.29 | 2.51968 | -22.62 | 0.009 |
| PCBHEX | 5 | -2.457 | 1.06 | 0.3668 | 5.67704 | -9.38 | 0.273 |
| PCBHEPT | 3 | 0 | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 269 | -2.123 | 2.83 | 0.0936 | 1.488 | -12.156 | 0.033 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected
during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE LXXXIV**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, ALL DATA, TEMPERATURE IS LESS THAN ZERO

| Homolog | n | M | t | p | 95% CI | b | $r^2$ |
|---------|---|---|---|---|--------|---|-------|
| PCBDI | 273 | **-0.032** | 1.97 | 0.0504 | 0.3298 | -18.8 | 0.014 |
| PCBTRI | 273 | -0.29 | 1.07 | 0.28 | 0.5238 | -19.06 | 0.004 |
| PCBTET | 273 | 0.008 | 0.01 | 0.99 | 2.3668 | -19.78 | 0 |
| PCBPNT | 273 | 0.537 | 0.83 | 0.41 | 1.2416 | -22.2 | 0.003 |
| PCBHEX | 273 | 0.012 | 0.03 | 0.97 | 0.70034 | 0.000004 | 0.0 |
| PCBHEPT | 273 | 0.148 | 0.8 | 0.43 | 0.36084 | -20 | 0.002 |
| PCBOCT | 273 | **-0.267** | 1958 | <0.0001 | 0.000252 | -19.68 | 0.999 |
| PCBNON | n.a | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 273 | -0.003 | 0 | 0.997 | 1.164 | -18.2 | 0 |

**Notes:**
b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE LXXXV**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, ALL DATA, TEMPERATURE IS GREATER THAN ZERO

| Homolog | n | M | t | p | 95% CI | b | $r^2$ |
|---------|---|---|---|---|--------|---|-------|
| PCBDI | 1311 | **-2.46E+00** | 12.82 | <0.0001 | 0.376704 | -11.11 | 0.112 |
| PCBTRI | 1311 | **-2.605** | 10.81 | <0.0001 | 0.47088 | -10.7 | 0.176 |
| PCBTET | 1311 | -0.43 | 2.7 | 0.0301 | 0.3924 | -18.46 | 0.0036 |
| PCBPNT | 1311 | **-3.074** | 14.62 | <0.0001 | 0.41202 | -9.26 | 0.141 |
| PCBHEX | 1311 | **-0.285** | 5.85 | <0.0001 | 0.096138 | -19.43 | 0.026 |
| PCBHEPT | 1311 | **-0.285** | 5.85 | <0.0001 | 0.096138 | -19.52 | 0.034 |
| PCBOCT | 1311 | **-0.264** | 18.24 | <0.0001 | 0.02943 | -19.69 | 0.21 |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 1311 | **-2.451** | 14.18 | <0.0001 | 0.33354 | -9.46 | 0.133 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected
during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject $H_0$, Slope Is Equal To 0 at $\alpha = 0.05$

Tables LXXXVI through LXXXIX summarize linear regression analyses results for the detects only data by Site ID. Once again, the data for 23013 are noticeably different (very few detects and lower slopes) than those for the other 3 sampling stations. The vapor pressure relationship was also evaluated for the detects only data by average temperature range (<0, 0-15, and >15 °C) in Tables XC and XCI. It appears that most of the temperature effect (in terms of greater magnitude of slopes and n, the no. of samples with detects) are the greatest for the average temperature of >15 °C. The effect of using minimum temperature during a sampling period (not shown) was reviewed, and it basically gave the same results. The effect of wind sector score grouping (<0.1, 0.1-0.2, >0.2) was investigated, and the results are summarized in Tables XCII through XCIV. Finally, the detected data was analyzed based on average temperature (≥0 °C) and wind sector score grouping (<0.1, 0.1-0.2, >0.2) together, in Tables XCV through XCVII. Note that there was no effect on wind sector score or temperature for average temperatures <0°C.

The slopes for the CC plots for the detects only and all data are plotted by homolog group in Figures 67 and 68.

The enthalpies of vaporization ($\Delta H_{vap}$) were calculated from the relationship $\Delta H_{vap} = -M*R$ for the detects only data and tabulated in Table XCVIII. Literature values from Falconer and Bidleman [95] were also included in Table XCVIII for comparison purposes. The values calculated for this study were lower, in some cases, much lower.

## TABLE LXXXVI

### LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER TEMPERATURE, DETECTS ONLY, SITE IDENTIFICATION NUMBER 23007

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---------|---|---|-----|---|--------|---|-------|
| PCBDI | 46 | **-5.57E+00** | 2.47 | 0.0174 | 4.555 | -8.747 | 0.122 |
| PCBTRI | 40 | **-5.22** | 3.23 | 0.0025 | 3.262 | 0.557 | 0.216 |
| PCBTET | 40 | **-5.513** | 3.42 | 0.0015 | 3.262 | 9.35 | 0.235 |
| PCBPNT | 43 | 1.564 | 0.84 | 0.4081 | 3.779 | -23.43 | 0.017 |
| PCBHEX | 2 | -0.285 | n.a. | n.a. | n.a. | -17.14 | 1 |
| PCBHEPT | 1 | | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 98 | **-2.055** | 2.52 | 0.0134 | 1.581 | -10.214 | 0.062 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE LXXXVII**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, SITE IDENTIFICATION NUMBER 23009

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---------|-----|----------|------|--------|--------|---------|--------|
| PCBDI | 31 | **-6.21E+00** | 2.8 | 0.0091 | 4.766 | 3.655 | 0.212 |
| PCBTRI | 44 | **-3.47** | 2.8 | 0.008 | 2.516 | -5.394 | 0.156 |
| PCBTET | 44 | **-3.756** | 3.02 | 0.0043 | 2.516 | 3.38 | 0.178 |
| PCBPNT | 33 | -0.72 | 0.68 | 0.5 | 2.177 | -15.56 | 0.0145 |
| PCBHEX | 2 | -1.676 | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 87 | -1.484 | -1.7 | 0.0936 | 1.741 | -12.156 | 0.033 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected
during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject H$_0$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE LXXXVIII**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, SITE IDENTIFICATION NUMBER 23011

| Homolog | n | M | t | p | 95% CI | b | r² |
|---------|---|---|---|---|--------|---|----|
| PCBDI | 20 | **-1.28E+01** | 2.9 | 0.0095 | 9.131 | 25.93 | 0.319 |
| PCBTRI | 38 | **-3.491** | 2.81 | 0.0079 | 2.532 | -5.49 | 0.18 |
| PCBTET | 38 | **-3.775** | 3.04 | 0.0044 | 2.532 | 3.28 | 0.205 |
| PCBPNT | 29 | -1.379 | 1.26 | 0.2175 | 2.274 | -13.27 | 0.056 |
| PCBHEX | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 79 | **1.532** | 1.95 | 0.0553 | 1.566 | -12.13 | 0.047 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected
during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject H$_o$, Slope Is Equal To 0 at $\alpha$ = 0.05

**TABLE LXXXIX**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, SITE IDENTIFICATION NUMBER 23013

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---------|---|------|------|--------|---------|--------|--------|
| PCBDI | 6 | **-4.06E+00** | 1.74 | 0.158 | 5.726 | -31.64 | 0.43 |
| PCBTRI | 3 | -6.32 | 0.14 | 0.911 | 143.349 | -39.24 | 0.02 |
| PCBTET | 3 | -6.026 | 0.13 | 0.9153 | 143.349 | -30.44 | 0.018 |
| PCBPNT | 32 | -0.29 | 0.23 | 0.8194 | 2.553 | -17 | 0.0018 |
| PCBHEX | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 49 | 0.109 | 0.15 | 0.885 | 1.51 | -18.19 | 0.0 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE XC**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, AVERAGE TEMPERATURE IS GREATER THAN
ZERO AND LESS THAN OR EQUAL TO FIFTEEN DEGREES CELSIUS

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---------|---|---|-----|---|--------|---|-------|
| PCBDI | 4 | **-3.60E+00** | 6.15 | 0.0255 | 1.64 | -5.41 | 0.95 |
| PCBTRI | 18 | **-3.476** | 1.85 | 0.0829 | 3.99 | -16.7 | 0.013 |
| PCBTET | 18 | **-3.759** | 1.88 | 0.063 | 3.99 | 3.3 | 0.2 |
| PCBPNT | 4 | -5.26 | 0.23 | 0.37 | 62.46 | -36.9 | 0.026 |
| PCBHEX | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 3 | 0 | n.a. | n.a. | n.a. | n.a. | 0 |
| PCBOCT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 46 | **-1.068** | 0.59 | 0.56 | 3.68 | -13.8 | 0.008 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE XCI**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, AVERAGE TEMPERATURE IS GREATER THAN
FIFTEEN DEGREES CELSIUS

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---------|------|----------|-------|---------|--------|-------|-------|
| PCBDI   | 99   | -7.25E+00 | 4.08 | <0.0001 | 3.52   | 7.03  | 0.146 |
| PCBTRI  | 105  | -6.415   | 3.41  | 0.0009  | 3.73   | 4.55  | 0.102 |
| PCBTET  | 105  | -6.709   | 3.57  | 0.0006  | 3.73   | 13.35 | 0.11  |
| PCBPNT  | 124  | 2.611    | 1.19  | 0.23    | 4.36   | -26.9 | 0.011 |
| PCBHEX  | 3    | -82.9    | 13.54 | 0.0469  | 26.33  | 264   | 0.99  |
| PCBHEPT | 0    | n.a.     | n.a.  | n.a.    | n.a.   | n.a.  | n.a.  |
| PCBOCT  | 0    | n.a.     | n.a.  | n.a.    | n.a.   | n.a.  | n.a.  |
| PCBNON  | n.a. | n.a.     | n.a.  | n.a.    | n.a.   | n.a.  | n.a.  |
| PCBDEC  | n.a. | n.a.     | n.a.  | n.a.    | n.a.   | n.a.  | n.a.  |
| PCBTOT  | 223  | -6.911   | 7.68  | <0.0001 | 1.79   | 5.77  | 0.08  |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE XCII**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER
TEMPERATURE, DETECTS ONLY, WIND SECTOR SCORE LESS THAN 0.1

| Homolog | n | M | t | p | 95% CI | b | r² |
|---|---|---|---|---|---|---|---|
| PCBDI | 27 | **6.48E+00** | 2.98 | 0.0 0630 | 4.46 | 4.31 | 0.262 |
| PCBTRI | 14 | -4.802 | 1.25 | 0.235 | 8.24 | -0.867 | 0.115 |
| PCBTET | 14 | -5.095 | 1.33 | 0.2 | 8.24 | 7.93 | 0.128 |
| PCBPNT | 67 | -0.377 | 0.38 | 0.71 | 2.00 | -16.7 | 0.02 |
| PCBHEX | 3 | 1.88 | 0.9 | 0.542 | 6.84 | -24.7 | 0.43 |
| PCBHEPT | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 120 | -0.109 | 0.56 | 0.85 | 1.11 | -17.3 | 0.0 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject H$_0$, Slope Is Equal To 0 at $\alpha$ = 0.05

**TABLE XCIII**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS
ONE OVER TEMPERATURE, DETECTS ONLY,
SCORE IS 0.1, GREATER THAN OR EQUAL TO 0.1, AND LESS THAN 0.2

| Homolog | n | M | t | p | 95% CI | b | $r^2$ |
|---------|-----|-----------|------|-------|--------|--------|-------|
| PCBDI | 14 | **-9.08E+00** | 1.88 | 0.085 | 10.36 | 13.3 | 0.227 |
| PCBTRI | 16 | **-8.84** | 1.5 | 0.15 | 12.38 | 12.6 | 0.14 |
| PCBTET | 16 | **-9.131** | 1.56 | 0.14 | 12.30 | 21.4 | 0.148 |
| PCBPNT | 22 | -1.61 | 1.23 | 0.23 | 2.71 | -12.42 | 0.07 |
| PCBHEX | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 47 | **-1.388** | 1.4 | 0.168 | 2.00 | -12.7 | 0.04 |

<u>Notes:</u>

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

t = calculated value for t

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE XCIV**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS
ONE OVER TEMPERATURE, DETECTS ONLY,
SCORE IS 0.1 AND GREATER THAN OR EQUAL TO 0.2

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---|---|---|---|---|---|---|---|
| PCBDI | 62 | **-5.42E+00** | 2.91 | 0.005 | 3.20 | 0.87 | 0.124 |
| PCBTRI | 95 | **-3.829** | 5.07 | <0.0001 | 1.51 | -4.2 | 0.217 |
| PCBTET | 95 | **-4.115** | 5.45 | <0.0001 | 1.49 | 4.57 | 0.242 |
| PCBPNT | 48 | 0.626 | 0.53 | 0.59 | 3.66 | -20.3 | 0.006 |
| PCBHEX | 3 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 146 | **-2.6** | 3.81 | 0.0002 | 1.35 | -8.24 | 0.092 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_o$, Slope Is Equal To 0 at $\alpha = 0.05$

## TABLE XCV

### LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS ONE OVER TEMPERATURE, DETECTS ONLY, TEMPERATURE IS GREATER THAN ZERO, SCORE IS LESS THAN 0.1

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---|---|---|---|---|---|---|---|
| PCBDI | 27 | **-6.48E+00** | 2.98 | <0.0001 | 4.45 | 4.31 | 0.262 |
| PCBTRI | 14 | **-4.802** | 1.25 | 0.23 | 8.24 | -0.87 | 0.115 |
| PCBTET | 14 | **-5.095** | 1.33 | 0.21 | 8.26 | 7.9 | 0.127 |
| PCBPNT | 65 | -0.35 | 0.23 | 0.82 | 3.08 | -16.8 | 0.0 |
| PCBHEX | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 98 | **0.22** | 0.19 | 0.85 | 2.30 | -18.4 | 0.0 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE XCVI**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS
ONE OVER TEMPERATURE, DETECTS ONLY,
TEMPERATURE IS GREATER THAN ZERO, WIND SECTOR SCORE IS 0.1 TO 0.2

| Homolog | n | M | $t$ | p | 95% CI | b | $r^2$ |
|---------|-----|-----------|------|--------|--------|--------|-------|
| PCBDI | 14 | **-9.08E+00** | 1.88 | 0.08 | 10.30 | 13.3 | 0.227 |
| PCBTRI | 16 | **-8.836** | 1.51 | 0.15 | 12.38 | 12.6 | 0.14 |
| PCBTET | 16 | **-9.131** | 1.56 | 0.14 | 12.38 | 21.4 | 0.148 |
| PCBPNT | 18 | **-6.08** | 0.76 | 0.45 | 16.80 | -38.48 | 0.04 |
| PCBHEX | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 40 | **-4.952** | 1.97 | 0.0561 | 5.13 | -0.55 | 0.09 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$

**TABLE XCVII**

LINEAR REGRESSION RESULTS OF PARTIAL VAPOR VERSUS
ONE OVER TEMPERATURE, ALL DATA,
TEMPERATURE IS GREATER THAN ZERO, SCORE IS GREATER THAN 0.2

| Homolog | n | M | t | p | 95% CI | b | $r^2$ |
|---------|-----|----------|------|---------|--------|-------|-------|
| PCBDI | 62 | -5.42E+00 | 2.91 | 0.005 | 3.72 | 0.8 | 0.124 |
| PCBTRI | 93 | -4.208 | 4.81 | <0.0001 | 1.75 | -2.91 | 0.202 |
| PCBTET | 93 | -4.495 | 5.13 | <0.0001 | 1.75 | 527 | 0.225 |
| PCBPNT | 45 | -2.8 | 1.41 | 0.166 | 4.02 | -27.7 | 0.044 |
| PCBHEX | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBHEPT | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBOCT | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBNON | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBDEC | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| PCBTOT | 131 | -3.828 | 9.95 | <0.0001 | 0.77 | -4.4 | 0.201 |

**Notes:**

b = slope intercept

M = Slope (1000's)

n = number of observations

n.a. denotes 'Not Applicable' or 'Not Analyzed' (nona- and deca- PCB were not detected during this project)

PCBTOT = Ln (Sum Of Vapor Pressures)

$t$ = calculated value for $t$

**Bolded Values** are statistically significant, i.e., Reject $H_O$, Slope Is Equal To 0 at $\alpha = 0.05$
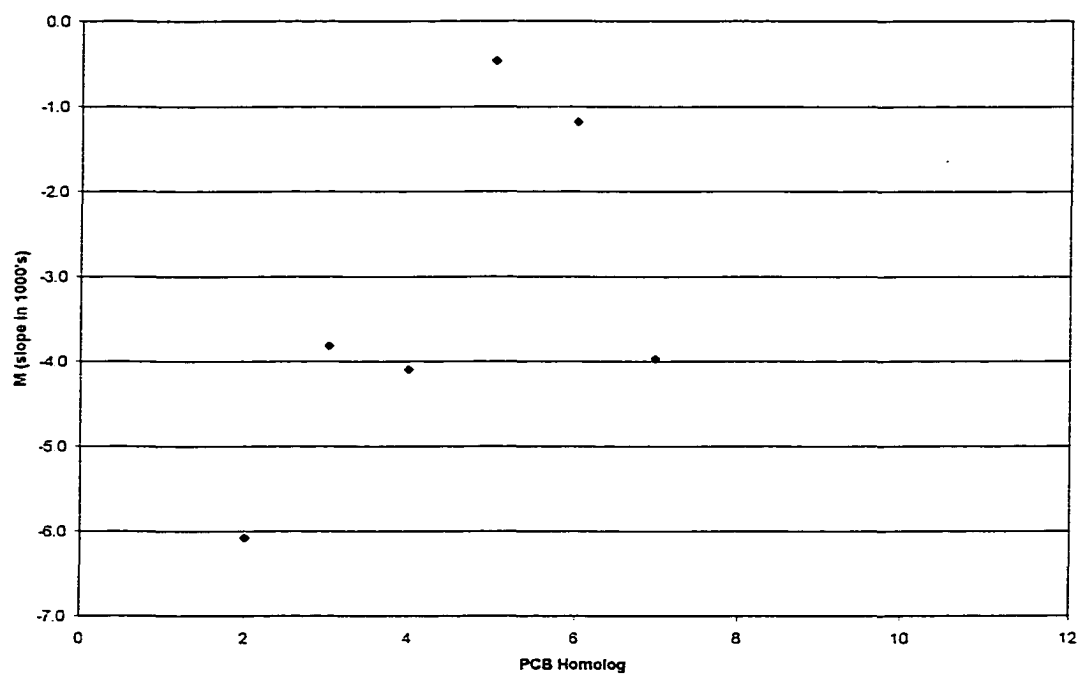
Figure 67.    Dependence of the slope (M) from Clausius-Clapeyron plot for detects only data.
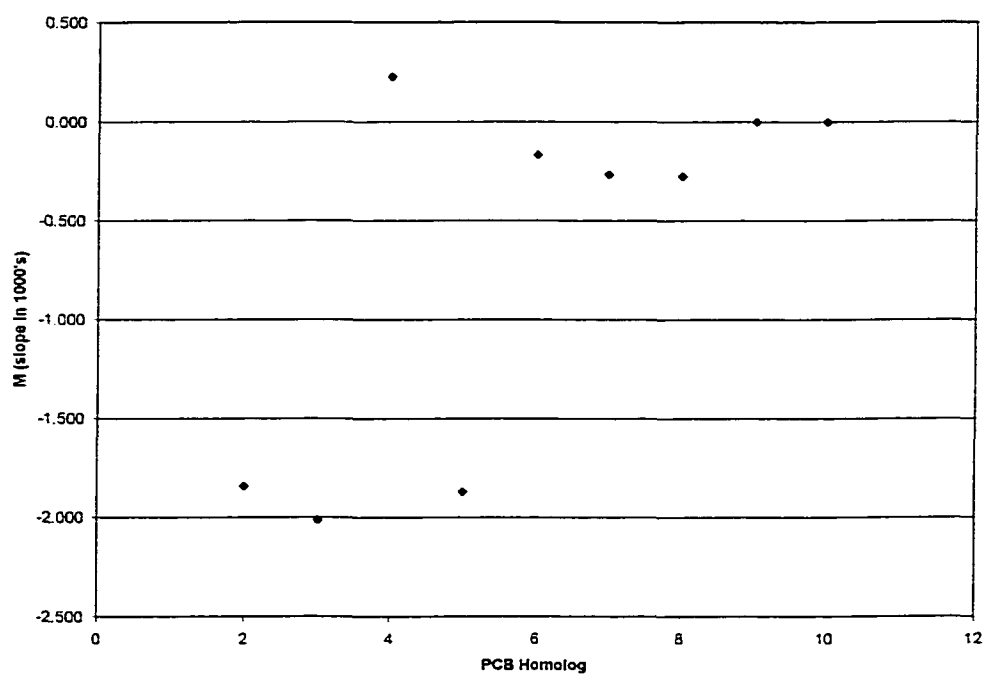
Figure 68.    Dependence of slope (M) from Clausius-Clapeyron plot, for all data.

**TABLE XCVIII**

CALCULATED ENTHALPY OF VAPORIZATION ($\Delta H_{VAP}$) FOR DETECTS,
VARIOUS SCENARIOS COMPARED TO VALUES IN LITERATURE[a]

| Homolog | All Data | Detects Only | Ave. Temp. >0 | Ave. Temp. >15 | Ave. Temp. >15, Score >0.3 | Lower Value for Homolog[a] | Middle of Range for Homolog[a] | Upper Value for Homolog[a] |
|---|---|---|---|---|---|---|---|---|
| n = | 1584 | | | | | | | |
| PCBDI | 15.3 | 50.5 | 50.5 | 60.3 | 45.0 | 69.7 | 72.1 | 74.4 |
| PCBTRI | 16.7 | 31.7 | 34.8 | 53.3 | 35.0 | 73.5 | 77.3 | 81.2 |
| PCBTET | 1.9 | 34.1 | 37.2 | 55.8 | 37.4 | 71.8 | 79.9 | 88.0 |
| PCBPNT | 15.5 | 3.9 | 11.3 | 21.7 | 23.3 | 77.1 | 86.0 | 94.9 |
| PCBHEX | 1.4 | 9.8 | 20.4 | | -- | 82.4 | 92.1 | 101.7 |
| PCBHEPT | 2.2 | 33.0 | 0.0 | -- | -- | 87.7 | 94.6 | 101.5 |
| PCBOCT | 0.0 | -- | -- | -- | -- | 92.9 | 98.2 | 103.4 |
| PCBNON | 0.0 | -- | -- | -- | -- | 98.2 | 99.1 | 100.1 |
| PCBDEC | 0.0 | -- | -- | -- | -- | 103.4 | 103.4 | 103.4 |
| PCBTOT | 12.8 | 11.5 | 17.7 | 57.5 | 31.8 | 66.3[b] | 84.9[b] | 103.4[b] |

**Notes:**

[a]   Data Summarized from Falconer and Bidleman [95]

[b]   Maximum and Minimum Values for PCB homolog group

### 4.5.3.2 Conclusions on Temperature Effects

For the Smithville air monitoring data, the temperature dependence for a number of PCB homologs and PCBTOT were highly significant (p <0.001) for both *detects only* and *all data*. The data that show the strongest temperature relationship are for detects only, average temperature >15°C, and wind sector score >0.2 (Table XCVII). The slope for PCBTOT for detects only data and average temperature ≥0°C range from −1400 K (Table XCIII) to -7000 K (Table XCI), which is in the range reported by Wania, et al. [102] in their review. Wania noted that for the North America data "there seemed to be a clear decline in slope m, with increasing distance from suspected PCB sources." On this basis, even higher slopes than were observed here would have been expected. It is likely that the reason the slopes were not higher is multifactorial, but most certainly includes factors such as amount of time downwind and/or impacted from the site, wind speed (and other meteorological factors), and site activities (such as source strength). Wind speed is discussed further in Section 4.6 and site activities are discussed in Section 4.7.

A number of researchers have noted that the temperature dependence of the CC plots for PCB and some other SVOCs disappeared (or became non-linear) at lower temperatures. The exact temperature at which the temperature dependence disappeared was chemical dependent. When the Smithville $P_{vap}$ data was stratified by temperature (ave-tempC) <0°C (~3.66 on the 1000*1/T scale), the data showed no temperature dependence. The temperature dependence cutoff of approximately 0°C has been observed previously for PCB compounds in Canadian data. In one study, Hoff, et al. observed that while the concentrations for PCB and other SVOCs increased with temperature during the warmer

months, this temperature dependence disappeared at lower temperatures (typical of winter months in Ontario). This resulted in nonlinearity in the CC plots. For PCB-52, they found that the temperature was linear and disappeared by approximately 5°C. These types of plots are referred to as "hockey stick diagrams" due to the similarity in appearance to the shape of a hockey stick. In another paper, Hoff, et al. [105] has proposed that when the slopes of the CC plot mimics the Pvap or Hvap slopes, one can assume "local volatilization and sources" (where local is in the range of a few hundred km or less) are important.

The trend in slope of the CC plot with degree of chlorination was also examined. In three studies referenced by Wania [102], the magnitude of calculated slopes (in absolute value) from CC plots for various PCB homologs became increasingly negative for the **increasing** degree of chlorination by a factor of 1200-2000 K per additional chlorine. However, studies for Egbert, Ontario [56], and other urban areas [76, 268],[264] did not find the same relationship. For the Smithville data, the slope for PCBDI was in the range of that reported for the Norwegian data; however, for the other homologs, the values of the slope actually decreased in magnitude for this data. The reason for this decrease is not clear.

Despite the limitations of the data for the Smithville project (which was never intended to look at gas vs. particle phase issues), a temperature relationship was observed. However, the data does not exactly match other studies. There are a number of possible reasons why this data does not match these studies:

1)    The sampling method used was for total PCBs instead of "particulate" and "vapor" phases. The phase the PCB is in may not have been primarily vapor.

Having information on filter borne vs. sorbent concentrations would have been helpful.

2) Although analysis was originally carried out for 70+ PCB congeners, the results were only available for homologs. The use of homolog vapor pressure and $H_{vap}$ is less accurate because of the difference in $P_{vap}$ within homolog groups due to the ortho chlorine effect [95].

3) The DL (~<W) and QL (~<T) of 0.2-0.6 ng/m$^3$ is relatively high compared to the ranges in which the linear CC plots have been found. This meant that for <W or <T values, there may have been a relationship, but it just could not be seen. For the higher homologs, the DL may have been too high to provide reliable data for calculating the slope. The homologs above penta were not detected very often in the Smithville data and the DL is higher than most results that have been seen reported for these homolog groups.

4) Non-equilibrium behavior.

5) Changes in source strength from other than the incinerator could have been an issue. Data presented in Sections 4.7 and 4.8 will show that the incinerator emissions were reasonably constant and not related to temperature.

6) The effect of relative humidity (RH) was not considered. Hornbuckle and Eisenreich [68] have shown that concentrations of PCB and other SVOCs are strongly correlated with temperature and RH. Hippelein and Mclachlan [269] have also shown that RH has an effect.

7) There may have been high levels of particulates present, into which vapor phase is then being partitioned. The TSP concentrations were higher in the warmer months and had an $r^2$ value of 0.25 vs. temperature.

8) Differences in the relative importance of different deposition mechanisms. For example, the stack gas was supersaturated in moisture and one could detect it "raining" when it passed above. Wet deposition could have been a much more significant process here than at sites with low wet deposition rates.

## 4.6 Polychlorinated Biphenyl Concentrations and Wind Speed

Wania [102] and Honrath [270] have shown that wind speed appears to affect the relationship of temperature with PCB concentrations. In this section 4.6, the effect of wind speed on PCB concentration is examined for the Smithville data.

The PCBTOT concentrations and average wind speed (m/s) for the Smithville data set are plotted on the same graph in Figure 69. Although there is a considerable amount of scatter in the data, there appears to be an inverse relationship, with samples obtained during periods of lower wind speeds having higher PCBTOT concentrations. To reduce the effect of data scatter, the monthly mean PCBTOT concentrations and monthly mean average wind speeds are plotted on the same graph in Figure 70. This Figure 70 suggests that periods with lower mean wind speeds have higher mean PCB concentrations. As mentioned previously, the monthly mean PCBTOT concentrations were higher during 1991 than in 1992. The monthly mean PCBTOT concentrations and monthly mean average wind speeds are plotted against year and month in Figure 71. As seen in Figure 71, the plots for both years and the

monthly mean wind speeds are very close to each other. Therefore, it does not appear that wind speed can explain the difference in concentrations between years.
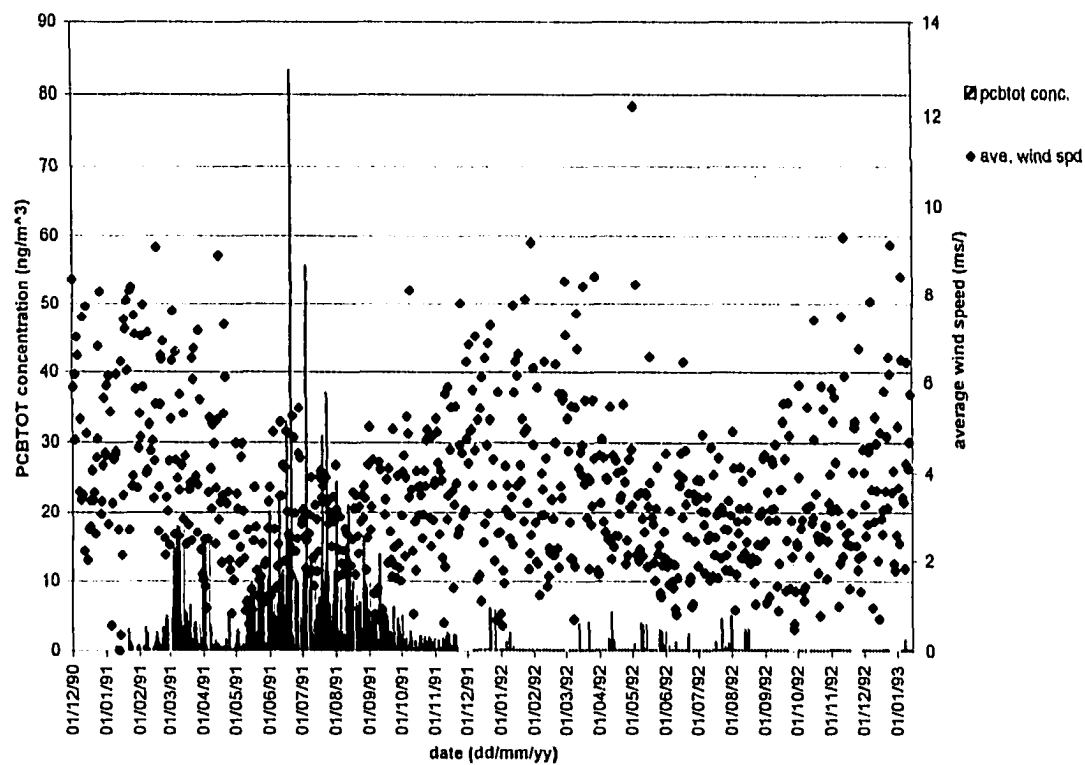
Figure 69.    Total polychlorinated biphenyl concentrations and average wind speed (meters per second) by sample date, all sites.
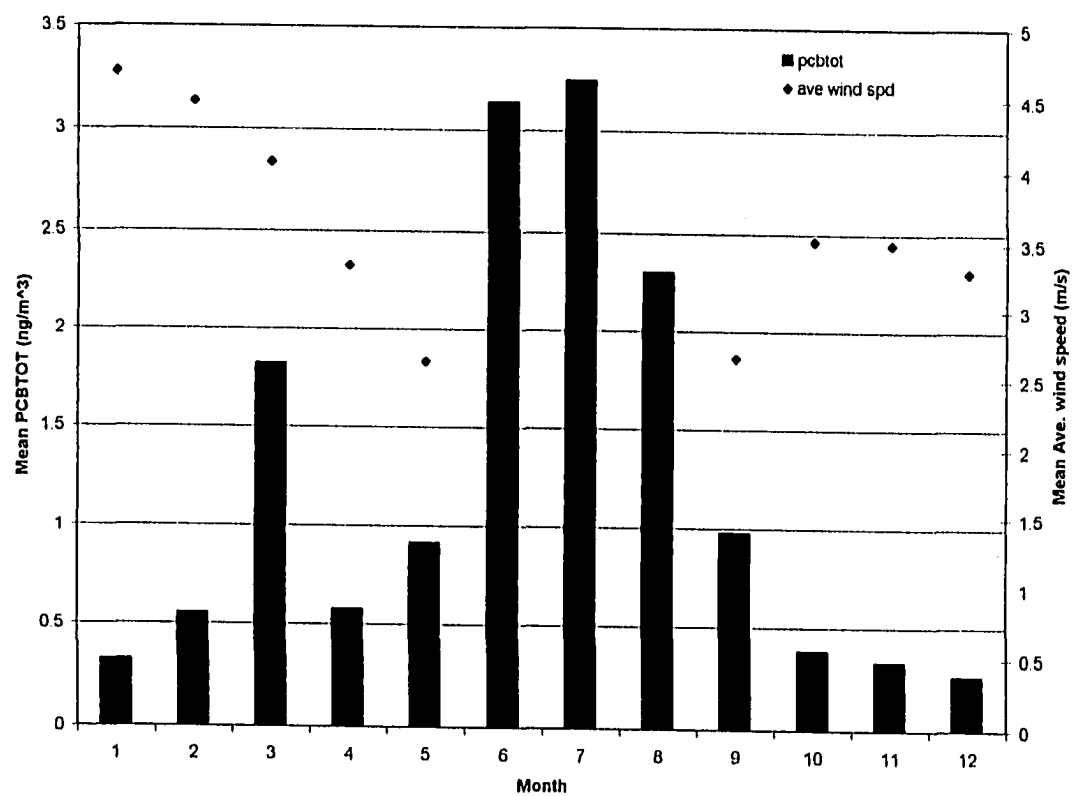
Figure 70.    Mean monthly total polychlorinated biphenyl concentrations (all sites) and average wind speeds.
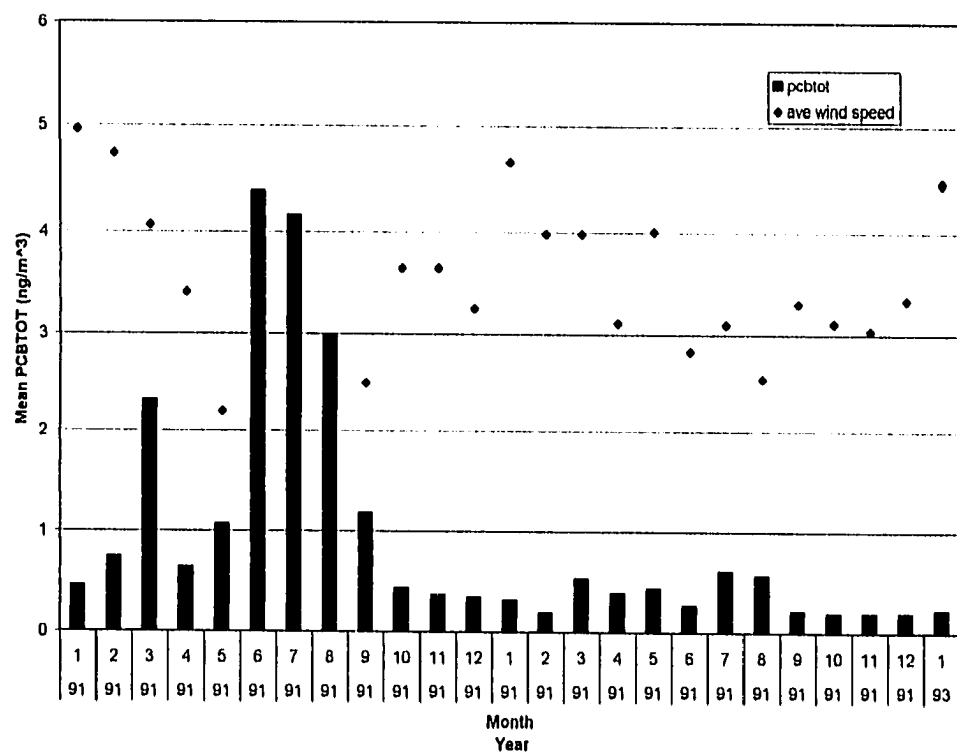
Figure 71.    Mean monthly total polychlorinated biphenyl concentrations (all sites) and average wind speeds concentrations versus wind speed by year and month.

Low wind speeds result in poor atmospheric mixing, or "stable" conditions. In North America, stable conditions are generally more common during the warm summer months. Therefore, caution must be exercised in interpreting data with regards to wind speed because the low wind speeds may simply be associated with higher temperatures. The average temperature ($^{\circ}$C) and the average wind speed (m/s) from the Smithville meteorological data set are plotted on the same graph in Figure 72. A visual inspection of Figure 72 does indicate that the periods of time with low wind speed are associated with higher average temperatures. When the monthly mean wind speed vs. monthly mean average temperature is analyzed by linear regression (Figure 73), there is a strong linear relationship with $r^2$=0.70.

The CC relationship of vapor pressure vs. inverse temperature, as a function of wind speed, was investigated for detects only and for all data. The results from the statistical analyses are summarized in Table XCIX (for detects only) and Table C (for all data). Wind speed groupings used followed those of Wania, et al. [102] in order to allow for comparison of data. Selected data from Wania, et al., for PCB samples obtained in Norway for 1992-95 at varying speeds are summarized in Table CI.

The data in Tables XCIX and C show that, in general, the slopes for the CC plots and mean PCB homolog concentrations are highest during periods of relatively still winds (<3 m/s). As wind speed increases, the PCB concentrations and slopes of the CC plot decrease. Only a small fraction (84/1584) of samples were taken during periods of very high wind speeds (>9m/s). It is worth noting that no detections of PCB occurred during the periods of very high wind speeds.

While the preliminary review of the Smithville data does tend to indicate a wind speed effect, when the mean average temperature is compared to the mean wind speed for each wind speed grouping in Table CII, it can be seen that the wind speed appears to be a linear function of temperature, with an $r^2$ value of 0.8. Therefore, the wind speed effect in this case is most likely related to temperature.

Wania, et al., concluded that for the data shown in Table CI, the temperature dependence of Ln ($P_{vap}$) for PCBs changes with wind speed. The data contained in Table CI are not clearly identified in terms of the PCB compound (i.e., are they congeners, homologs, totals?). However, the general trends seen in Table CI are also observed for the Smithville data in Tables XCIX and C. If the Norway locations had meteorological behavior similar to Smithville, it is possible that another explanation could be that wind speed was a surrogate for temperature. Unfortunately, the wind speed and temperature information were not presented in the paper by Wania, et al., so it cannot be determined whether or not this explanation is correct.
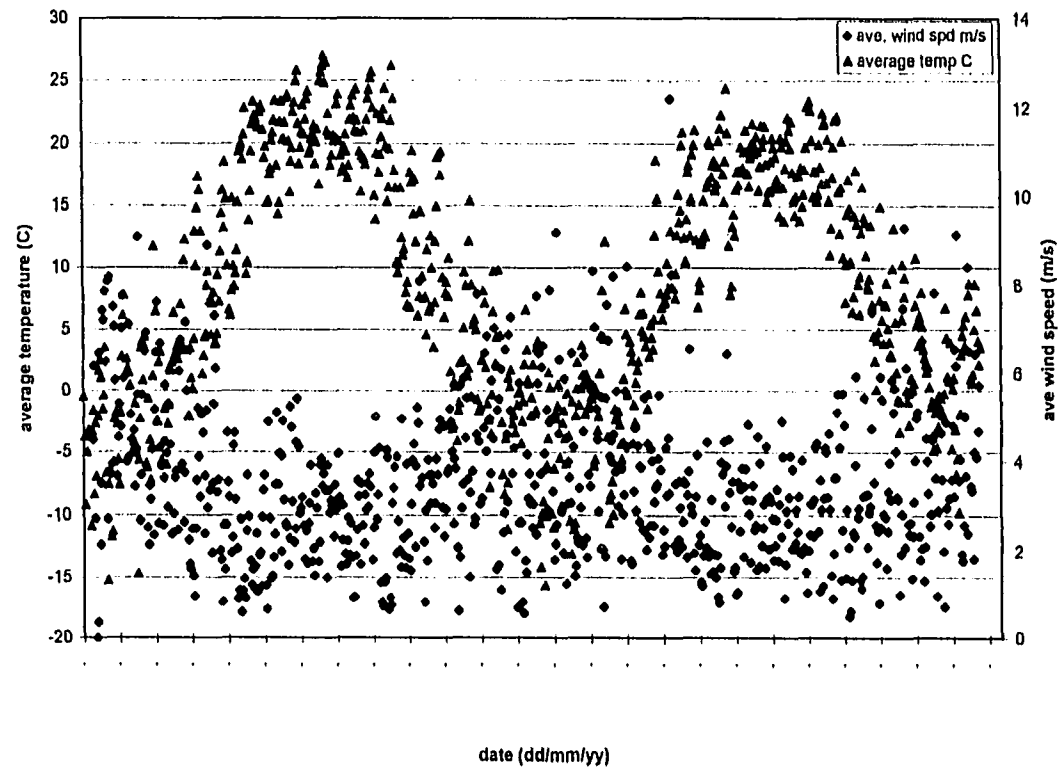
Figure 72.    Average temperature and wind speed by date.
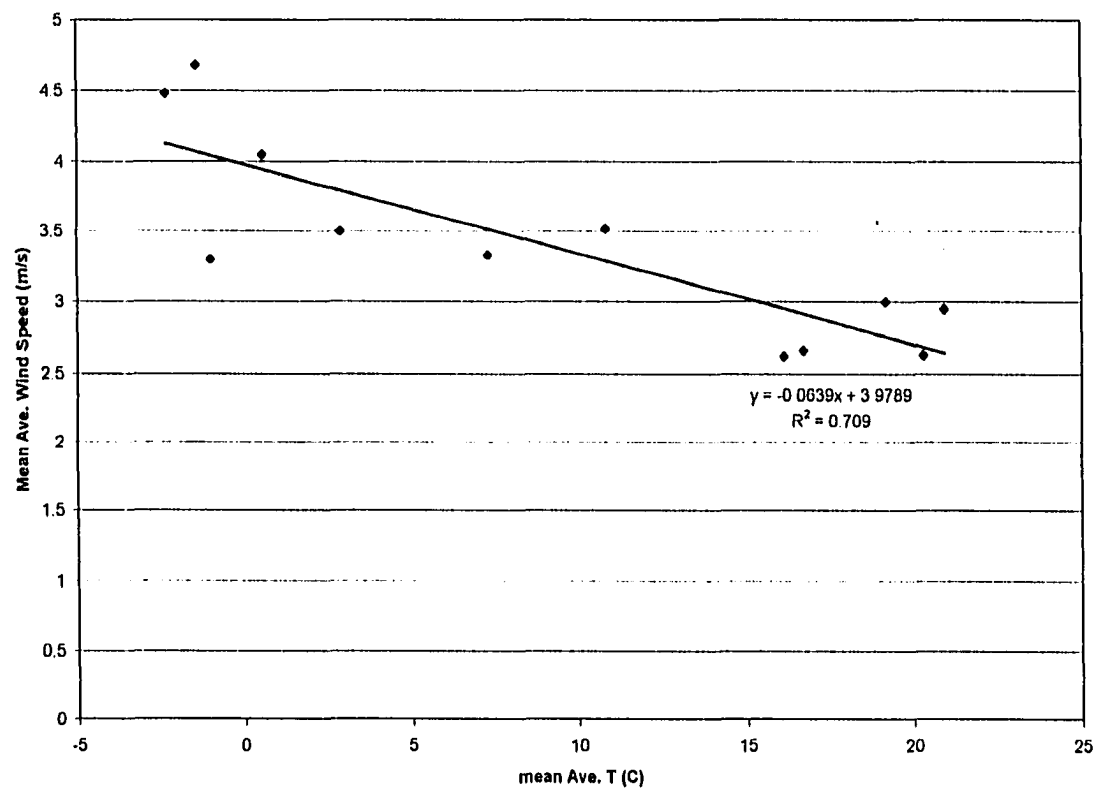
Figure 73.    Mean wind speed versus mean average temperature, all sites by month.

# TABLE XCIX

## TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| DETECTS ONLY | Mean PCBTOT conc. (ng/m$^3$) | n | M | std. error | t | p | 95% CI | b | r$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **PCBDI** | | | | | | | | | |
| all data | 2.7 | 103 | -6.07E+00 | 1.41E+00 | 4.3 | 0.0001 | 2.80 | 3.057 | 0.146 |
| ave. wind speed <3 m/s | 2.5 | 58 | -6.533 | 1.98 | 3.29 | 0.0017 | 3.98 | 4.6 | 0.162 |
| ave. wind speed 3-6 m/s | 3 | 45 | -5.486 | 2.1 | 2.61 | 0.012 | 4.24 | 1.12 | 0.137 |
| ave. wind speed >6 & ≤9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| ave. wind speed >9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| **PCBTRI** | | | | | | | | | |
| all data | 4.1 | 125 | -3.813 | 0.71 | 5.34 | 0.0001 | 1.42 | -4.277 | 0.188 |
| ave. wind speed <3 m/s | 3.8 | 65 | -4.363 | 1.31 | 3.32 | 0.0015 | 2.62 | -2.45 | 0.149 |
| ave. wind speed 3-6 m/s | 4.4 | 58 | -3.525 | 0.93 | 3.77 | 0.0004 | 1.87 | -5.19 | 0.203 |
| ave. wind speed >6 & ≤9 m/s | 1.4 | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| ave. wind speed >9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

TABLE XCIX (Continued)

TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE
GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| DETECTS ONLY | Mean PCBTOT conc. (ng/m³) | n | M | std. error | t | p | 95% CI | b | r² |
|---|---|---|---|---|---|---|---|---|---|
| **PCBTET** | | | | | | | | | |
| all data | 1.3 | 125 | -4.099 | 0.72 | 5.74 | 0.0001 | 1.43 | -4.496 | 0.211 |
| ave. wind speed <3 m/s | 1.1 | 65 | -4.651 | 1.3 | 3.54 | 0.0008 | 2.60 | 6.33 | 0.166 |
| ave. wind speed 3-6 m/s | 1.6 | 58 | -3.81 | 0.93 | 4.08 | 0.0001 | 1.87 | 3.58 | 0.229 |
| ave. wind speed >6 & ≤9 m/s | 0.6 | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| ave. wind speed >9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| **PCBPNT** | | | | | | | | | |
| all data | 2.7 | 137 | -0.469 | 0.63 | 0.74 | 0.4596 | 1.23 | -16.43 | 0.004 |
| ave. wind speed <3 m/s | 3.2 | 82 | -1.277 | 1.1 | 1.15 | 0.2534 | 2.19 | -13.6 | 0.016 |
| ave. wind speed 3-6 m/s | 1.9 | 53 | 0.81 | 0.57 | 1.43 | 0.159 | 1.15 | -20.9 | 0.04 |
| ave. wind speed >6 & ≤9 m/s | 1.3 | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| average wind speed >9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

## TABLE XCIX (Continued)

### TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| DETECTS ONLY | Mean PCBTOT conc. (ng/m$^3$) | n | M | std. error | t | p | 95% CI | b | r$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **PCBHEX** | | | | | | | | | |
| all data | 2.8 | 7 | -1.181 | 1.71 | 0.69 | 0.519 | 4.17 | -13.78 | 0.087 |
| ave. wind speed <3 m/s | 2.7 | 5 | -2.976 | 2.01 | 1.47 | 0.237 | 5.58 | -7.6 | 0.41 |
| ave. wind speed 3-6 m/s | 3 | 2 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| ave. wind speed >6 & ≤9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| average wind speed >9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| **PCBHEPT** | | | | | | | | | |
| all data | 3.2 | 4 | -3.971 | 1.68 | 2.36 | 0.1424 | 5.35 | -3.8 | 0.754 |
| ave. wind speed <3 m/s | 3.8 | 3 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| ave. wind speed 3-6 m/s | 1.4 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| ave. wind speed >6 & ≤9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| average wind speed >9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

TABLE XCIX (Concluded)

TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE
GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| DETECTS ONLY | Mean PCBTOT conc. (ng/m$^3$) | n | M | std. error | t | p | 95% CI | b | r$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **PCBOCT** | | | | | | | | | |
| all data | 1.2 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| average wind speed <3 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| average wind speed 3-6 m/s | 1.2 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| average wind speed >6 & ≤9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| average wind speed >9 m/s | n.a. | 0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| **PCBTOT[a]** | | | | | | | | | |
| all data | 5.4 | 313 | -1.389 | 0.42 | 3.35 | 0.0009 | 0.82 | -12.61 | 0.035 |
| average wind speed <3 m/s | 5.4 | 173 | -1.748 | 0.64 | 2.73 | 0.007 | 1.27 | -11.4 | 0.04 |
| average wind speed 3-6 m/s | 5.6 | 125 | 0.85 | 0.64 | 1.32 | 0.19 | 1.27 | -14.4 | 0.02 |
| average wind speed >6 & ≤9 m/s | 3.4 | 14 | -0.398 | 1.99 | 0.2 | 0.84 | 4.30 | -16.4 | 0.003 |
| average wind speed >9 m/s | 2.6 | 1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

**Note:**

[a] While a total of 366/1584 samples were detected for PCBTOT, not all had a detected homolog

## TABLE C

TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE
FOR ALL DATA GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| ALL DATA | Mean PCBTOT conc. (ng/m³) | n | M | std. error | t | p | 95% CI | b | r² |
|---|---|---|---|---|---|---|---|---|---|
| **PCBDI** | | | | | | | | | |
| all data | 0.4 | 1584 | -1.84E+00 | 1.24E-01 | 14.91 | <0.0001 | 0.243 | -13.263 | 0.123 |
| wind speed <3 m/s | 0.4 | 738 | -1.97 | 0.2 | 9.96 | <0.0001 | 0.397 | -12.8 | 0.119 |
| wind speed 3-6 m/s | 0.4 | 751 | 1.815 | 0.18 | 10.2 | <0.0001 | 0.357 | -13.4 | 0.122 |
| wind speed >6 & ≤9 m/s | 0.2 | 84 | -0.281 | 0.29 | 0.98 | 0.3 | 0.577 | -18.95 | 0.012 |
| wind speed >9 m/s | 0.2 | 11 | -0.277 | 0.001 | 439 | <0.0001 | 0.0013 | -19 | 0.99 |
| **PCBTRI** | | | | | | | | | |
| all data | 0.52 | 1584 | -2.013 | 0.16 | 12.99 | <0.0001 | 0.304 | -12.747 | 0.096 |
| wind speed <3 m/s | 0.54 | 738 | -2.1 | 0.25 | 8.52 | <0.0001 | 0.496 | -12.5 | 0.09 |
| wind speed 3-6 m/s | 0.55 | 751 | -2.021 | 0.23 | 8.98 | <0.0001 | 0.456 | -12.71 | 0.1 |
| wind speed >6 & ≤9 m/s | 0.24 | 84 | -0.706 | 0.47 | 1.49 | 0.14 | 0.935 | -17.5 | 0.03 |
| wind speed >9 m/s | 0.2 | 11 | -0.277 | 0.001 | 439 | <0.0001 | 0.001 | -19.1 | 0.99 |

## TABLE C (Continued)

### TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE FOR ALL DATA GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| ALL DATA | Mean PCBTOT conc. (ng/m$^3$) | n | M | std. error | t | p | 95% CI | b | r$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **PCBTET** | | | | | | | | | |
| all data | 0.5 | 1584 | 0.226 | 0.15 | 1.5 | 0.1329 | 0.295 | -20.72 | 0.001 |
| wind speed <3 m/s | 0.5 | 738 | 0.33 | 0.23 | 1.41 | 0.16 | 0.462 | -21 | 0.003 |
| wind speed 3-6 m/s | 0.43 | 751 | 0.044 | 0.21 | 0.22 | 0.83 | 0.417 | -20.1 | 0.0 |
| wind speed >6 & ≤9 m/s | 0.63 | 84 | -0.505 | 1.2 | 0.42 | 0.68 | 2.388 | -17.9 | 0.002 |
| wind speed >9 m/s | 0.5 | 11 | -2.46 | 2.41 | 1.02 | 0.34 | 5.304 | -10.8 | 0.103 |
| **PCBPNT** | | | | | | | | | |
| all data | 0.46 | 1584 | -1.87 | 0.14 | 13.01 | <0.0001 | 0.283 | -13.43 | 0.097 |
| wind speed <3 m/s | 0.58 | 738 | -2.404 | 0.25 | 9.46 | <0.0001 | 0.496 | -11.5 | 0.109 |
| wind speed 3-6 m/s | 0.36 | 751 | -1.575 | 0.17 | 9.01 | <0.0001 | 0.337 | -14.52 | 0.1 |
| wind speed >6 & ≤9 m/s | 0.29 | 84 | 0.769 | 0.63 | 1.22 | 0.22 | 1.254 | -23 | 0.018 |
| wind speed >9 m/s | 0.25 | 11 | 1.064 | 1.22 | 0 27 | 0.4 | 2.685 | -24 | 0.08 |

## TABLE C (Continued)

### TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE FOR ALL DATA GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| ALL DATA | Mean PCBTOT conc. (ng/m³) | n | M | std. error | t | p | 95% CI | b | r² |
|---|---|---|---|---|---|---|---|---|---|
| **PCBHEX** | | | | | | | | | |
| all data | 0.21 | 1584 | -0.167 | 0.04 | 4.24 | <0.0001 | 0.077 | -19.84 | 0.011 |
| wind speed <3 m/s | 0.22 | 738 | -0.217 | 0.07 | 3.02 | 0.0027 | 0.141 | -19.7 | 0.012 |
| wind speed 3-6 m/s | 0.21 | 751 | -0.17 | 0.04 | 4.05 | <0.0001 | 0.083 | -19.8 | 0.02 |
| wind speed >6 & ≤9 m/s | 0.22 | 84 | 0.481 | 0.3 | 1.55 | 0.13 | 0.597 | -22.2 | 0.03 |
| wind speed >9 m/s | 0.2 | 11 | -0.277 | 0.001 | 440 | <0.0001 | 0.001 | -19.5 | 0.99 |
| **PCBHEPT** | | | | | | | | | |
| all data | 0.21 | 1584 | -0.267 | 0.03 | 8.98 | <0.0001 | 0.058 | -19.58 | 0.049 |
| wind speed <3 m/s | 0.21 | 738 | -0.3 | 0.06 | 4.97 | <0.0001 | 0.119 | -19.5 | 0.03 |
| wind speed 3-6 m/s | 0.2 | 751 | -0.226 | 0.03 | 8.21 | <0.0001 | 0.06 | -19.74 | 0.09 |
| wind speed >6 & ≤9 m/s | 0.2 | 84 | -0.274 | 0.0 | 657 | <0.0001 | 0.001 | -19.6 | 0.999 |
| wind speed >9 m/s | 0.2 | 11 | -0.277 | 0.001 | 439 | <0.0001 | 0.001 | -19.6 | 0.99 |

## TABLE C (Concluded)

### TEMPERATURE DEPENDENCE OF POLYCHLORINATED BIPHENYL HOMOLOG PARTIAL PRESSURE FOR ALL DATA GROUPED ACCORDING TO AVERAGE WIND SPEED DURING SAMPLING PERIOD

| ALL DATA | Mean PCBTOT conc. (ng/m$^3$) | n | M | std. error | t | p | 95% CI | b | r$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| **PCBOCT** | | | | | | | | | |
| all data | 0.2 | 1584 | -0.274 | 0.01 | 29.73 | <0.0001 | 0.018 | -19.66 | 0.359 |
| wind speed <3 m/s | 0.2 | 738 | -0.28 | 0.0 | 1800 | <0.0001 | 0.0 | -19.6 | 0.999 |
| wind speed 3-6 m/s | 0.2 | 751 | -0.27 | 0.02 | 14 | <0.0001 | 0.038 | -19.7 | 0.21 |
| wind speed >6 & ≤9 m/s | 0.2 | 84 | -0.274 | 0.0 | 657 | <0.0001 | 0.001 | -19.65 | 0.99 |
| wind speed >9 m/s | 0.2 | 11 | -0.277 | 0.001 | 439 | <0.0001 | 0.001 | -19.64 | 0.99 |
| **PCBTOT** | | | | | | | | | |
| all data | 1.32 | 1584 | -1.535 | 0.12 | 12.87 | <0.0001 | 0.233 | -12.62 | 0.095 |
| wind speed <3 m/s | 1.5 | 738 | -1.83 | 0.19 | 9.47 | <0.0001 | 0.377 | -11.6 | 0.11 |
| wind speed 3-6 m/s | 1.2 | 751 | -1.383 | 0.17 | 8.4 | <0.0001 | 0.337 | -13.2 | 0.09 |
| wind speed >6 & ≤9 m/s | 0.9 | 84 | -0.16 | 0.6 | 0.3 | 0.79 | 1.194 | -17.6 | 0.001 |
| wind speed >9 m/s | 0.6 | 11 | -0.49 | 0.96 | 0.51 | 0.63 | 2.113 | -16.4 | 0.03 |

## TABLE CI

### TEMPERATURE DEPENDENCE OF PARTIAL PRESSURE OF POLYCHLORINATED BIPHENYL[a]

| | Mean PCB conc.[b] (ng/m$^3$) | n | M | std. error | t | p | 95% CI | b | r$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| all data | 0.115 | 201 | -6.746 | n.s. | n.s. | <0.0001 | n.s. | n.s. | 0.43 |
| wind speed <3 m/s | 0.1311 | 30 | -1.83 | n.s. | n.s. | <0.0001 | n.s. | n.s. | 0.6 |
| wind speed 3-6 m/s | 0.1231 | 94 | -1.383 | n.s. | n.s. | <0.0001 | n.s. | n.s. · | 0.44 |
| wind speed >6 & ≤9 m/s | 0.1096 | 53 | -0.16 | n.s. | n.s. | 0.79 | n.s. | n.s. | 0.4 |
| wind speed >9 m/s | 0.0839 | 23 | -0.49 | n.s. | n.s. | 0.63 | n.s. | n.s. | 0.01 |

**Note:**

[a] Data from Table 4 in Wania, et al.

[b] It is not clear from the paper if this is one congener, several congeners, or total PCB congeners.

n.s. = not specified

## TABLE CII

### MEAN AVERAGE TEMPERATURE OBSERVED FOR EACH WIND SPEED GROUPING

| | Mean ave_tempC | Mean average wind speed (m/s) |
|---|---|---|
| all data | 10.3 | 3.33 |
| wind speed <3 m/s | 11.55 | 2.022 |
| wind speed 3-6 m/s | 10.19 | 4.1 |
| wind speed >6 & ≤9 m/s | 1.53 | 7.1 |
| wind speed >9 m/s | 2.7 | 10.3 |

**4.7    Polychlorinated Biphenyl Concentrations and Site Activities**

In previous sections of this chapter, it was shown that there were large variations in concentrations of PCBTOT observed at the off-site air monitoring stations. It was also shown that the variation in concentration was associated with the wind sector score and ambient air temperature (the wind speed was inversely related to temperature). However, in 1992, the concentrations of PCBTOT observed at the off-site air monitoring stations were quite a bit lower than in 1991, even though the temperature and wind sector scores were similar. This suggests that there are other factors besides just temperature affecting the emissions and/or that the source strength was not constant.

The site activities were an obvious source of PCB emissions and were classified into two types: 1) a point source, i.e., the incinerator stack itself; and 2) fugitive emissions, i.e., non-specific emissions from site activities. Potential fugitive emission sources initially identified included stockpiled contaminated soil, soil excavation activities, feed preparation area, the shredding/shearing operations, and the tank farm building.

**4.7.1    Incinerator Performance**

The incinerator operations were carried out on a 24-hour a day, 7 days per week basis. Normal operations were considered to be "steady state" and were not expected to be affected by changes in weather. In order to evaluate whether or not this was true, the PCBTOT emissions results from the 9 Source (or Stack) Tests were plotted along with the average temperature for the testing period in Figure 74. Figure 74 can be interpreted to support the hypothesis that the incinerator emissions are not related to temperature. The

effect of PCB feed rate on PCB DRE was evaluated in Figure 75. While it appears that higher DRE was achieved with higher feed rates, this is primarily as a result of detection limit limitations for the lower feed rate. The effect of feed rate on PCBTOT emission concentrations was evaluated in Figure 76. Despite a change in feed rate of almost 10 times over the course of the source testing, the PCBTOT emissions were relatively constant. The conclusion from these results is that the incinerator stack emissions were not changing with temperature or feed rate and, therefore, were not the source of the fluctuations in PCB ambient air concentrations observed during summers of 1991 and, to a lesser extent, 1992.
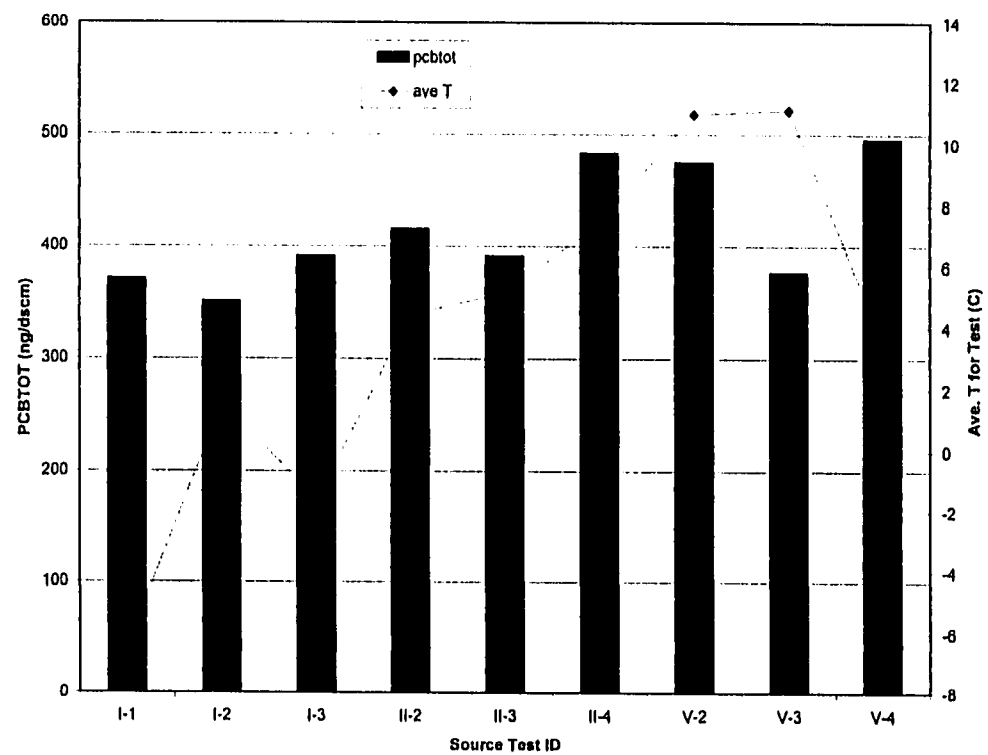
Figure 74.  Concentration of total polychlorinated biphenyls in incinerator stack emissions and average temperature.
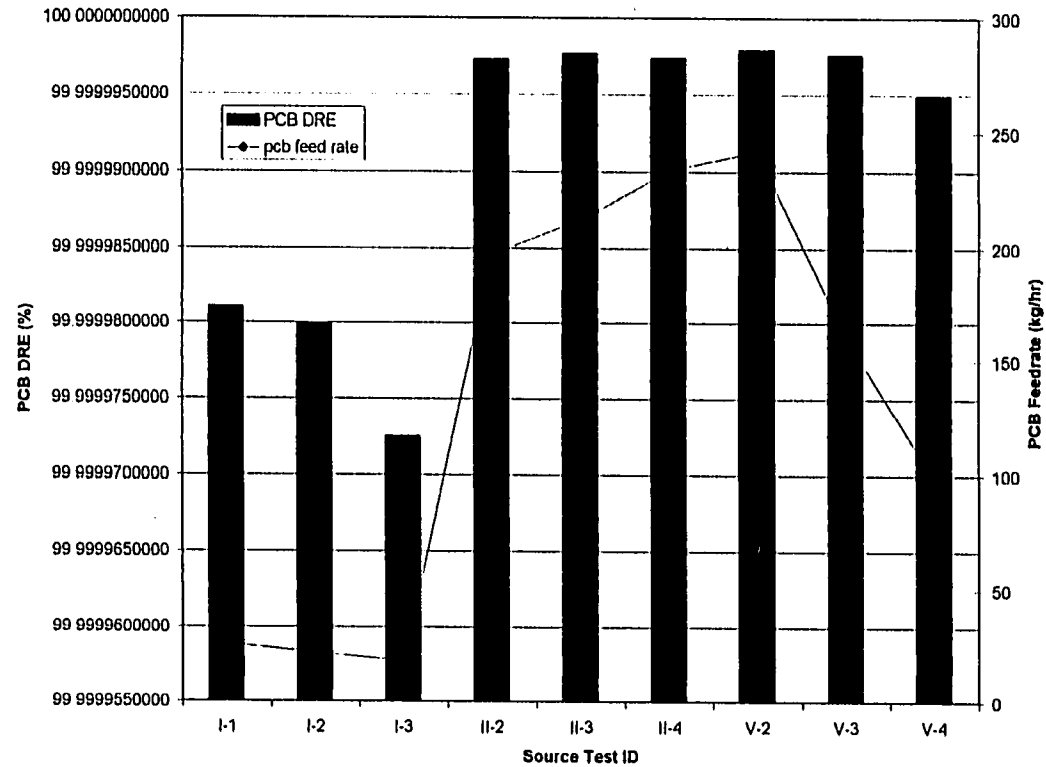
Figure 75. Incinerator destruction removal efficiency for polychlorinated biphenyls and polychlorinated biphenyl feed rate.
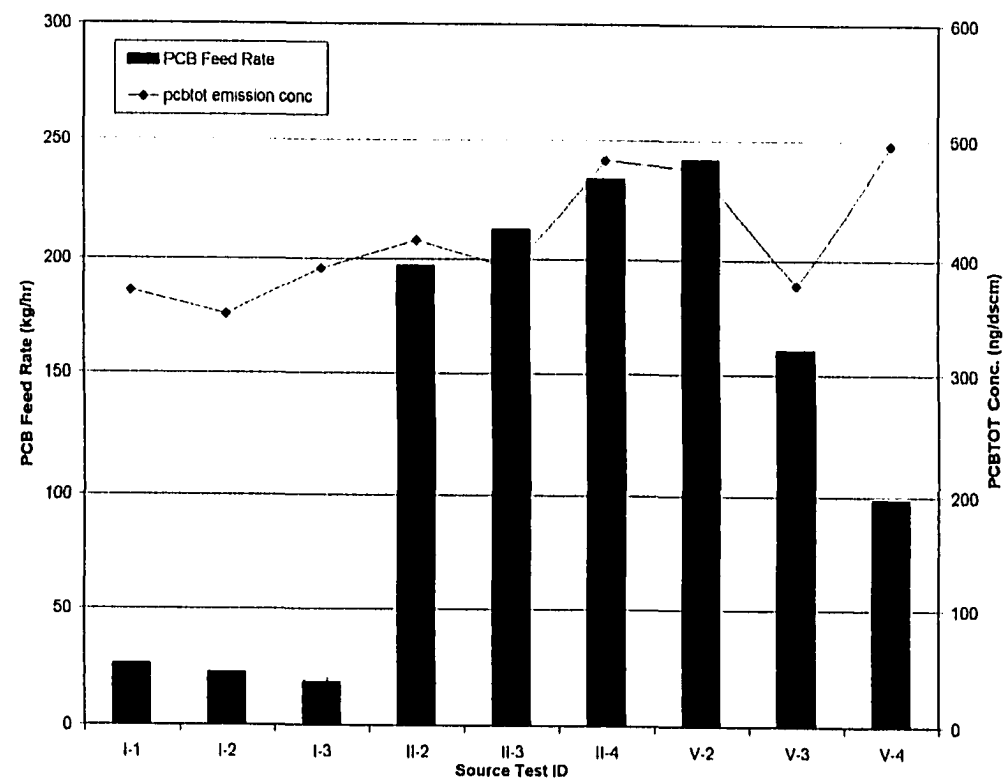
Figure 76.    Polychlorinated biphenyl feed rate and total polychlorinated biphenyl emissions concentration.

## 4.7.2 Site Activity Records

The Phase 3 of the Smithville Cleanup was the first commercial mobile PCB incineration project in Ontario and only the second in Canada. It also was the first time that the O.Reg. 148/86 provisions for incineration had been implemented. As a result of these factors and the notoriety that the Smithville site had gained, there was intense public and regulatory scrutiny of the project. While this scrutiny sometimes made it difficult to move quickly on issues, it also meant that when a decision was reached, there was generally a consensus. One of the unique things that sets this project apart from many other incineration projects is the existence of extensive documentation of site activities. There were regulatory inspectors on-site 24 hours a day. These inspectors filed a Daily Report (DR) to the deputy minister's (DM) office of MOE every morning at 0800 hrs. These Daily Reports exist from February 11, 1991 to December 18, 1992.

The DR contained general information on what material was being incinerated, the feed rates, "unusual" events (such as opening of the thermal relief vent (TRV), high CO, loss of kiln negative pressure, etc.), and any other information that was deemed to be significant, such as source testing, complaints received, etc. From April, 1991 onwards, the DRs contained information on the daily, monthly and project totals for the quantities of soil (tons), liquids (lbs), drums (no.), and vaults (no.). In addition to the DR, Occurrence Reports (OR) were prepared by project staff for events that resulted from deviations from normal work practices, permit conditions, and/or events that may have resulted in a release to the environment.

The existence of the DR and OR documents provided an opportunity to examine site activities to see if there were any effect associated with events or activities on the observed off-site PCBTOT concentrations. Because the DR and OR were all in written form, they were of little use as they existed. Therefore, the first challenge was getting the information in the 373 DRs and the 184 ORs entered into an electronic data format that could be used in conjunction with the air monitoring results. For the DRs, the fields in Table CIII were used to prepare an Excel$^{tm}$ spreadsheet summary. For the ORs, the fields in Table CIV were used to prepare a summary, also in Excel$^{tm}$. The DR and OR spreadsheets were then merged by date with the SAS$^{tm}$ data set for ambient air results and analyzed using SAS$^{tm}$.

There were 4 site activities that were examined: AWFSO events, opening of the TRV, issuance of an OR, and issuance of an OR identified to have potential air impacts (e.g., spill of high level PCB oil on site). The variables that were examined were PCBTOT conc., wind sector score, average wind speed (m/s), and average temperature ($^{o}$C). Summary statistics are provided in Tables CV-CVIII. None of these variables show an effect from a specific event identified as having a potential air impact. This suggests that the emissions sources on the site were either: a) rather long-lived, and not the short-term (<1 hour) type events that were examined by the type of analysis carried out here (however, a recent paper by Blumenstock, et al. [80] indicates that the effect from these short term excursion can be seen in emissions over a period of several hours); or b) if they were short-term emissions, they were of much higher concentration than any of the events examined above.

**TABLE CIII**

FIELDS FOR DAILY REPORT SPREADSHEET

| Date | Year, Month, Day | |
|---|---|---|
| Type of Feed for period (4 Fields, for up to 4 different feed types per DR) | 0 | no feed |
| | 11 | warm, standby (no PCB feed) |
| | 21 | soil, not specified |
| | 22 | soil, low level |
| | 23 | soil, high level (>5000 ppm) |
| | 24 | copper contaminated soil |
| | 25 | soil + concrete |
| | 26 | carbon |
| | 31 | liquids, not specified |
| | 32 | liquids, low level (<0.58% PCB) |
| | 33 | liquids, high level (>0.58% PCB) |
| | 34 | sludge lance liquids, conc. not specified |
| | 35 | waste water |
| | 41 | shredded material, conc. not specified |
| | 42 | 5 gallon pails, low level |
| | 43 | 5 gallon pails, high level |
| | 44 | 5 gallon pails, tyvek |
| | 45 | 5 gallon pails, shredded tire, tyvek |
| | 46 | 5 gallon pails, miscellaneous |
| | 47 | copper |
| | 51 | metals |
| | 61 | drums |
| | 71 | vaults |
| | 80 | ash discharge |
| | 90 | questions |
| | 99 | no information available |
| Daily totals | liquids (lbs.), solids (tons), soils (tons) | |
| Monthly | soil (tons), liquids (lbs.), drums (no.), vaults (no.) | |
| Project to Date | soil (tons), liquids (lbs.), drums (no.), vaults (no.) | |
| TRV event | 0 = no, 1 = yes | |
| AWFSO event(s) | 0 = no, 1 = yes | |
| Occurrence Report(s) | 0 = no, 1 = yes | |
| Source Testing | Summary Information | |
| Complaint received | 0 = no, 1 = yes | |
| Comments fields | 4 fields with summary info | |

**TABLE CIV**

FIELDS FOR OCCURRENCE REPORT SPREADSHEET

| Date | Year, Month, Day |
|---|---|
| Occurrence Report 1 | OR number |
| Possible Air Emission1 | The OR was reviewed to see if there was a potential for air emissions from the occurrence<br>0 = no, 1 = yes |
| Comments1 | Brief description or comment on OR |
| same information as above for 5 additional ORs | .<br>.<br>.<br>. |

## TABLE CV

### SUMMARY STATISTICS FOR VARIABLES FOR DATES,
### WITHOUT AND WITH AUTOMATIC WASTE FEED SHUT-OFF EVENTS

**AWFSO=0 (no events)**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 1498 | 1.3 | 3.9 | 0.2 | 83.2 | 83 | 0.2 | 174 | 11 |
| wind sector score | 1498 | 0.17 | 0.24 | 0 | 1 | 1 | 0.06 | 2 | 1 |
| ave. wind speed (m/s) | 1498 | 3.3 | 1.6 | 0.6 | 12.2 | 11.6 | 3.2 | 2.9 | 1 |
| ave. temperature °C | 1498 | 10.4 | 9.7 | -15.3 | 27 | 42.3 | 11 | -1 | 0 |

**AWFSO=1 (event occurred)**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 86 | 1.6 | 1.9 | 0.2 | 10 | 9.8 | 0.9 | 6 | 2 |
| wind sector score | 86 | 0.19 | 0.26 | 0 | 0.94 | 0.94 | 0.63 | 1 | 2 |
| ave. wind speed (m/s) | 86 | 3.4 | 2 | 0.7 | 7.2 | 6.5 | 3 | -1 | 1 |
| ave. temperature °C | 86 | 0.1 | 10.1 | -7.2 | 24.8 | 32 | 6.5 | -1 | 0 |

# TABLE CVI

SUMMARY STATISTICS FOR VARIABLES FOR DATES WITHOUT AND WITH THERMAL RELIEF VENT EVENTS

**TRV=0 (no events)**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 1291 | 1.4 | 4.1 | 0.2 | 83.2 | 83 | 0.2 | 158 | 10 |
| wind sector score | 1291 | 0.17 | 0.24 | 0 | 1 | 1 | 0.06 | 2 | 2 |
| ave. wind speed (m/s) | 1291 | 3.36 | 1.62 | 0.6 | 12.2 | 11.6 | 3.2 | 3 | 1 |
| ave. temperature °C | 1291 | 10.2 | 9.9 | -15.3 | 27.0 | 42.3 | 10.6 | -1 | 0 |

**TRV=1 (event occurred)**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 293 | 0.9 | 1.8 | 0.2 | 13.8 | 13.6 | 0.2 | 18 | 4 |
| wind sector score | 293 | 0.17 | 0.23 | 0 | 1 | 1 | 0.08 | 2 | 2 |
| ave. wind speed (m/s) | 293 | 3.2 | 1.8 | 0.8 | 9.2 | 8.5 | 2.7 | 1 | 1 |
| ave. temperature °C | 293 | 10.9 | 9 | -1 | 24.4 | 34.4 | 10.2 | -1 | 0 |

# TABLE CVII

## SUMMARY STATISTICS FOR VARIABLES FOR DATES WITHOUT AND WITH OCCURRENCE REPORTS

**Occurrence Report =0 (no OR)**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 1221 | 1.3 | 3.8 | 0.2 | 83.2 | 83 | 0.2 | 202 | 11 |
| wind sector score | 1221 | 0.17 | 0.24 | 0 | 1 | 1 | 0.06 | 2 | 2 |
| ave. wind speed (m/s) | 1221 | 3.2 | 1.6 | 0.6 | 12.2 | 11.6 | 3 | 4 | 1 |
| ave. temperature °C | 1221 | 11.3 | 9.5 | -15.3 | 27.0 | 42.3 | 10.6 | -1 | 0 |

**Occurrence Report=1 (OR was issued)**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 363 | 1.4 | 3.9 | 0.2 | 55.8 | 55.6 | 0.2 | 110 | 9 |
| wind sector score | 363 | 0.18 | 0.24 | 0 | 1 | 1 | 0.06 | 2 | 9 |
| ave. wind speed (m/s) | 363 | 3.9 | 1.6 | 0.6 | 9.1 | 8.5 | 3.7 | 1 | 1 |
| ave. temperature °C | 363 | 7 | 9.9 | -14.7 | 26.5 | 41.2 | 3.6 | -1 | 0 |

# TABLE CVIII

## SUMMARY STATISTICS FOR VARIABLES FOR DATES WITHOUT AND WITH OCCURRENCE REPORTS IDENTIFIED AS HAVING POTENTIAL FOR AIR EMISSIONS

**Dates with No OR**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 1347 | 1.3 | 3.9 | 0.2 | 83.2 | 83 | 0.2 | 176 | 11 |
| wind sector score | 1347 | 0.17 | 0.24 | 0 | 1 | 1 | 0.06 | 2 | 2 |
| ave. wind speed (m/s) | 1347 | 3.3 | 1.7 | 0.6 | 12.2 | 11.6 | 3.1 | 3 | 1 |
| ave. temperature °C | 1347 | 10.8 | 9.7 | -15.3 | 27.0 | 42.3 | 11.5 | -1 | 0 |

**Dates with Air Emission Related OR**

|  | n | Mean | std. dev. | MIN. | MAX. | Range | Median | Kurtosis | Skewness |
|---|---|---|---|---|---|---|---|---|---|
| PCBTOT | 237 | 1.2 | 2.7 | 0.2 | 24.4 | 24.2 | 0.2 | 37 | 6 |
| wind sector score | 237 | 0.18 | 0.24 | 0 | 1 | 1 | 0.06 | 2 | 1 |
| ave. wind speed (m/s) | 237 | 3.7 | 1.5 | 0.6 | 9.1 | 8.5 | 3.6 | 1 | 1 |
| ave. temperature °C | 237 | 5.8 | 9.9 | -14.7 | 26.5 | 41.2 | 2.3 | -1 | 1 |

One of the issues that continued to be puzzling up to this point was the question of why the ambient air PCB concentrations were so much lower in 1992 than in 1991. This occurred even though the temperatures and wind speeds observed in both years were very similar. The on-site activities related to feed preparation and decontamination operations were also very similar in both years. This difference suggests a change in source strength at the site. This issue was examined in more detail by making use of the quantities of materials treated for the project to date that were contained in the DRs. Figure 77 shows the ambient air PCBTOT concentrations and daily PCB soil feed amounts for the course of the project. It is notable that PCB soil feed amounts were very similar in 1992 to 1991. Under the permit conditions, the soil incinerated had concentrations ranging up to a maximum of 20,000 mg/kg. There was no information in the available records on the average concentrations for the PCB soil feed in 1991 compared to 1992. It is worth noting, however, that for the Source Tests that were carried out for soil feed, the concentrations of PCB in the feed had to be augmented with PCB oil.

This suggests that most of the soil on-site had relatively low concentrations of PCB (<500-1000 mg/kg). When the off-site ambient air PCBTOT concentrations and project-to-date PCB soil quantities are shown on the same plot (Figure 78), it can be seen that the amount of PCB-contaminated soil treated in both years was approximately the same. Because large changes in the PCB feed rate did not result in significant differences in measured PCBTOT emissions (see Figure 76 above), it would be expected that emissions related to the soil should be approximately the same and, therefore, not responsible for the large differences in ambient air concentrations between 1991 and 1992.

However, when ambient air concentrations of PCBTOT and the amount of high concentration (~20-60%; ~200,000-600,000 ppm) PCB liquids incinerated for the project to date were shown on the same plot (Figure 79), a clearer relationship emerges. It appears that once the PCB liquids were incinerated in the fall of 1991, the off-site ambient air concentrations began to diminish. While this was probably due, in part, to the cooler temperatures, it does not explain why the concentrations in the summer of 1992 did not approach those of 1991. One hypothesis of this thesis is that with the high concentration PCB oil gone, there was not as much PCB available for volatilization, and the source strength is reduced. This appears to be the main reason that the ambient air concentrations were lower in 1992 than 1991. This conclusion is an extremely important finding from this research.
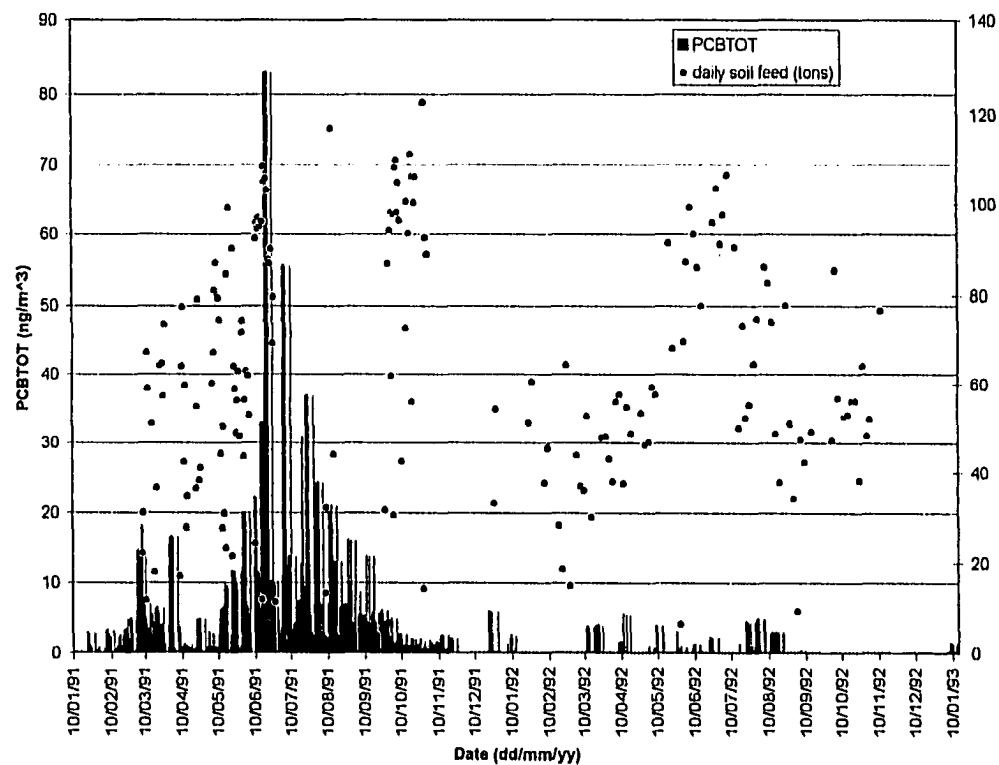
Figure 77. Ambient air total polychlorinated biphenyl concentration and daily polychlorinated biphenyl soil feed by date for project.
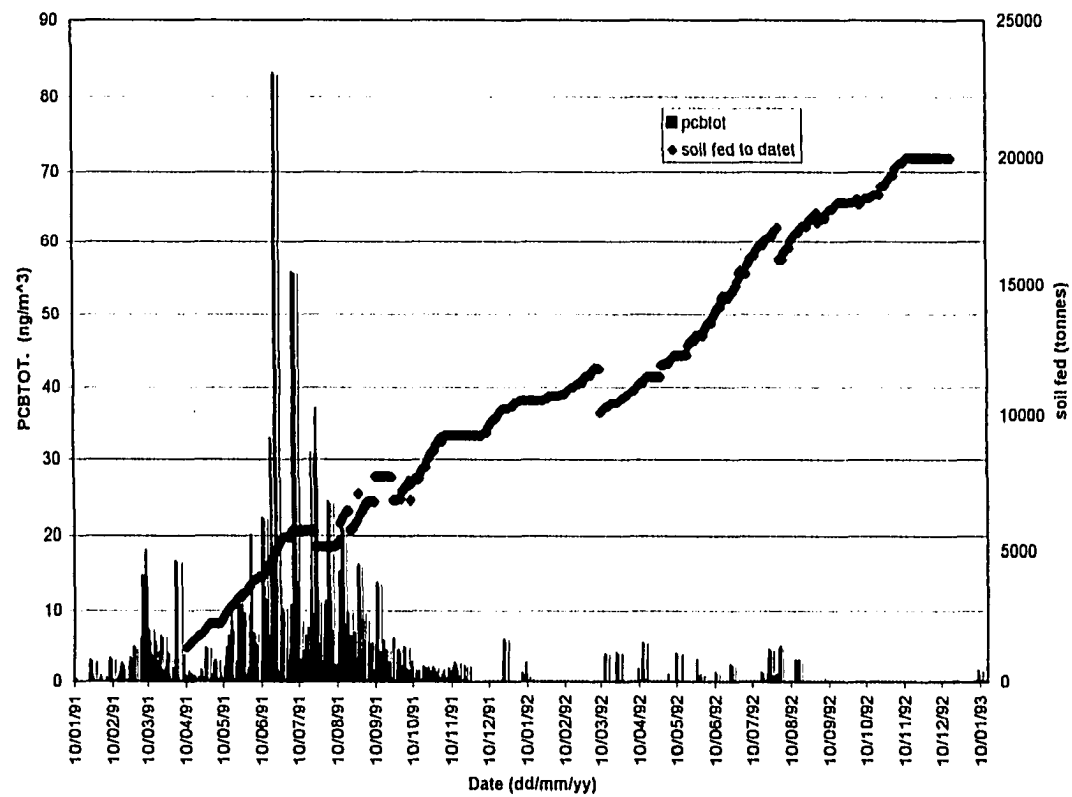
Figure 78.    Ambient air total polychlorinated biphenyl concentrations and project to date soil amounts, by date.
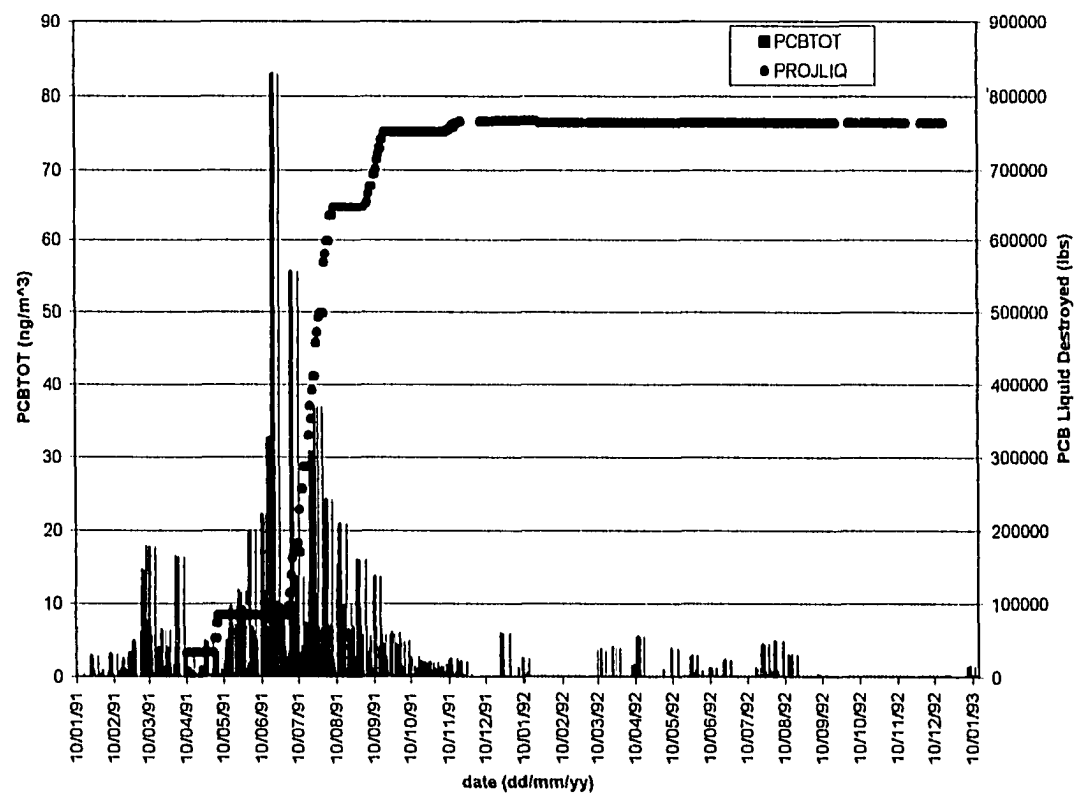
Figure 79.    Off-site total polychlorinated biphenyl concentrations and cumulative amount of polychlorinated biphenyl liquids destroyed by date.

### 4.7.3  On-Site Total Polychlorinated Biphenyl Air Monitoring Results

From the very beginning of the Phase 3 Cleanup, emissions from on-site activities, other than just the incinerator itself, were recognized as being cause for concern. This concern was heightened when ambient air monitoring by the TAGA unit detected concentrations of approximately 600 ng/m$^3$ (1/2 hr average) in early February, 1991, **prior** to the incinerator beginning to process **any** PCB-contaminated materials. At the time, it was suspected that the main source of the fugitive emissions was the shredder operations. Investigations were carried out to identify the sources of these fugitive emissions more fully. These investigations did identify the shredder operations as a fugitive emissions source. However, the investigations also identified a number of other sources of fugitive emissions on-site. These included the tank farm building (where the high level PCB oils were stored) and unexpectedly high concentrations of PCBs in the air of the building (referred to as the Thomas Quonset or Waste Water Treatment building) being used to treat the existing ground water PCB contamination at the site as part of the Phase 4 cleanup.

In response to these preliminary findings, additional on-site sampling, utilizing ambient air samplers, was implemented in an effort to identify typical site conditions and additional opportunities for controlling or reducing fugitive emissions. The on-site monitoring results for 94 air samples for PCBs, obtained on-site on 74 different occasions, are shown in Table CIX along with some summary statistics for these samples. The PCB concentrations observed on-site were typically 2-3 orders of magnitude greater than the off-site ambient air monitoring (Figure 80) during the same period. Some of the on-site samples

had concentrations 100X greater than the maximum concentration observed in the incinerator stack (while feeding high concentration PCB oil).

In response to the concerns about fugitive emissions from the shredder (and other tasks) operations in the containment building, a carbon filtration unit (CFU) was installed in the Spring of 1991 and commenced operations on May 25, 1991. The CFU did help to reduce fugitive emissions from the containment building. In Figure 81, the on-site PCBTOT concentrations are plotted along with the average temperatures. Up to the start of CFU operations, the PCBTOT concentrations were increasing with temperature. Additional sampling carried out in the containment building (not shown) during this period showed PCBTOT concentrations in the tens of thousands of ng/m$^3$. It should be noted that some of the samples obtained inside the containment building during the 1985-90 time period were over 100,000 ng/m$^3$. Despite the high concentrations in the containment building, once the CFU was operating, the magnitude of the on-site PCBTOT concentrations fluctuations was reduced. The CFU exhaust was sampled approximately monthly up until May, 1992 and the concentrations never exceeded 1000 ng/m$^3$.

Although the PCBTOT concentrations observed on-site were generally below the MOL limit, they still represented a significant source to the environment. They were certainly much higher in concentration than those that were encountered in the incinerator stack. These on-site air samples give an indication of the concentrations that can be encountered at PCB storage sites and (potentially) during clean up operations, regardless of the technology being used.

**TABLE CIX**

SUMMARY OF ON-SITE AIR MONITORING FOR FUGITIVE EMISSIONS

| DATE SAMPLED | Samples for date | LOCATION OF SAMPLER | Sample period | PCBTOT (ng/m³) | Site average PCBTOT conc. for sampling period (ng/m³) |
|---|---|---|---|---|---|
| Feb 5-6/91 | 1 | Southeast of the CWML Site, 76' west of hut #1 | 1 | 63.7 | 63.7 |
| Feb 6-7/91 | 1 | Next to shredder pad | 2 | 145.3 | 145.3 |
| Feb 7-8/91 | 1 | Next to shredder pad | 3 | 4.6 | 4.6 |
| Feb 8-9/91 | 1 | NE corner, near tank farm | 4 | 76.6 | 76.6 |
| Feb 11-12/91 | 1 | At the Thomas Quonset exhaust vent | 5 | 611 | 611 |
| Feb 14-16/91 | 3 | In Dome next to control trailer | 6 | 556 | 196.7 |
| Feb 14-16/91 | | Next to shredder pad | | 23 | |
| Feb 14-16/91 | | SE corner of site | | 11 | |
| Feb 16-18/91 | 3 | In Dome next to control trailer | 7 | 840 | 336.3 |
| Feb 16-18/91 | | Next to shredder pad | | 74 | |
| Feb 16-18/91 | | SE corner of site | | 95 | |
| Feb 19-21/91 | 1 | In Dome next to control trailer | 8 | 916 | 916 |
| Feb 22-23/91 | 1 | At the Thomas Quonset exhaust vent | 9 | 159.8 | 159.8 |
| Feb 23-24/91 | 1 | SE corner of site | 10 | 5.2 | 5.2 |
| Feb 24-25/91 | 2 | SE corner of site | 11 | 9.9 | 67.5 |
| Feb 23-25/91 | | SE corner of site | 12 | 125 | 125 |
| Feb 25-26/91 | 1 | Next to shredder pad | 13 | 245.7 | 245.7 |
| Feb 25-27/91 | 3 | In Dome next to control trailer | 14 | 58 | 92.7 |
| Feb 25-27/91 | | Next to shredder pad | | 117 | |
| Feb 25-27/91 | | SE corner of site | | 103 | |
| Mar 3-5/91 | 3 | In Dome next to control trailer | 15 | 108 | 96 |
| Mar 3-5/91 | | Next to shredder pad | | 81 | |
| Mar 3-5/91 | | SE corner of site | | 99 | |
| Mar 5-7/91 | 3 | In Dome next to control trailer | 16 | 413 | 165 |
| Mar 5-7/91 | | Next to shredder pad | | 81 | |
| Mar 5-7/91 | | SE corner of site | | 1 | |
| Mar 7-9/91 | 2 | In Dome next to control trailer | 17 | 335 | 172.5 |
| Mar 7-9/91 | | Next to shredder pad | | 10 | |
| Mar 9-11/91 | 1 | In Dome next to control trailer | 18 | 197 | 197 |
| Mar 11-13/91 | 1 | In Dome next to control trailer | 19 | 461 | 461 |
| Mar 13-15/91 | 1 | In Dome next to control trailer | 20 | 255 | 255 |
| Mar 15-16/91 | 1 | In Dome next to control trailer | 21 | 1142 | 1142 |
| Mar 16-18/91 | 1 | In Dome next to control trailer | 22 | 1389 | 1389 |
| Mar 18-20/91 | 1 | In Dome next to control trailer | 23 | 944 | 944 |
| Mar 20-22/91 | 1 | In Dome next to control trailer | 24 | 1020 | 1020 |

## TABLE CIX (Continued)

## SUMMARY OF ON-SITE AIR MONITORING FOR FUGITIVE EMISSIONS

| DATE SAMPLED | Samples for date | LOCATION OF SAMPLER | Sample period | PCBTOT $(ng/m^3)$ | Site average PCBTOT conc. for sampling period $(ng/m^3)$ |
|---|---|---|---|---|---|
| Mar 22-24/91 | 1 | In Dome next to control trailer | 25 | 1707 | 1707 |
| Mar 24-26/91 | 1 | In Dome next to control trailer | 26 | 1615 | 1615 |
| Mar 25-27/91 | 1 | In Thomas Quonset Hut | 27 | 763.3 | 763.3 |
| Mar 26-28/91 | 1 | In Dome next to control trailer | 28 | 1466 | 1466 |
| Mar 25-28/91 | 1 | Next to shredder pad | 29 | 350 | 350 |
| Mar 28-30/91 | 1 | Next to shredder pad | 30 | 215 | 215 |
| Mar 30-Apr 1/91 | 2 | Next to shredder pad | 31 | 232 | 754.5 |
| Mar 30-Apr 1/91 | | In Dome next to control trailer | | 1277 | |
| Apr 1-3/91 | 2 | In Dome next to control trailer | 32 | 1010 | 614 |
| Apr 1-3/91 | | Next to shredder pad | | 218 | |
| Apr 3-5/91 | 2 | In Dome next to control trailer | 33 | 1997 | 1117.5 |
| Apr 3-5/91 | | Next to shredder pad | | 238 | |
| Apr 7-9/91 | 1 | In Dome next to control trailer | 34 | 2659 | 2659 |
| Apr 8-10/91 | 1 | Next to shredder pad | 35 | 308 | 308 |
| Apr 9-11/91 | 1 | In Dome next to control trailer | 36 | 1221 | 1221 |
| Apr 11-13191 | 2 | Next to shredder pad | 37 | 329 | 281 |
| Apr 11-13/91 | | In Dome next to control trailer | | 233 | |
| Apr 13-15/91 | 1 | In Dome next to control trailer | 38 | 1479 | 1479 |
| Apr 15-17/91 | 2 | In Dome next to control trailer | 39 | 1235 | 688 |
| Apr 15-17/91 | | Next to shredder pad | | 141 | |
| Apr 17-19/91 | 3 | In Dome next to control trailer | 40 | 378 | 181 |
| Apr 17-19/91 | | Next to shredder pad | | 135 | |
| Apr 17-19/91 | | SE corner of site | | 30 | |
| Apr 19-21/91 | 1 | In Dome next to control trailer | 42 | 171 | 171 |
| Apr 21-23/91 | 1 | In Dome next to control trailer | 43 | 1405 | 1405 |
| Apr 23-25/91 | 2 | Next to shredder pad | 44 | 642 | 1039 |
| Apr 23-25/91 | | In Dome next to control trailer | | 1436 | |
| Apr 30-May 1/91 | 1 | Next to shredder pad | 45 | 405 | 405 |
| May 1-3/91 | 2 | In Dome next to control trailer | 46 | 2384 | 1441 |
| May 1-3/91 | | Next to shredder pad | | 498 | |
| May 3-6/91 | 1 | In Dome next to control trailer | 47 | 1070 | 1070 |
| May 6-7/91 | 1 | In Dome (during incident) | 48 | 6439 | 6439 |
| May 7-9/91 | 1 | In Dome next to control trailer | 49 | 3723 | 3723 |
| May 8-10/91 | 1 | Next to shredder Pad | 50 | 3077 | 3077 |
| May 9-11/91 | 1 | In Dome next to control trailer | 51 | 3561 | 3561 |
| May 11-13/91 | 1 | In Dome next to control trailer | 52 | 4232 | 4232 |

**TABLE CIX (Concluded)**

## SUMMARY OF ON-SITE AIR MONITORING FOR FUGITIVE EMISSIONS

| DATE SAMPLED | Samples for date | LOCATION OF SAMPLER | Sample period | PCBTOT (ng/m³) | Site average PCBTOT conc. for sampling period (ng/m³) |
|---|---|---|---|---|---|
| May 14-16/91 | 1 | In Dome next to control trailer | 53 | 1221 | 1221 |
| May 16-17/91 | 1 | Thomas Quonset Hut | 54 | 704 | 704 |
| May 16-18/91 | 1 | Thomas Quonset Hut | 55 | 420 | 420 |
| May 17-19/91 | 1 | In Dome next to control trailer | 56 | 403 | 403 |
| May 28-29/91 | 1 | CFU (location not specified) | 57 | 685.3 | 685.3 |
| May 29-30/91 | 1 | CFU (location not specified) | 58 | 690.8 | 690.8 |
| Jun 18-19/91 | 1 | In Dome next to control trailer | 59 | 1588 | 1588 |
| Jun 19-20/91 | 1 | In Dome next to control trailer | 60 | 1435 | 1435 |
| Jun 27-28/91 | 1 | CFU Exhaust | 61 | 805 | 805 |
| Jul 17-18/91 | 2 | In Dome next to control trailer | 62 | 452.9 | 966.3 |
| Jul 18-19/91 | | In Dome next to control trailer | 63 | 1479.7 | 1479.7 |
| Jul 24-25/91 | 1 | SE Site corner | 64 | 125.3 | 125.3 |
| Jul 25-26/91 | 1 | SE Site corner | 65 | 40.6 | 40.6 |
| Jul 31-Aug 1/91 | 1 | CFU Exhaust | 66 | 835.6 | 835.6 |
| Aug 27-28/91 | 1 | CFU Outlet | 67 | 396 | 396 |
| Sept 10-11/91 | 1 | Thomas Quonset Exhaust | 68 | 76 | 76 |
| Oct 1-2/91 | 1 | CFU Exhaust | 69 | 484 | 484 |
| Nov 23-24/91 | 1 | CFU Exhaust | 70 | 348.3 | 348.3 |
| Nov 27-28/91 | 1 | CFU Exhaust | 71 | 42 | 42 |
| Dec 26-27/91 | 1 | CFU Exhaust | 72 | 326.1 | 326.1 |
| Feb 1-2/92 | 1 | CFU Exhaust | 73 | 23 | 23 |
| Mar 28-29/92 | 1 | CFU Exhaust | 74 | 37.3 | 37.3 |
| May 1-2/92 | 1 | CFU Exhaust | 75 | 72 | 72 |

**Notes:**

Summary Statistics for data in Table CIX:

| | | |
|---|---|---|
| n | 94 | 74 |
| n not blank | 94 | 74 |
| n blank | 0 | 20 |
| mean | 763.3 | 865.9 |
| std. dev. | 1040.66 | 1100.72 |
| 95% CI | 210.37 | 250.79 |
| MIN. | 1.0 | 4.6 |
| MAX. | 6439.0 | 6439.0 |
| range | 6438.0 | 6434.4 |
| kurtosis | 10 | 10 |
| skewness | 3 | 3 |
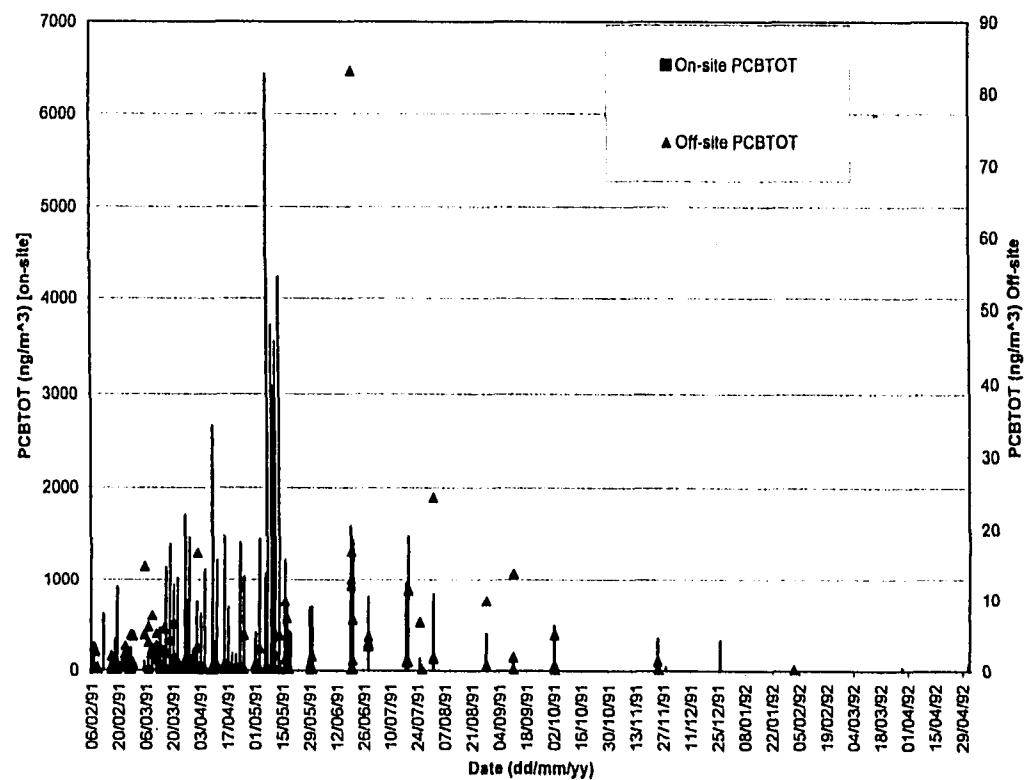
Figure 80.  Total polychlorinated biphenyl concentrations for off- and on-site monitoring (Note: carbon filtration unit (CFU) installed and operated as of May 25, 1991)
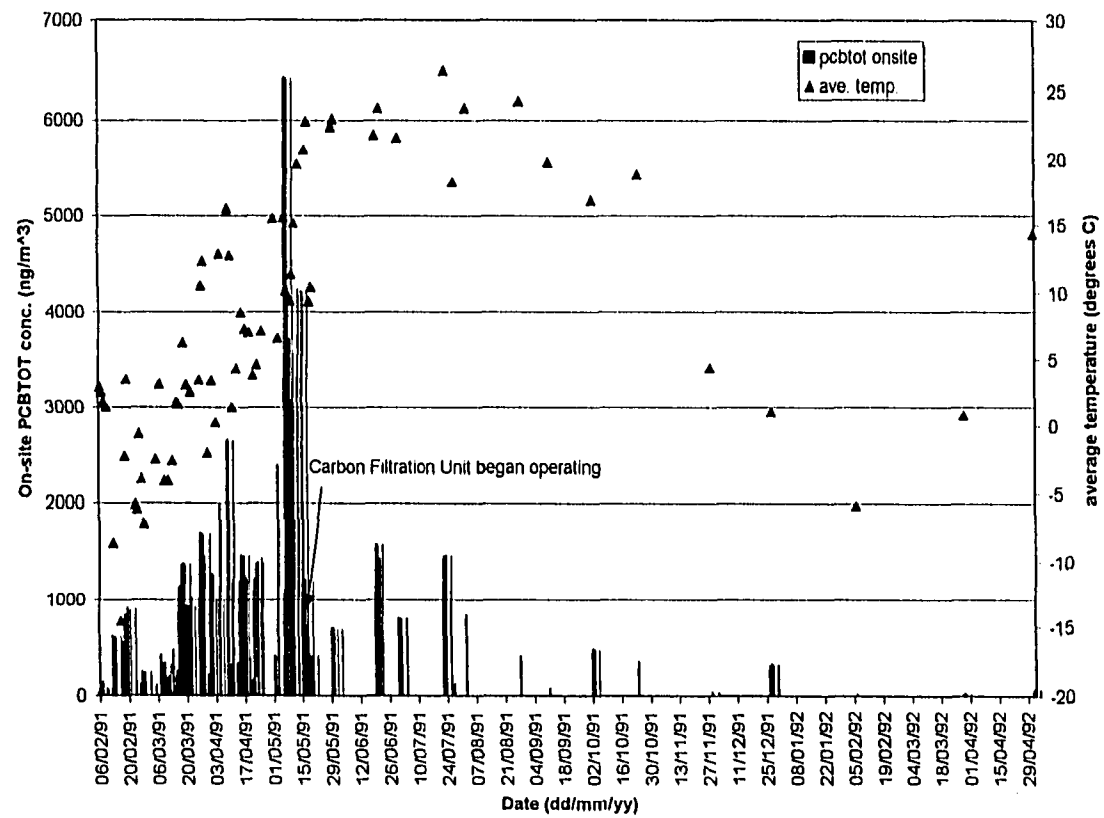
Figure 81. On-site total polychlorinated biphenyl concentrations and average temperatures.

The results presented above lead to several important conclusions about PCB storage:

1) High concentration PCB liquids are an important source of PCBs to the environment, even when "properly" stored (recall that this was the largest PCB storage site in Ontario and represented a state of the art facility).

2) Where PCB liquids and PCB contaminated soils exist at a location, the PCB liquids are probably a much more important source of PCBs in terms of concentrations seen in the air.

3) The proper destruction of the PCB liquids results in a discernible reduction in ambient air concentrations, almost to background, within the year.

4) PCB storage sites, especially those containing high concentration PCB liquids are probably "breathing" PCBs into the surrounding environment. The concentrations observed from on-site fugitive emissions often were much higher than those observed in the incinerator stack. These on-site fugitive emissions would most likely occur regardless of the cleanup technology used. Therefore, delaying destruction of the PCBs while waiting for the development of an alternative to a proven (but controversial) destruction technology, such as incineration, results in on-going PCB emissions that could have been prevented. In such instances, waiting for a "better" or at least more acceptable technology may, in fact, result in larger amounts of PCBs being emitted to the environment.

## 4.8     Modeling For Polychlorinated Biphenyl Ambient Air Data

In the previous sections of this chapter, the ambient air data was analyzed without incorporating specific information on PCB patterns or concentrations for source (or sources) on the CWML site. Still, the data tends to indicate that the incinerator operation itself was not a major source of PCBs, but rather, it was fugitive emissions associated with other activities (such as PCB liquid storage) that were primarily responsible. While persuasive, this evidence can be considered somewhat circumstantial because it does not consider what was actually known to be emitted from the stack.

During the course of the Phase 3 Cleanup, a number of Source (or Stack) Tests of the ENSCO incinerator took place. For nine of the testing "runs" (on nine different dates), data was obtained for PCBs (and other SVOC) emissions. Off-site ambient air sampling data for PCBs existed for 35 of a possible 36 samples (i.e., from 4 off-site sampling locations times 9 dates). In this Section 4.8, the emissions data for the incinerator (and some other on site emission sources) were analyzed, and the off-site ambient air data from these 9 dates/35 samples were reanalyzed, taking the source information into account. This analysis was carried out by modeling the emissions data on both a qualitative and quantitative basis using air dispersion modeling (ADM) and receptor modeling (RM). A major purpose of this modeling was to see if the incinerator emissions might be responsible for observed PCB concentrations based on the PCB homolog patterns and concentrations, and if they were, to assign a percentage to the contribution. Some additional modeling using vapor pressures and fugacity principles was carried out in an attempt to compare transport mechanisms for PCB volatilization from soil versus oils.

### 4.8.1 Air Dispersion Modeling

The ISC3 short term (ISC3ST) model developed by USEPA [232] was used to perform air dispersion modeling for each of the 9 Source Test dates. Only the 9 Source Test dates were looked at because of the existence of comprehensive, quantitative emissions data for these dates. The ISC3ST model is based on Gaussian dispersion principles and has been applied to numerous air emissions sources, including incinerators, for transport distances of less than 50 km [42, 271]. This model is one of the most often used regulatory ADM.

### 4.8.1.1 Source Testing Data

The ISC3ST model uses source(s) specific physical and emission information for its calculations. The SVOC sampling train times for the 9 Source Tests are shown in Table CX. Physical parameters for the stack for all Source Tests are shown in Table CXI. The PCB and TSP emissions information, including DRE, are summarized in Table CXII. The PCB homolog data for each Source Test are shown in Table CXIII. The PCB DRE is compared to the PCB feed rate in Figure 82. This figure shows that the PCB DRE was not affected by increases of the feed rate of almost 2 orders of magnitude. The concentration of PCBTOT in the emissions is shown along with the PCB feed rate in Figure 83. In the same manner as for PCB DRE, the emission concentration does not appear to be affected significantly by large changes in PCB feed rates. The PCBTOT concentration and average ambient air temperature are shown in Figure 84. Figure 84 clearly shows that the PCBTOT concentrations do not vary as a function of temperature, unlike for the ambient air data. The PCBTOT concentrations are shown along with the TSP concentrations in Figure 85. There is no effect

from increases in TSP concentration, suggesting that the PCBs are not associated to any great degree with the particulate phase for these Source Tests. In Figure 86, the average PCBTOT emission rate (in g/s) is compared to the average PCB feed rate (in g/s). Here once again, there is no relationship between increases in feed rate and emissions rate

**TABLE CX**

SEMIVOLATILE ORGANIC COMPOUND SAMPLE TRAIN
SOURCE TEST TIME INFORMATION

| Date (mm/dd/yy) | series | run | TEST ID | start time (SVOC train) | end time (SVOC train) | total elapsed time |
|---|---|---|---|---|---|---|
| 02/16/91 | 1 | 1 | I-1 | 18:21 | 23:58 | 5:37 |
| 02/19/91 | 1 | 2 | I-2 | 13:16 | 22:04 | 8:48 |
| 02/20/91 | 1 | 3 | I-3 | 14:02 | 22:11 | 8:09 |
| 02/22/91 | 2 | 1 | II-1 | | | |
| 02/24/91 | 2 | 2 | II-2 | 14:50 | 19:15 | 4:25 |
| 02/25/91 | 2 | 3 | II-3 | 13:27 | 18:22 | 4:55 |
| 02/26/91 | 2 | 4 | II-4 | 13:12 | 19:00 | 5:48 |
| 07/9/91 | 5 | 1 | V-1 | | | |
| 07/10/91 | 5 | 2 | V-2 | 12:50 | 18:50 | 6:00 |
| 07/12/91 | 5 | 3 | V-3 | 13:52 | 18:54 | 5:02 |
| 07/13/91 | 5 | 4 | V-4 | 14:39 | 19:19 | 4:40 |

## TABLE CXI

INCINERATOR STACK PHYSICAL PARAMETERS FOR SOURCE TESTS

| Test Designa-tion | Feed Material | Stack Height (m) | Stack velocity (m/s) | Stack diameter (m) | Stack area (m$^2$) | Stack flow rate (acm/s) | % moisture | RH (%) | Stack flow rate (dscm/s) | Stack temp (C) |
|---|---|---|---|---|---|---|---|---|---|---|
| I-1 | soils | 21.9 | 17.48 | 0.762 | 0.456 | 7.972 | 45.2 | >100 | 3.694 | 79.2 |
| I-2 | soils | 21.9 | 17.61 | 0.762 | 0.456 | 8.031 | 47.8 | >100 | 3.528 | 80.9 |
| I-3 | soils | 21.9 | 18.07 | 0.762 | 0.456 | 8.241 | 48.9 | >100 | 3.583 | 81.1 |
| II-2 | solids/liquids | 21.9 | 16.1 | 0.762 | 0.456 | 7.342 | 44.7 | >100 | 3.5 | 79 |
| II-3 | solids/liquids | 21.9 | 16.13 | 0.762 | 0.456 | 7.356 | 45.3 | >100 | 3.389 | 79.4 |
| II-4 | solids/liquids | 21.9 | 16.93 | 0.762 | 0.456 | 7.721 | 44.7 | >100 | 3.472 | 78.6 |
| V-2 | solids/liquids | 21.9 | 16.29 | 0.762 | 0.456 | 7.429 | 52.4 | >100 | 2.9 | 82.4 |
| V-3 | solids/liquids | 21.9 | 16.13 | 0.762 | 0.456 | 7.356 | 53.2 | >100 | 2.83 | 81.9 |
| V-4 | solids/liquids | 21.9 | 16.2 | 0.762 | 0.456 | 7.388 | 53.3 | >100 | 2.81 | 82.7 |

**Notes:**

acm/s          actual cubic meter/second

dscm/s         dry standard cubic meter/second, std. temperature = 25 C , std. pressure = 101.325 kPa

RH             relative humidity

RH >100%       supersaturated with water

## TABLE CXII

POLYCHLORINATED BIPHENYL AND TOTAL SUSPENDED PARTICULATE EMISSION SUMMARY FOR SOURCE TESTS

| Test Designation | Feed Material | PCB Feed rate (kg/hr) | PCB Feed rate (g/s) | Average Oxygen (%) | TSP (mg/dscm) | TSP (mg/dscm) @ 11% $O_2$ | PCBTOT emissions (ng/dscm) | PCBTOT emission rate (g/s) | DRE (%) |
|---|---|---|---|---|---|---|---|---|---|
| I-1 | soils | 26.0703 | 7.2 | 8.0 | 16.0 | 12.3 | 371.47 | 1.37E-06 | 99.999981 |
| I-2 | soils | 22.2384 | 6.2 | 5.8 | 0.6 | 0.4[a] | 350.62 | 1.24E-06 | 99.999980 |
| I-3 | soils | 18.3128 | 5.1 | 6.0 | 2.9 | 1.9 | 391.3 | 1.4E-06 | 99.999973 |
| II-1 | solids/liquids | n.a. | n.a. | 8.7 | 41.0 | 33.3 | n.a. | n.a. | n.a. |
| II-2 | solids/liquids | 197.4 | 54.8 | 7.9 | 59.9 | 45.6 | 416.2 | 1.46E-06 | 99.999997 |
| II-3 | solids/liquids | 212.9 | 59.1 | 6.7 | 91.8 | 64.0 | 391.8 | 1.33E-06 | 99.999998 |
| II-4 | solids/liquids | 233.8 | 64.9 | 6.8 | n.a.[b] | n.a. | 482.9 | 1.68E-06 | 99.999997 |
| V-2 | solids/liquids | 241.92 | 67.2 | 6.9 | 23.0 | 23.0 | 475 | 1.38E-06 | 99.999998 |
| V-3 | solids/liquids | 160.56 | 44.6 | 6.9 | 16.6 | 16.5 | 377 | 1.07E-06 | 99.999998 |
| V-4 | solids/liquids | 98.64 | 27.4 | 8.4 | 44.1 | 44.1 | 496 | 1.39E-06 | 99.999995 |

__Note:__

g/s             grams/second

mg/dscm         milligram /dry standard cubic meter

ng/dscm         nanogram/dry standard cubic meter

# TABLE CXIII

## POLYCHLORINATED BIPHENYL HOMOLOG SOURCE TEST EMISSION DATA

| TEST ID | I-1 | | I-2 | | I-3 | | II-2 | | II-3 | | II-4 | | V-2 | | V-3 | | V-4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Date (dd/mm/yy) | 16/2/91 | | 19/2/91 | | 20/2/91 | | 24/2/91 | | 25/2/91 | | 26/2/91 | | 10/07/91 | | 12/07/91 | | 13/07/91 |
| | flag | ng/dscm | flag | ng/dscm | flag | ng/dscm | flag | ng/dscm | flag | ng/dscm | flag | ng/dscm | flag | ng/dscm | flag | ng/dscm | flag | ng/dscm |
| Mono- | < | 0.03 | | 0.90 | < | 0.60 | < | 0.04 | < | 0.04 | < | 0.04 | | 9.21 | < | 8.58 | < | 8.53 |
| Di- | | 21.10 | | 50.70 | | 18.70 | < | 15.30 | | 27.10 | | 27.60 | | 12.80 | | 23.40 | < | 8.53 |
| Tri- | | **230.00** | | **167.40** | | **230.40** | | **285.10** | < | 83.40 | | **201.20** | | 44.70 | | 38.90 | | 25.00 |
| Tetra- | | 84.00 | | 125.80 | | 136.20 | < | 115.10 | | **153.30** | | 133.40 | | **193.00** | | **131.00** | | 118.00 |
| Penta- | | 23.00 | | 5.20 | < | 4.70 | < | 0.05 | | 57.90 | | 44.50 | | 124.00 | | 91.50 | | **176.00** |
| Hexa- | < | 10.00 | < | 0.05 | < | 0.06 | < | 0.06 | < | 48.80 | < | 49.30 | | 44.90 | | 40.00 | | 95.90 |
| Hepta- | < | 2.90 | < | 0.07 | < | 0.07 | < | 0.07 | < | 19.10 | < | 25.70 | | 21.50 | | 18.00 | | 37.80 |
| Octa- | < | 0.05 | < | 0.05 | < | 0.06 | < | 0.06 | < | 0.06 | < | 0.06 | < | 8.37 | < | 8.58 | | 10.20 |
| Nona- | < | 0.04 | < | 0.05 | < | 0.06 | < | 0.05 | < | 1.00 | < | 0.06 | < | 8.37 | < | 8.58 | < | 8.53 |
| Deca- | < | 0.35 | < | 0.40 | < | 0.45 | < | 0.45 | < | 1.20 | < | 1.20 | < | 8.37 | < | 8.58 | < | 8.53 |
| sum mono-deca PCB | < | 371.47 | < | 350.62 | < | 391.30 | < | 416.28 | < | 391.90 | < | 483.06 | < | 475.22 | < | 377.12 | < | 497.02 |
| sum di-dec PCB | | 371.44 | | 349.72 | | 390.70 | | 416.24 | | 391.86 | | 483.02 | | 466.01 | | 368.54 | | 488.49 |
| difference | | 0.03 | | 0.90 | | 0.60 | | 0.04 | | 0.04 | | 0.04 | | 9.21 | | 8.58 | | 8.53 |

**Notes:**

**Bolded** number is homolog group with maximum concentration
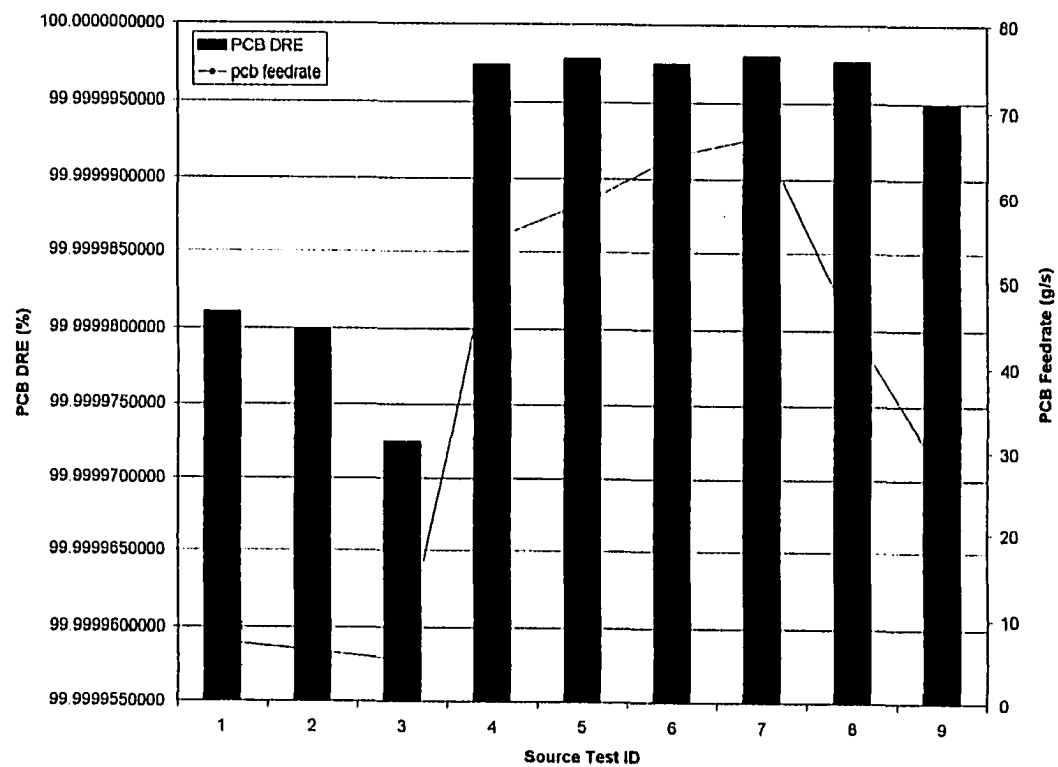
Figure 82.    Polychlorinated biphenyl destruction and removal efficiency and polychlorinated biphenyl feed rate for source tests.
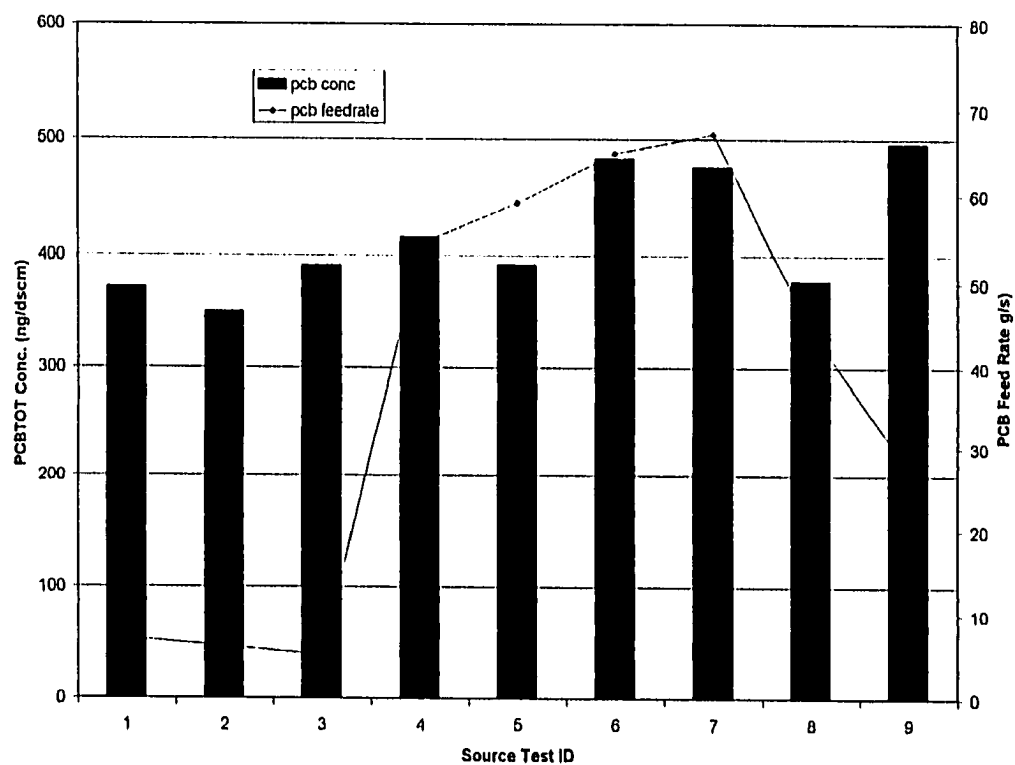
Figure 83. Polychlorinated biphenyl feed rate and total polychlorinated biphenyl concentration for source tests.
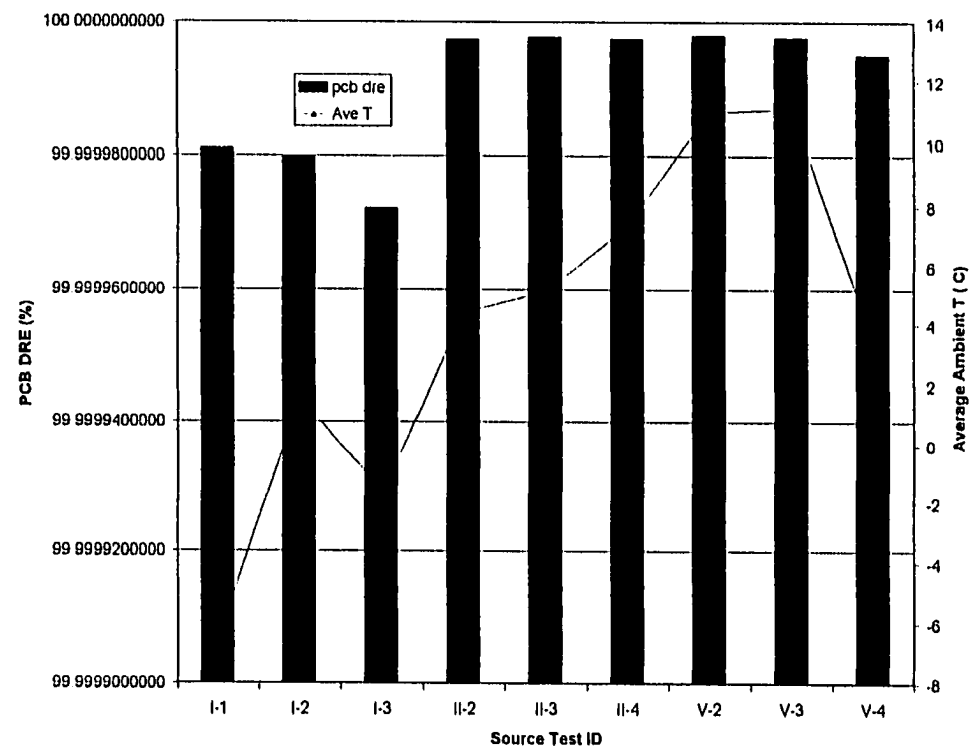
Figure 84.    Total polychlorinated biphenyl and average ambient temperature for source tests.
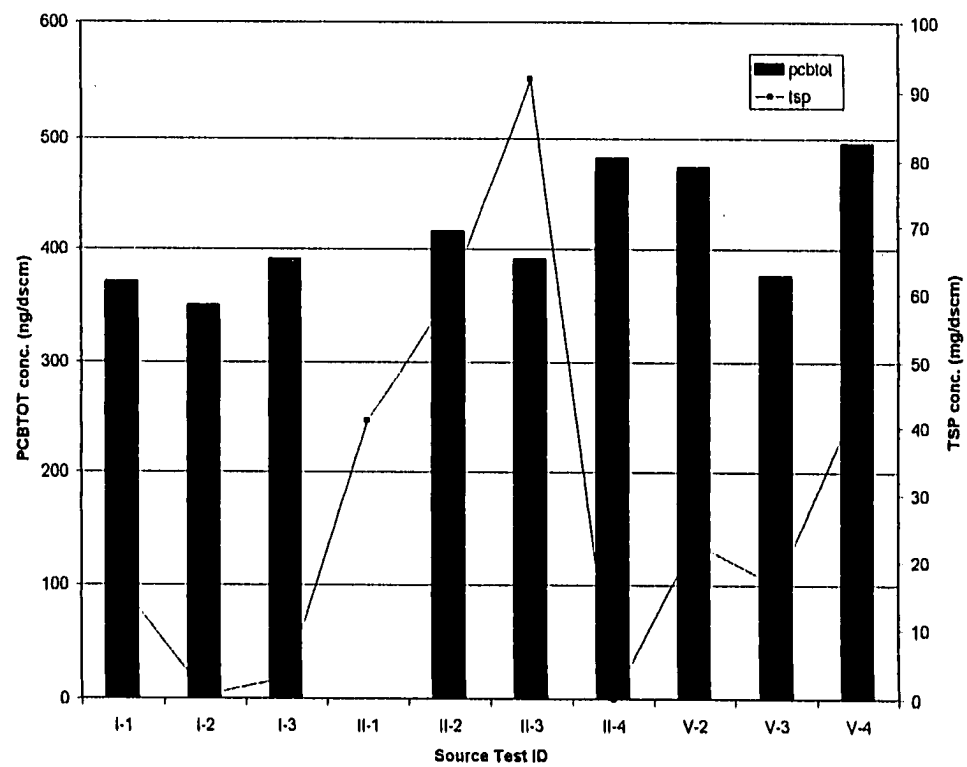
Figure 85.    Total polychlorinated biphenyl concentration and total suspended particulate concentrations for source tests.
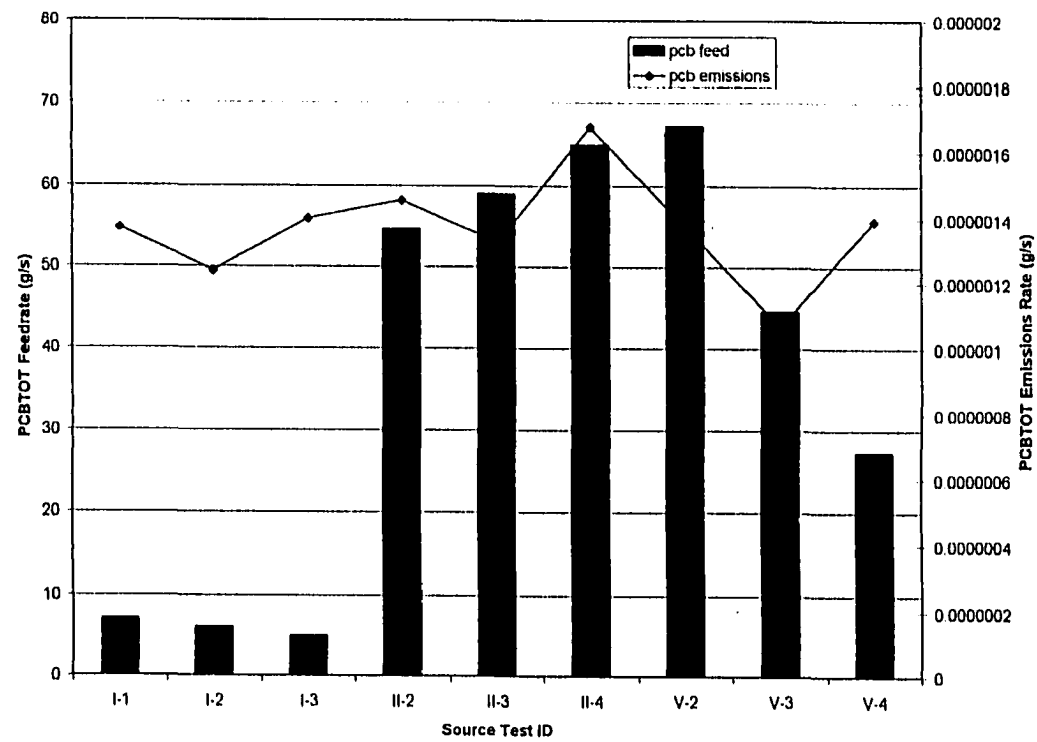
Figure 86.    Total polychlorinated biphenyl emission rate and polychlorinated biphenyl feed rate.

### 4.8.1.2 <u>ISC3View<sup>tm</sup> Modeling</u>

The ISC3ST model is a DOS executable program written in FORTRAN. As such, it can prove to be quite difficult to use if one is not a programmer. A number of companies, including Lakes Environmental, Trinity Consultants and Bowman Environmental, have developed Windows<sup>tm</sup>-based interfaces for the ISC3 model to allow for improved ease of use and data manipulation. Dr. Jesse The' of Lakes Environmental kindly provided a copy of their ISCVIEW<sup>tm</sup> software for setting up and performing the ISC3ST modeling. The meteorological data for the Smithville site was used for wind speed, wind direction, and ambient air temperature. Additional meteorological data (including twice daily upper air soundings) from the Buffalo International Airport, which is located approximately 80 km from the site, were combined with the SV MET data to create the required meteorological inputs files for ISC3. While this is a simple process in principle, it was in practice an extremely challenging undertaking because of differences in file formats, units, and the large volume of data that were involved. After a great deal of trial and error, the required meteorological input files were produced in the proper format and the files required for ISC3 were created using Lakes' RAMMETVIEW<sup>tm</sup> preprocessor. The RAMMETVIEW<sup>tm</sup> preprocessor also contained a program that produces a worst case meteorological data set for a site based upon the meteorological data that is provided.

### 4.8.1.2.1 <u>Worst Case Modeling with Screen3 and Industrial Source Complex 3-Short Term</u>

The worst case dispersion concentrations were first determined for the ENSCO incinerator stack conditions using the SCREEN3VIEW<sup>tm</sup> (kindly donated by Lakes

Environmental) interface for the USEPA SCREEN3 model [272, 273]. The worst case (i.e.,

MAX. ground level concentration) meteorological data set produced by RAMMETVIEW[tm]

for the 1991 data were also used by ISC3ST to model worst case concentrations. The

SCREEN3 model results are shown in Figures 87 and 88. The ISC3ST model results for

worst case dispersion are shown in Figure 89. Table CXIV shows a comparison of the

concentrations calculated by the two models. As expected, SCREEN3, which makes more

conservative assumptions, produced higher concentrations. Note that the models treat the

calculated ambient air concentration as a linear function of the emission rate, such that

halving the emission rate will result in an air concentration of ½ of the previous value. Using

an emission rate of 1.67E-6 g/s (the maximum measured in any of the 9 source tests), the

maximum concentration predicted was 0.04 ng/m$^3$. This concentration is several orders of

magnitude less than the maximum concentrations actually observed during the project. This

is a significant difference and another piece of evidence that the incinerator stack is not the

major source of the PCBs observed in the ambient air.

### 4.8.1.2.2    Industrial Source Complex 3-Short Term Results for Source Test Dates

After determining the "worst case" scenario results, ADM was carried out for

each of the 9 Source Test dates. The information used for setting up receptors for the off-site

air monitoring locations in the ISC3 model is summarized in Table CXV. The other general

parameters used for the ISC3 model are shown in Table CXVI. The actual stack gas exit

velocity and exit temperature were input for each of the 9 source tests.

```
SIMPLE TERRAIN INPUTS:
   SOURCE TYPE          =        POINT
   EMISSION RATE (G/S)  =     1.00000      ********************************************
   STACK HEIGHT (M)     =    21.9000       *** SUMMARY OF SCREEN MODEL RESULTS ***
   STK INSIDE DIAM (M)  =      .7620        ********************************************
   STK EXIT VELOCITY (M/S)= 17.4800
   STK GAS EXIT TEMP (K)=   352.0000       CALCULATION      MAX CONC   DIST TO  TERRAIN
   AMBIENT AIR TEMP (K) =   293.0000       PROCEDURE        (UG/M**3)  MAX (M)  HT (M)
   RECEPTOR HEIGHT (M)  =      .0000        ----------      ---------  -------  -------
   URBAN/RURAL OPTION   =      RURAL        SIMPLE TERRAIN    26.05     247.      0.
   BUILDING HEIGHT (M)  =      .0000
   MIN HORIZ BLDG DIM (M) =    .0000
   MAX HORIZ BLDG DIM (M) =    .0000
```

**Automated Distances Vs. Concentration**
**Terrain Height = 0. m**
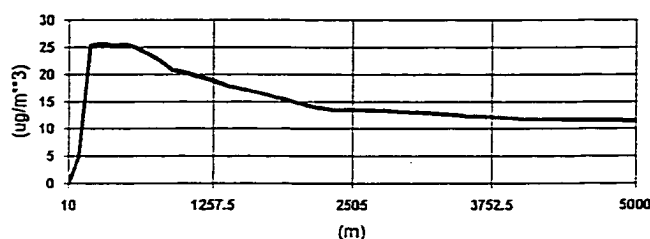


Figure 87.    Air dispersion modeling results from Screen3 for emission rate equal to one gram per second.

```
SIMPLE TERRAIN INPUTS:
   SOURCE TYPE          =        POINT          **************************************
   EMISSION RATE (G/S)  =    .167000E-05        *** SUMMARY OF SCREEN MODEL RESULTS ***
   STACK HEIGHT (M)     =    21.9000            **************************************
   STK INSIDE DIAM (M)  =      .7620
   STK EXIT VELOCITY (M/S)= 17.4800            CALCULATION      MAX CONC   DIST TO  TERRAIN
   STK GAS EXIT TEMP (K)=   352.0000           PROCEDURE        (UG/M**3)  MAX (M)  HT (M)
   AMBIENT AIR TEMP (K) =   293.0000           ----------      ---------  -------  -------
   RECEPTOR HEIGHT (M)  =      .0000           SIMPLE TERRAIN   .4350E-04   247.     0.
   URBAN/RURAL OPTION   =      RURAL
   BUILDING HEIGHT (M)  =      .0000
   MIN HORIZ BLDG DIM (M) =    .0000
   MAX HORIZ BLDG DIM (M) =    .0000
```

**Automated Distances Vs. Concentration**
**Terrain Height = 0. m**
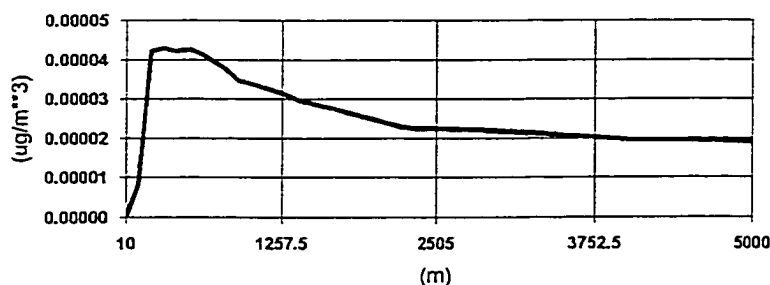


Figure 88.    Worst case air dispersion modeling for emission rate equals 1.67 E-6 grams per second using Screen3.

emission rate=1 g/s

max. conc. =20.85 ug/m^2 at x=225m, y=268 m
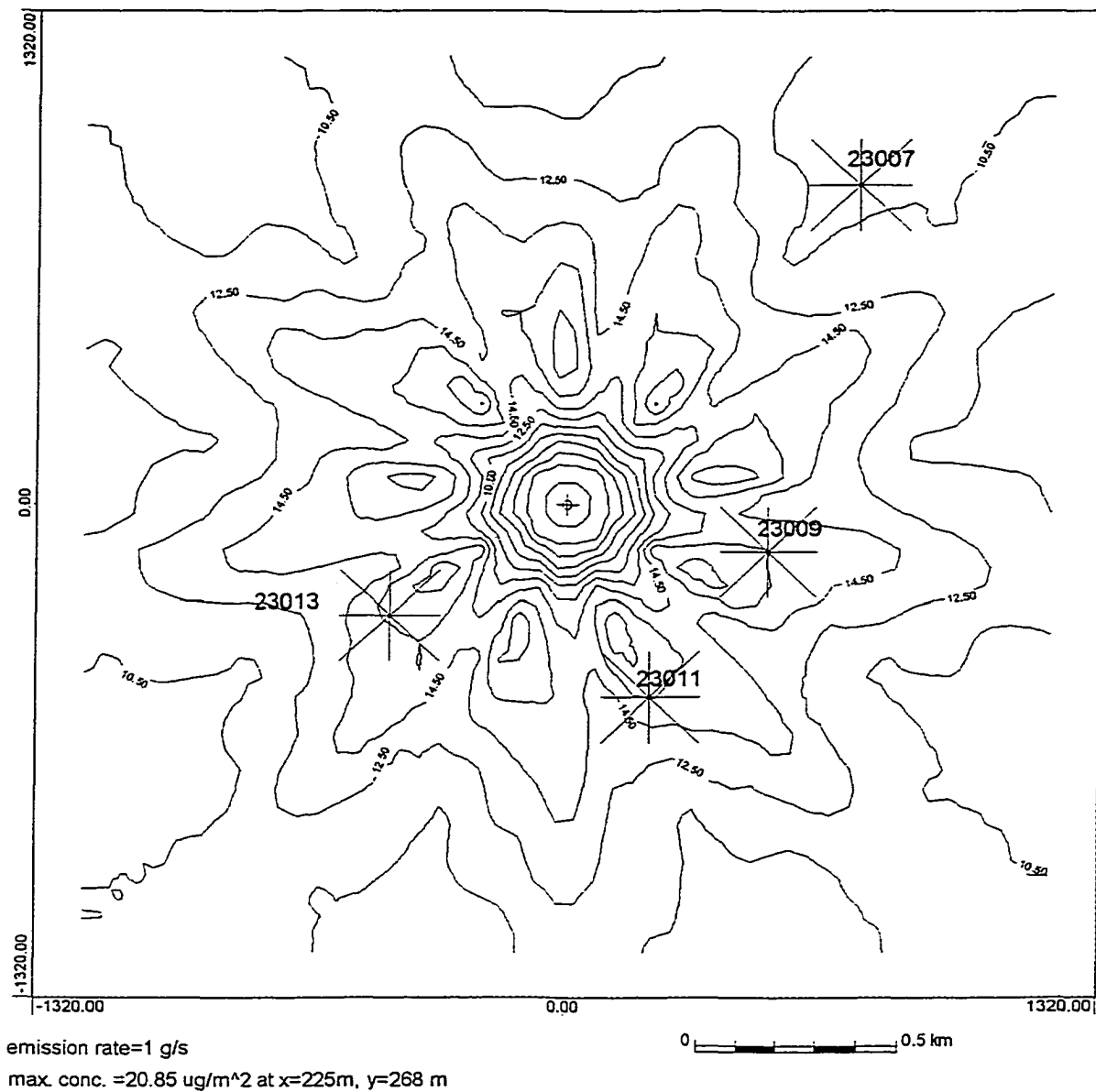
Figure 89.    Worst case modeling results with Industrial Source Complex 3 — short term using emission rate of one (1) gram per second.

**TABLE CXIV**

SUMMARY OF WORST CASE DISPERSION MODELING RESULTS

| Model | Emission rate (g/s) | Stack Height (m) | Stack velocity (m/s) | Stack diameter (m) | Stack temp (C) | Ambient T (K) | Receptor Height (m) | MAX. conc. (ug/m^3) | MAX. conc. (ng/m^3) | x (m) | y (m) | Distance from stack |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SCREEN3 | 1 | 21.9 | 17.48 | 0.762 | 79.2 | 293 | 0 | 26.05 | 26050 | -- | -- | 247 |
| ISC3ST | 1 | 21.9 | 17.48 | 0.762 | 79.2 | screen.met[a] | 0 | 20.85 | 20850 | 225 | 268 | 350 |
| SCREEN3 | 1.67E-06 | 21.9 | 17.48 | 0.762 | 79.2 | 293 | 0 | 4.35E-05 | 0.044 | -- | -- | 247 |
| ISC3ST | 1.67E-06 | 21.9 | 17.48 | 0.762 | 79.2 | screen.met[a] | 0 | 3.48E-05 | 0.035 | 225 | 268 | 350 |

**Note:**

[a] Worst case meteorological data file produced using RAMMETVIEW[tm]

## TABLE CXV

### AIR MONITORING STATION LOCATION INFORMATION FOR INDUSTRIAL SOURCE COMPLEX 3 MODELING

| SiteID | Name | Easting | Plus | Northing | Plus | Est. distance (m) | Center heading from stack | Distance used for ISC3 (m) | Direction used for ISC3 (degrees) | ISC x (m) | ISC y (m) |
|--------|------|---------|------|----------|------|------|------|------|------|------|------|
| 23005 | Met. Stn. | 19 | 0.1 | 75.0 | 0.1 | 1410 | 357 | 1400 | | | |
| 23007 | Mud Rd. | 19 | 0.7 | 74.0 | 0.8 | 1210 | 29 | 1150 | 30 | 575.0 | 995.9 |
| 23009 | Witmer | 19 | 0.5 | 73.0 | 0.7 | 390 | 91 | 390 | 91 | 389.9 | -6.8 |
| 23011 | Winery | 19 | 0.0 | 73.0 | 0.3 | 390 | 168 | 390 | 169 | 74.4 | -382.8 |
| 23013 | School | 18 | 0.6 | 73.0 | 0.5 | 590 | 253 | 590 | 253 | -564.2 | -172.5 |

**TABLE CXVI**

GENERAL MODELING PARAMETERS USED FOR INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM MODELING

| Dispersion option | Output type | Dispersion coefficient | Plume depletion | Pollutant | Averaging time |
|---|---|---|---|---|---|
| regulatory default | concentration | rural | none | PCB | 24 hrs |
| exponential decay | terrain hgt options | terrain calc algorithm | x coord | y coord | base elevation |
| no | simple | simple terrain only | 0 | 0 | 0 |
| emission rate (g/s) | release hgt (m) | gas exit temperature (K) | gas exit velocity (m/s) | stack inside diameter (m) | particle info |
| 1 | 21.9 | 352.35 | 17.48 | 0.762 | none |
| uniform polar grid no. of rings | uniform polar grid spacing (m) | discrete polar receptor distance (m) and degrees | windspd categories | windprofile exponents | Vertical Temp. gradient |
| 24 | 50 | 1140　　30<br>　　　　91<br>　　　　169<br>610　　243 | default | n.a. due to reg default option | n.a. due to regulatory default option |

**Note:**

Exit gas temperature and gas exit velocity shown for Series I Run1; actual values used differed for each modeled run.

Although there was information available on the stack TSP concentration, there was no information available on particle size. Discussions with the designer of the ENSCO unit indicated that it was his feeling that most of the particulate should be sub-micron in size [213]. In any event, there does not appear to be any effect of TSP concentrations on PCBTOT concentrations based on Figure 85. Therefore, no particulate size information was used for this modeling. In addition, the dry and wet deposition algorithms were also not used for this modeling. This is believed to be a conservative treatment since the effects of wet and dry deposition would most likely be to reduce concentrations farther from the site, below that calculated without these algorithms. There were not expected to be any effects from environmental half-life and/or degradation reactions for PCBs because of the short distances and time spans involved.

The results from ISC3ST modeling using a PCB emission rate of 1 g/s are summarized in Table CXVII. The calculated concentrations using the actual emission rates are shown in Table CXVIII. Figures 90 through 107 contain wind roses and ISC3ST concentration isopleths for each of the dates with both ambient air sampling and source testing information.

The observed vs. modeled ambient air concentrations are compared by SiteID in Tables CXIX-CXXII. The highest concentration sites observed and modeled are shown in bold. The observed mean and maximum concentrations are 3 orders of magnitude greater than the modeled concentrations, which again indicate that the incinerator stack is not a major source for the observed PCB concentrations on these dates.

It must be noted that the observed and modeled concentrations will be a function of wind direction, wind speed, and source strength. In the case of the incinerator stack, the source strength does not appear to fluctuate greatly. However, there could be other sources (e.g., fugitive emissions) that are time variant and could account for some of the differences. In any event, the results indicate that the Site is a source, but the concentrations observed cannot be adequately accounted for by the stack emissions.

# TABLE CXVII

## AMBIENT AIR CONCENTRATIONS CALCULATED USING INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM MODEL
### (1 GRAM PER SECOND EMISSION RATE)

| Test Designation | Feed Material | PCBTOT Emission Rate used for Model (g/s) | 23007 modeled (ug/m^3) | 23009 modeled (ug/m^3) | 23011 modeled (ug/m^3) | 23013 modeled (ug/m^3) | MAX. conc. modeled (ug/m^3) | MAX. conc. (x) Coordinates (m) | MAX. conc. (y) Coordinates (m) |
|---|---|---|---|---|---|---|---|---|---|
| I-1 | Soils | 1 | 1.18 | 0 | 0 | 0 | 5.8 | 321 | 383 |
| I-2 | Soils | 1 | 1.92 | 0.56 | 0 | 0 | 3.35 | 205 | 564 |
| I-3 | soils | 1 | 0.53 | 0 | 0 | 0 | 2.48 | 460 | 386 |
| II-2 | solids/liquids | 1 | 1.08 | 0 | 0.08 | 0.16 | 2.95 | -766 | -643 |
| II-3 | solids/liquids | 1 | 0 | 0 | 0 | 0.013 | 8.67 | -612 | -514 |
| II-4 | solids/liquids | 1 | 0 | 1.34 | 0 | 0 | 3.32 | 800 | 0 |
| V-2 | solids/liquids | 1 | 0.92 | 3.28 | 0 | 0 | 4.74 | 321 | 383 |
| V-3 | solids/liquids | 1 | 0 | 0 | 0 | 2.07 | 7.91 | -421 | -353 |
| V-4 | solids/liquids | 1 | 0 | 0 | 0 | 0.33 | 3.34 | -375 | -650 |

# TABLE CXVIII

## CALCULATED CONCENTRATIONS FROM INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM MODEL USING ACTUAL EMISSION RATES

| Test Designation | Feed Material | Actual PCBTOT emission rate (g/s) | 23007 modeled (ng/m^3) | 23009 modeled (ng/m^3) | 23011 modeled (ng/m^3) | 23013 modeled (ng/m^3) | MAX. conc. modeled (ng/m^3) | MAX. conc. Coordinates (x) | MAX. conc. Coordinates (y) |
|---|---|---|---|---|---|---|---|---|---|
| I-1 | soils | 1.37E-06 | 1.62E-03 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 7.96E-03 | 321 | 383 |
| I-2 | soils | 1.237E-06 | 2.37E-03 | 6.93E-04 | 0.00E+00 | 0.00E+00 | 4.14E-03 | 205 | 564 |
| I-3 | soils | 1.402E-06 | 7.43E-04 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 3.48E-03 | 460 | 386 |
| II-2 | solids/liquids | 1.457E-06 | 1.57E-03 | 0.00E+00 | 1.17E-04 | 2.33E-04 | 4.30E-03 | -766 | -643 |
| II-3 | solids/liquids | 1.328E-06 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 1.73E-05 | 1.15E-02 | -612 | -514 |
| II-4 | solids/liquids | 1.677E-06 | 0.00E+00 | 2.25E-03 | 0.00E+00 | 0.00E+00 | 5.57E-03 | 800 | 0 |
| V-2 | solids/liquids | 1.378E-06 | 1.27E-03 | 4.52E-03 | 0.00E+00 | 0.00E+00 | 6.53E-03 | 321 | 383 |
| V-3 | solids/liquids | 1.067E-06 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 2.21E-03 | 8.44E-03 | -421 | -353 |
| V-4 | solids/liquids | 1.394E-06 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 4.60E-04 | 4.66E-03 | -375 | -650 |
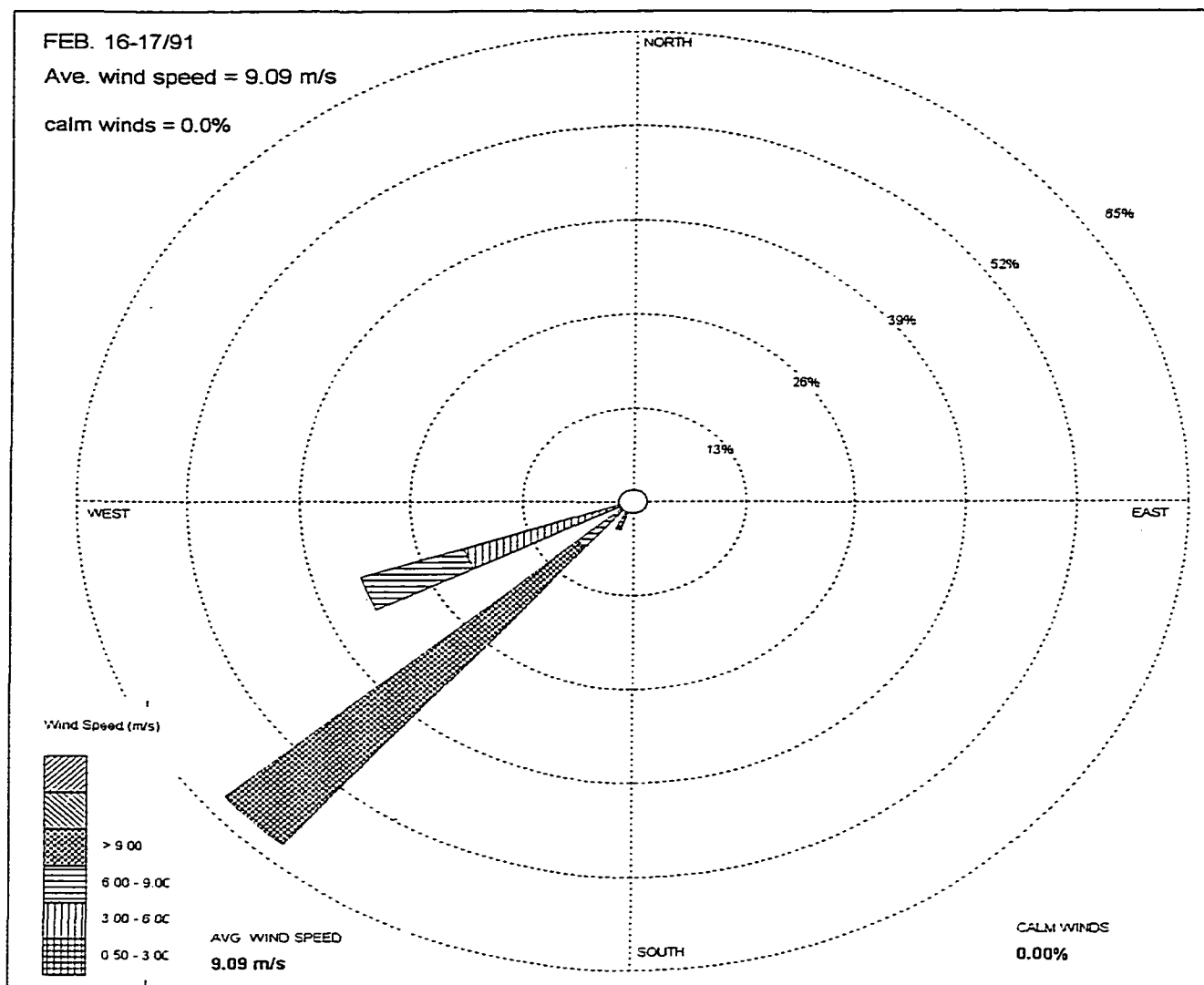
Figure 90.    Wind rose for February 16-17, 1991.
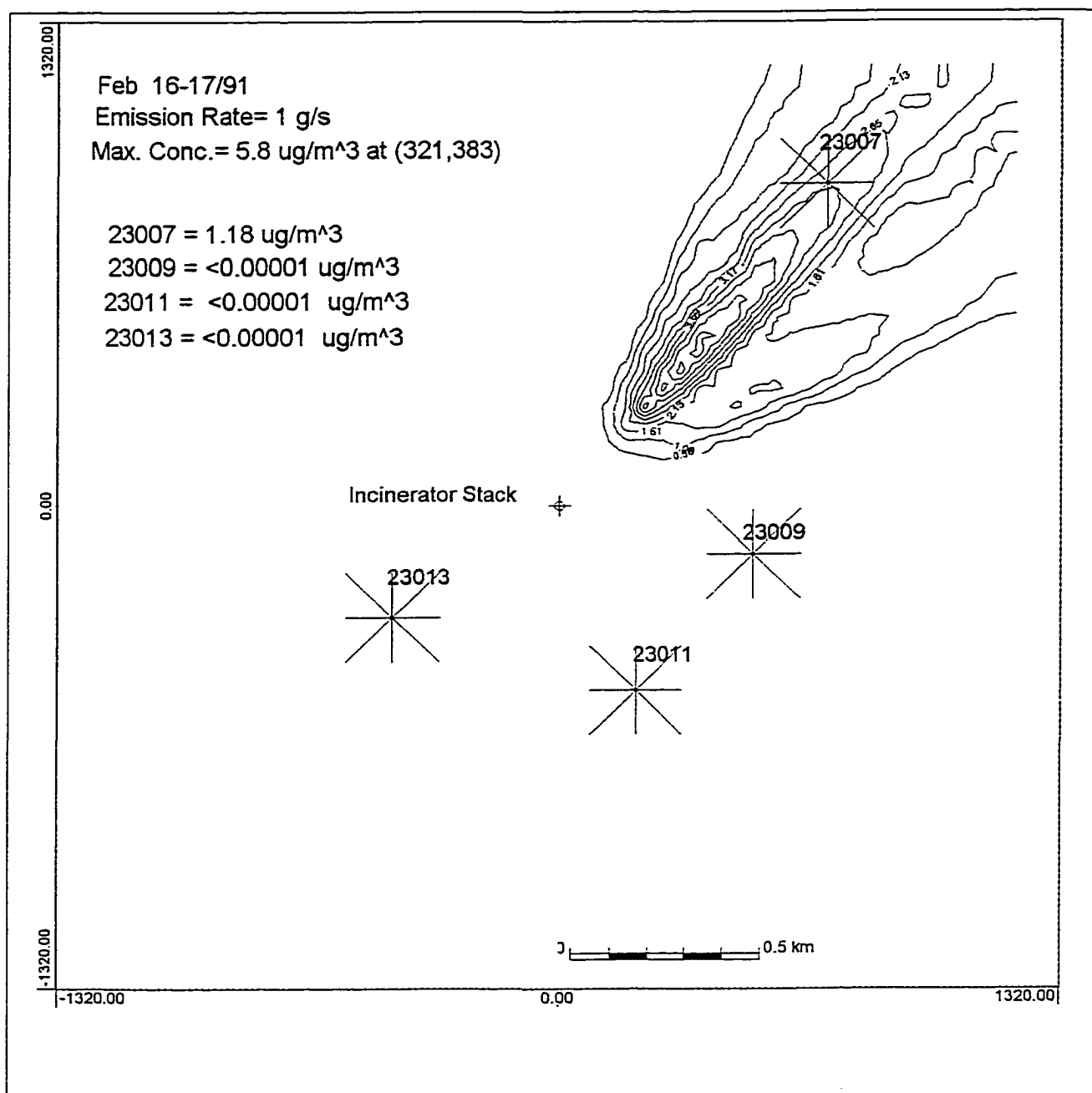
Figure 91.    Industrial Source Complex 3 — short term concentration isopleths for February 16-17, 1991.
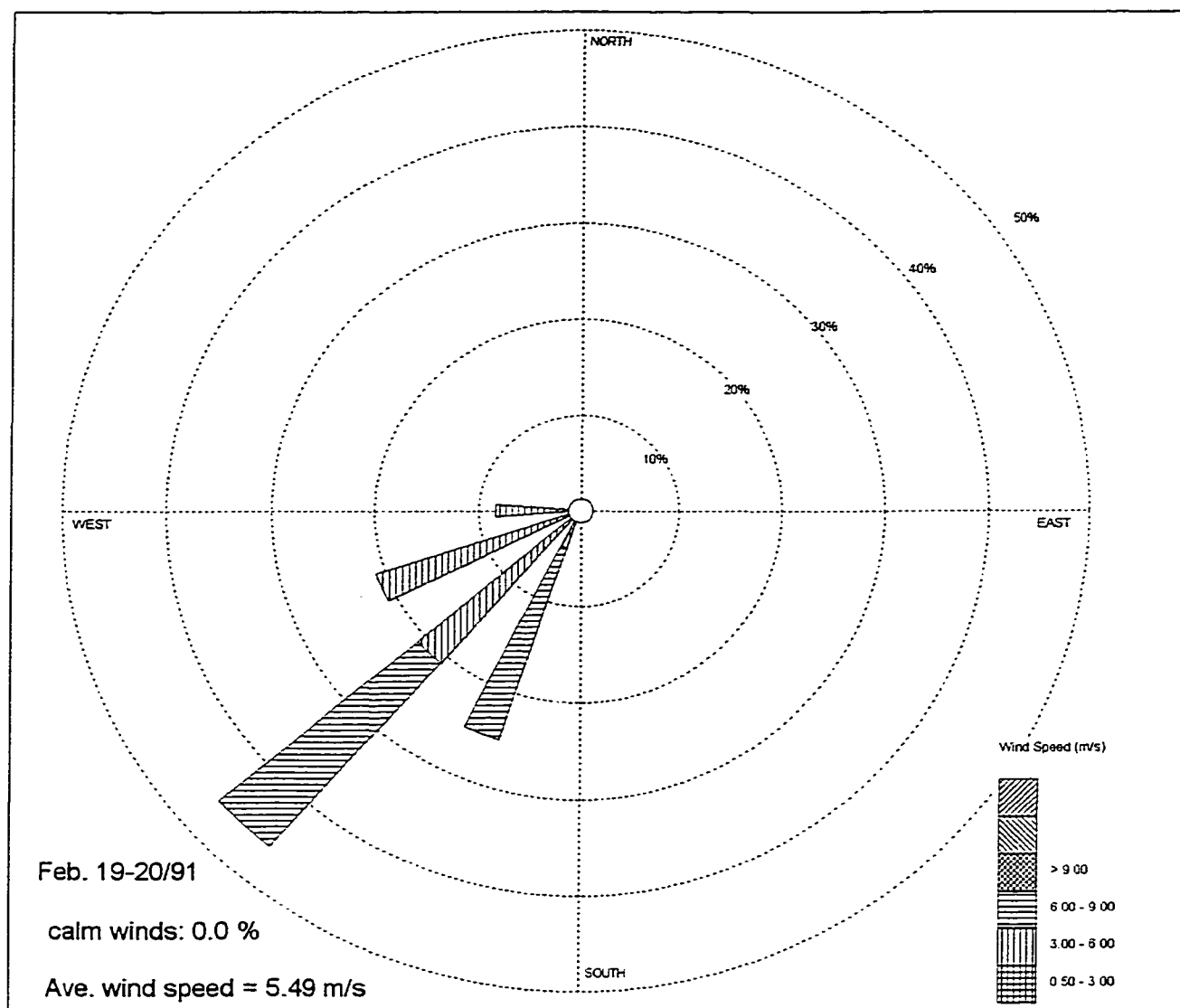
Figure 92.     Wind rose for February 19-20, 1991.
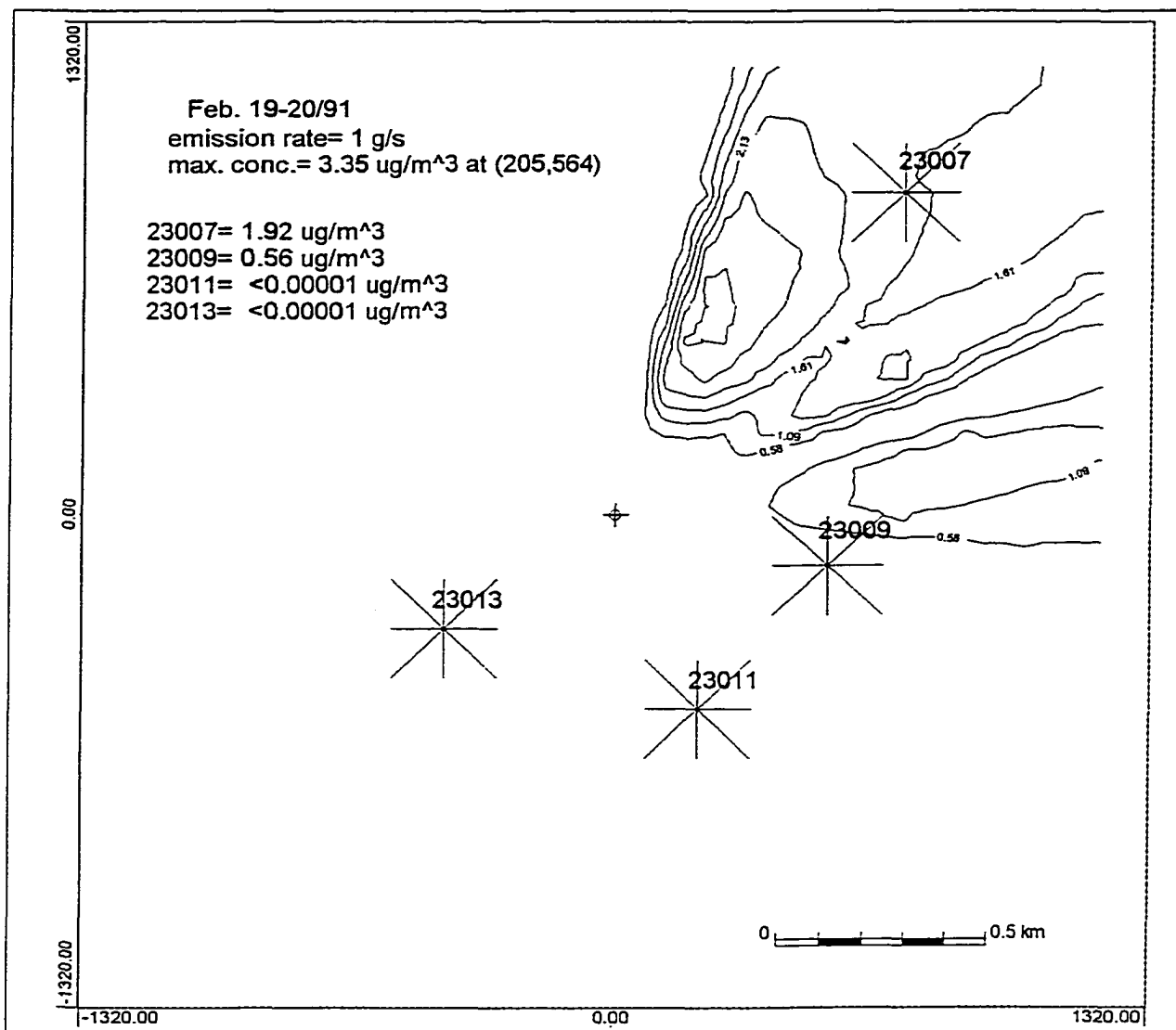
Figure 93.    Industrial  Source  Complex  3  —  short  term  concentration  isopleths  for
             February 19-20, 1991.
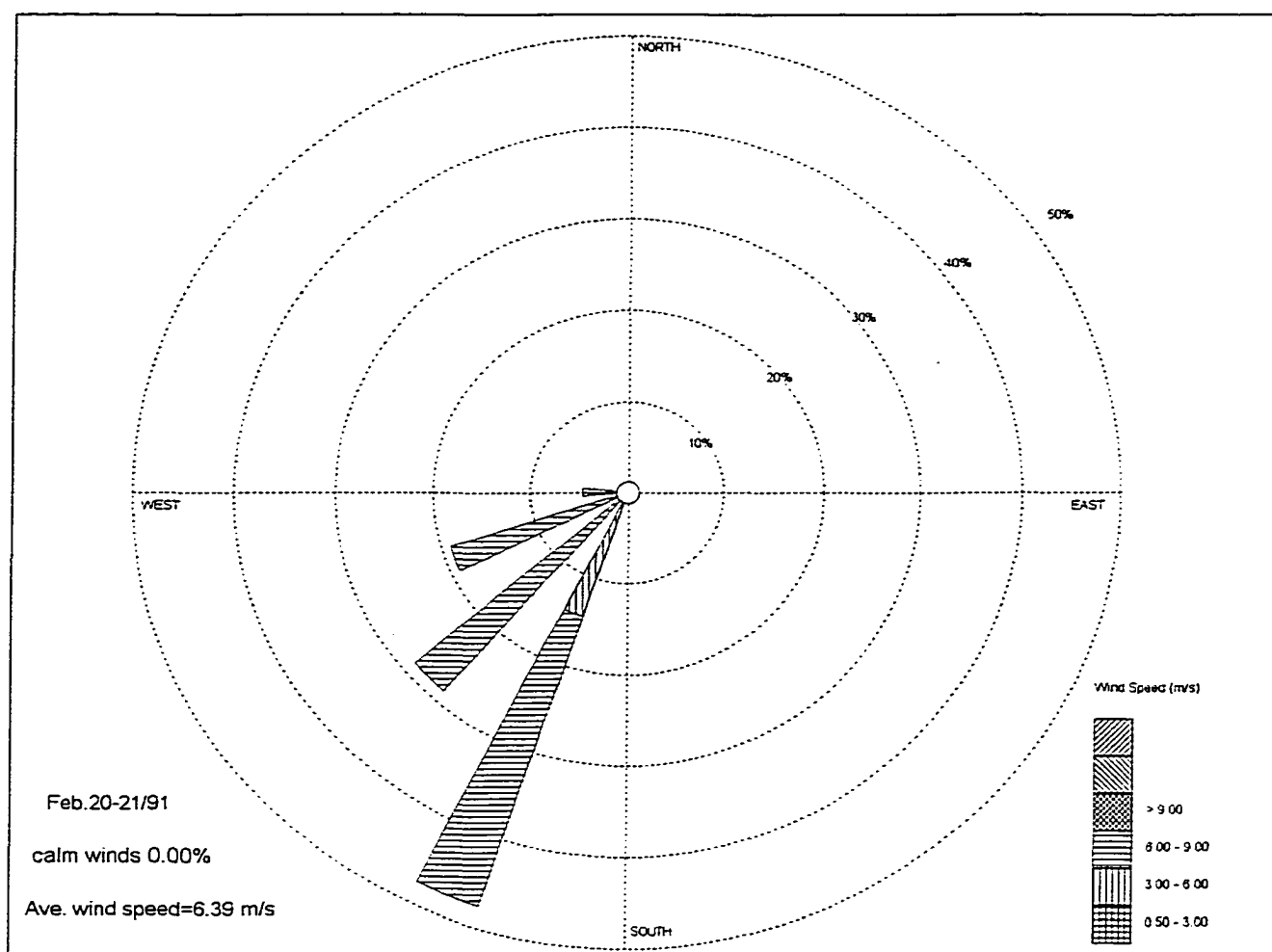
Figure 94.    Wind rose for February 20-21, 1991.

Feb 20-21/91
Emission rate= 1 g/s
Max . conc.=2.48 ug/m^3 at (460,386)

23007=0.53 ug/m^3
23009= <0.00001 ug/m^3
23011= < 0.00001 ug/m^3
23013= <0.00001 ug/m^3
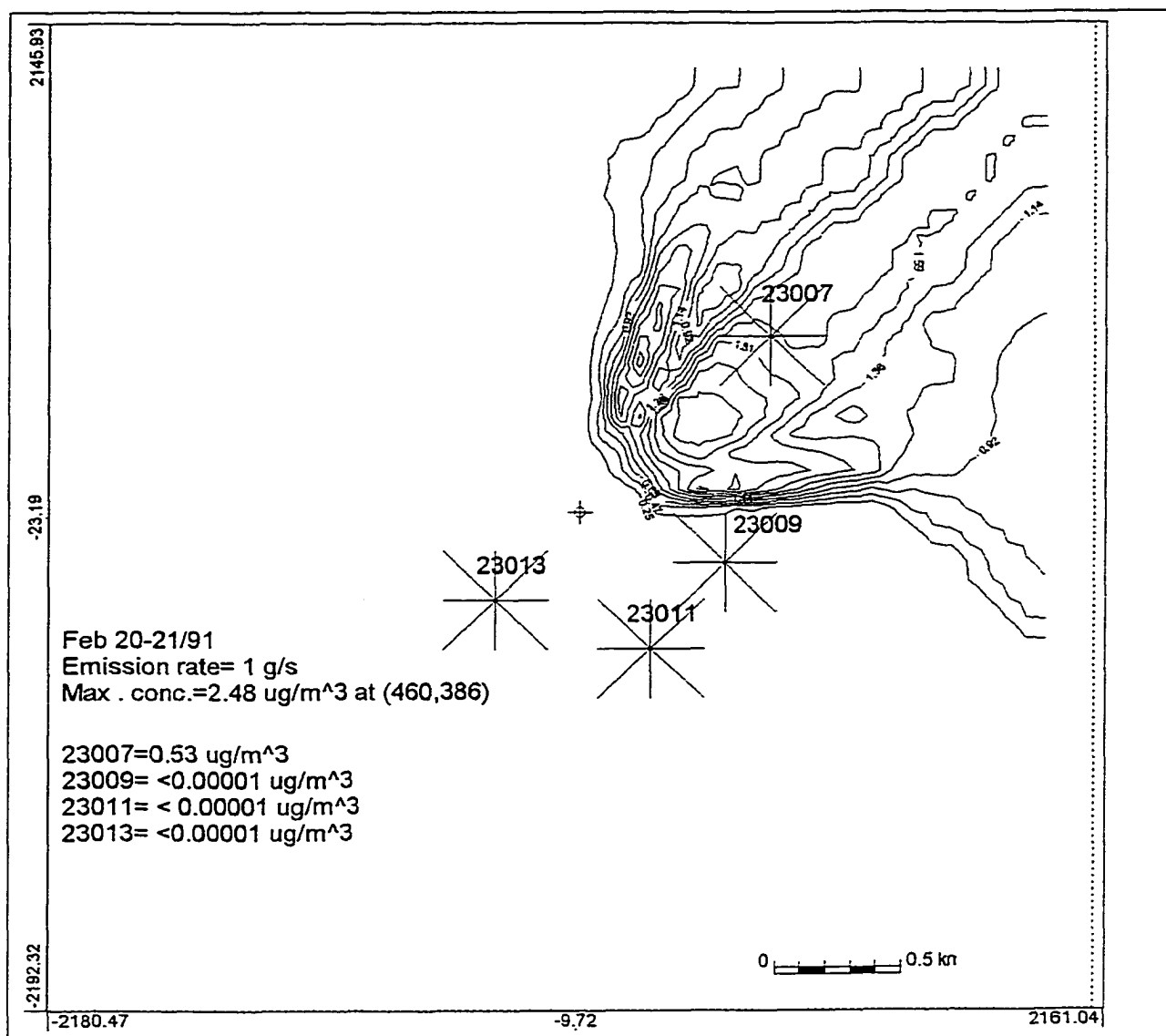
Figure 95.    Industrial Source Complex 3 — short term concentration isopleths for February 20-21, 1991.
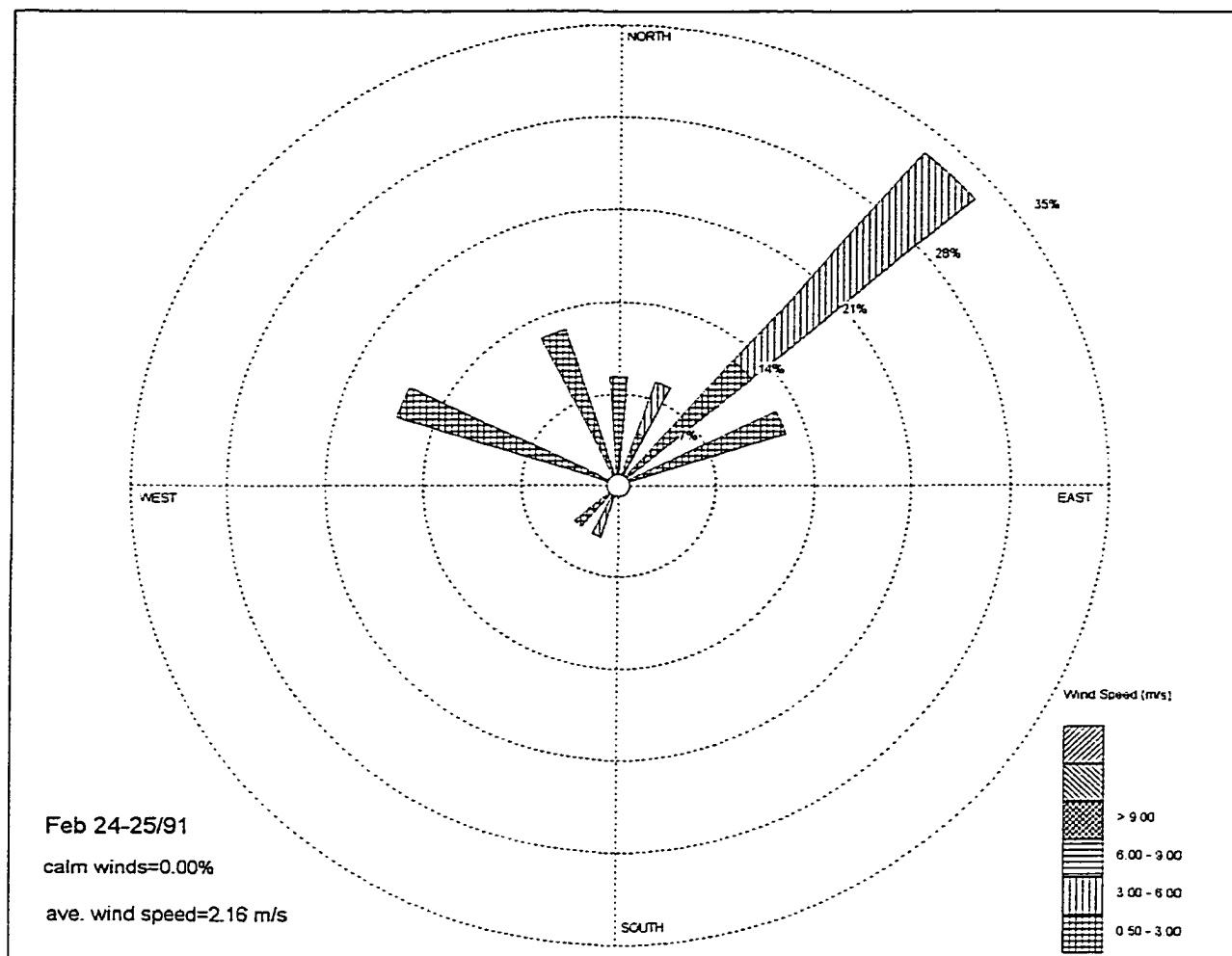
Figure 96.    Wind rose for February 24-25, 1991.
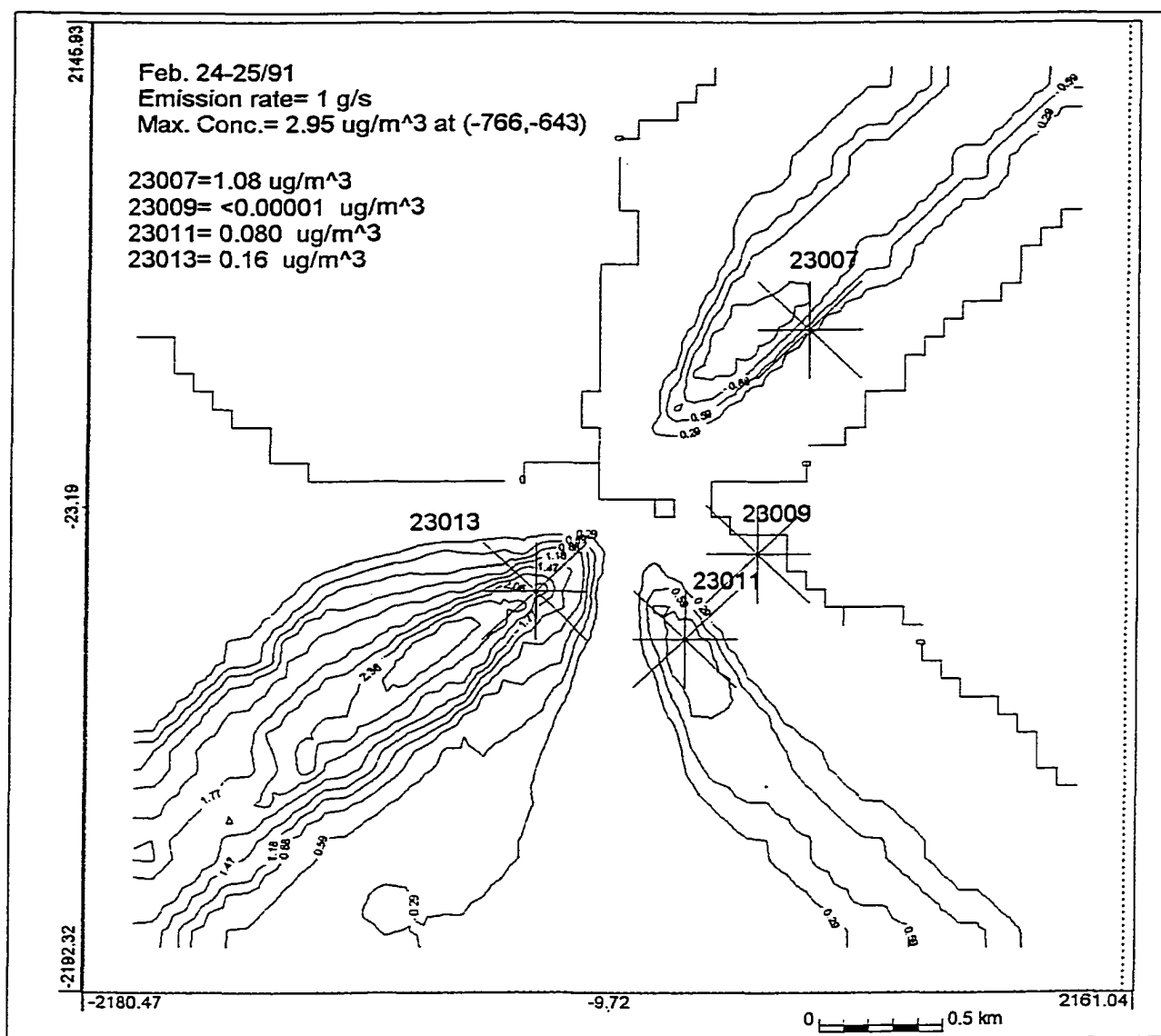
Figure 97.    Industrial Source Complex 3 – short term concentration isopleths for February 24-25, 1991.
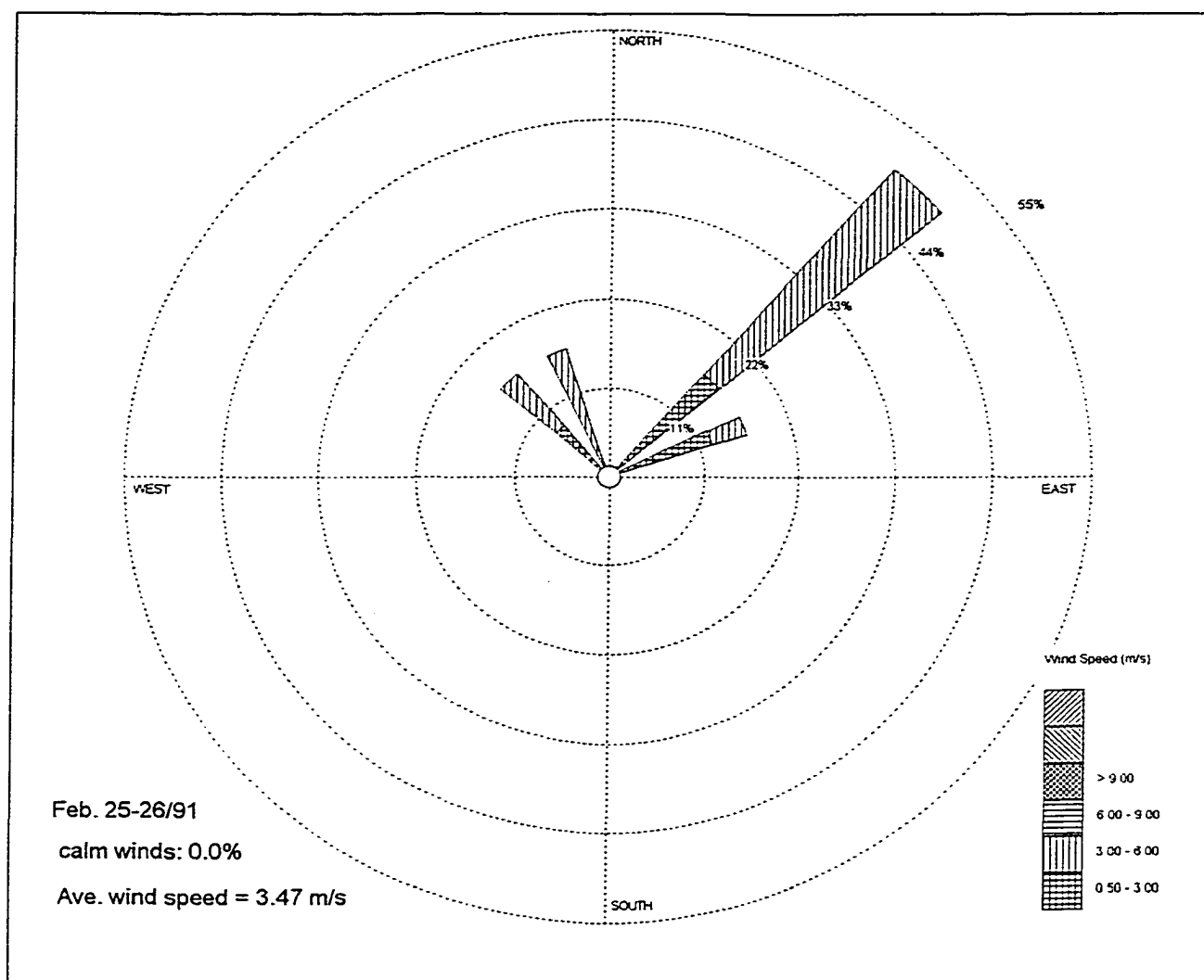
Figure 98.    Wind rose plot for February 25-26, 1991.
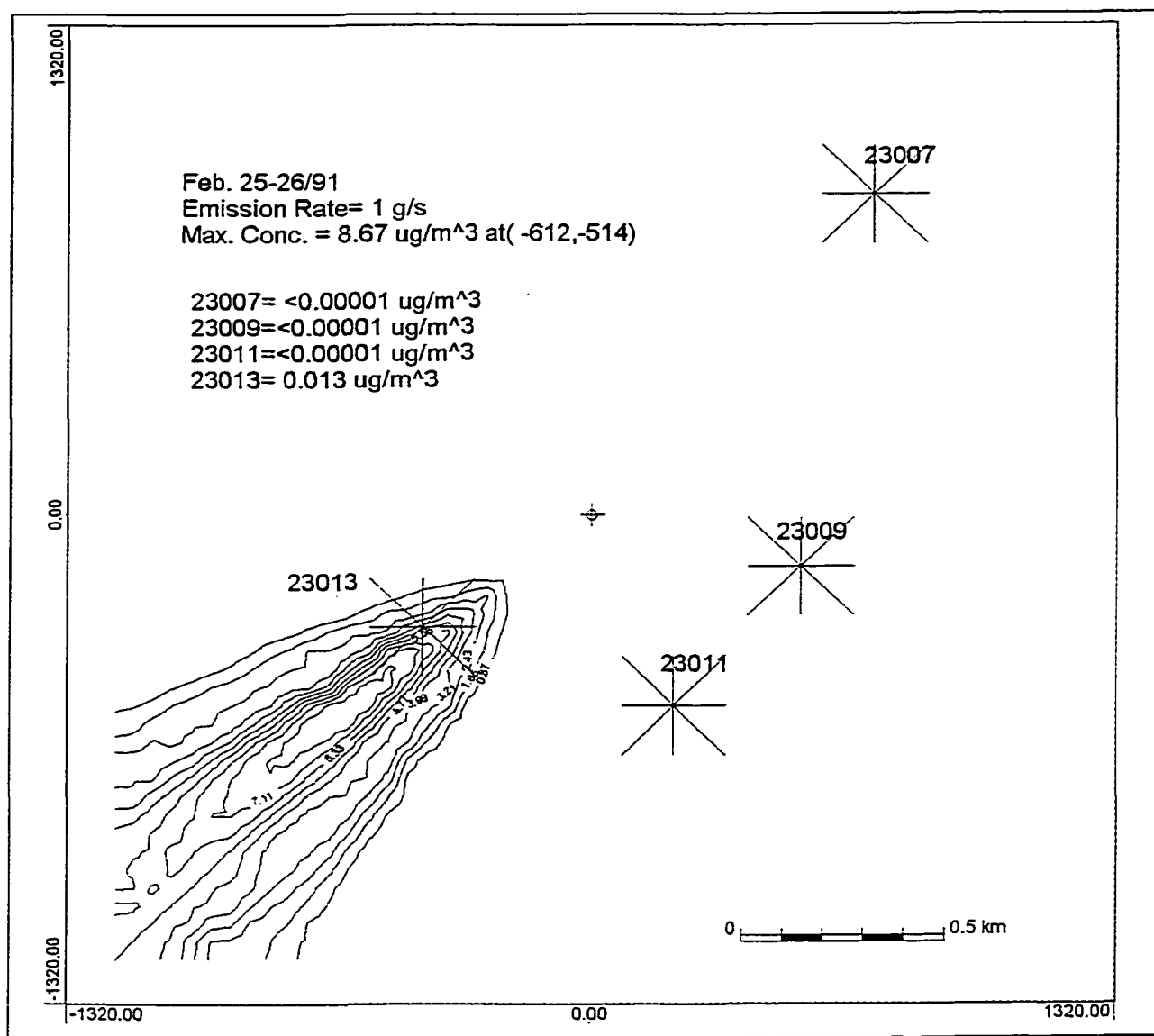
Figure 99.    Industrial Source Complex 3 − short term concentration isopleths for February 25-26, 1991.
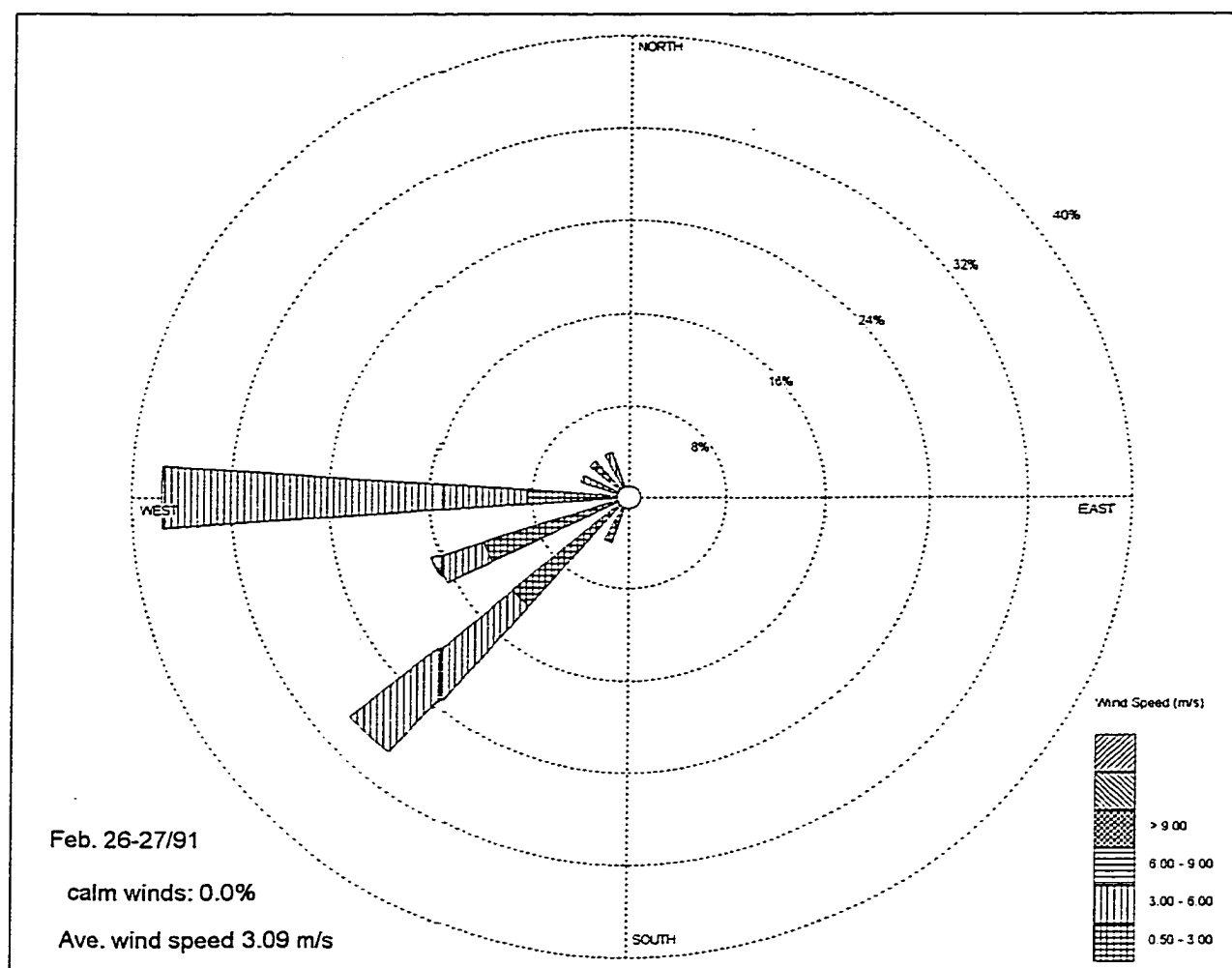
Figure 100.    Wind rose for February 26-27, 1991.
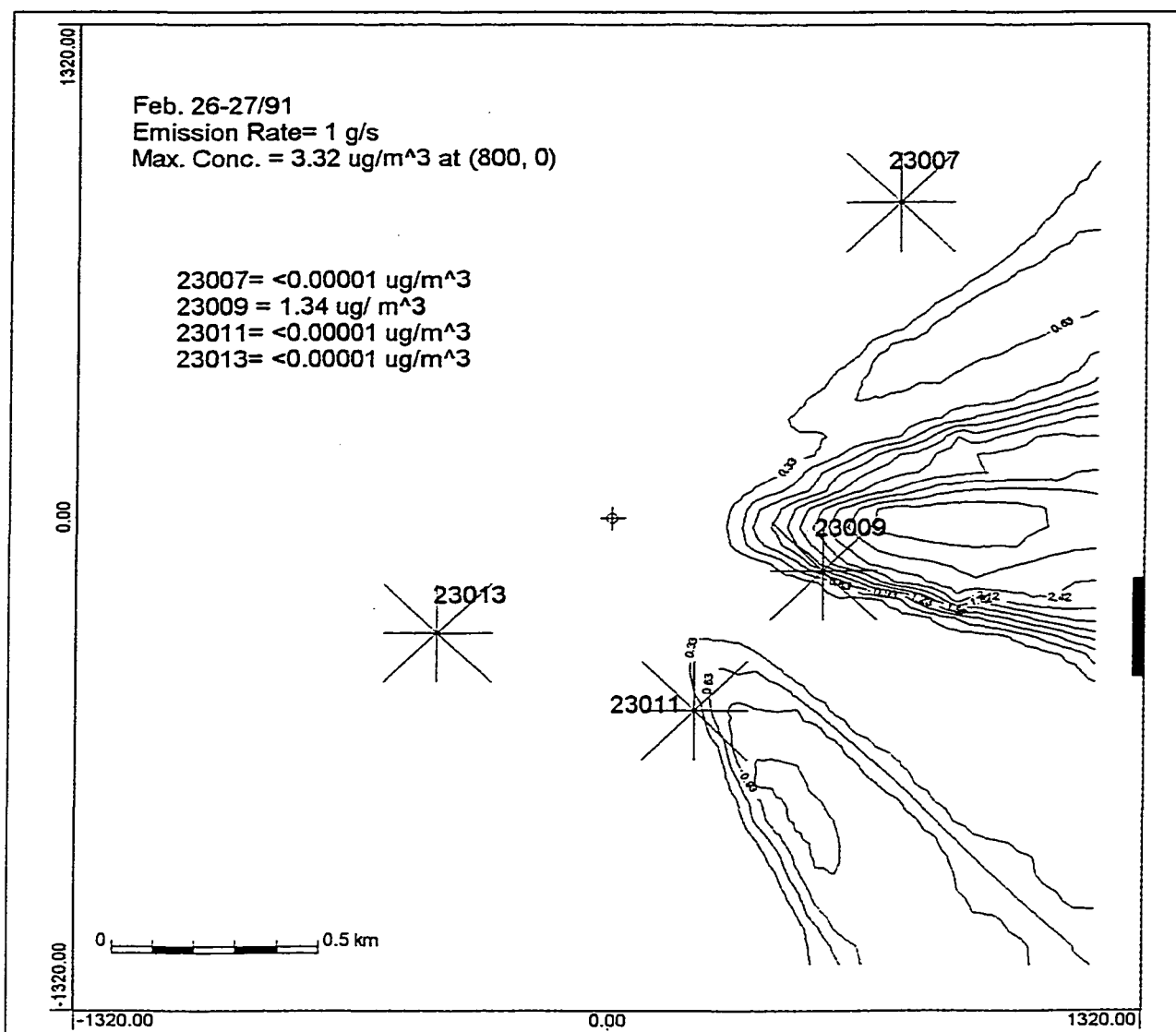
Figure 101.    Industrial Source Complex 3 — short term concentration isopleths for
February 26-27, 1991.

NORTH

35%

28%

21%

14%

7%

WEST

EAST

SOUTH

Wind Speed (m/s)

> 9 00

6 00 - 9 00

3 00 - 6 00

0 50 - 3 00

Jul. 10-11/91

calm winds: 0.0%

Ave. wind speed = 2.04 m/s
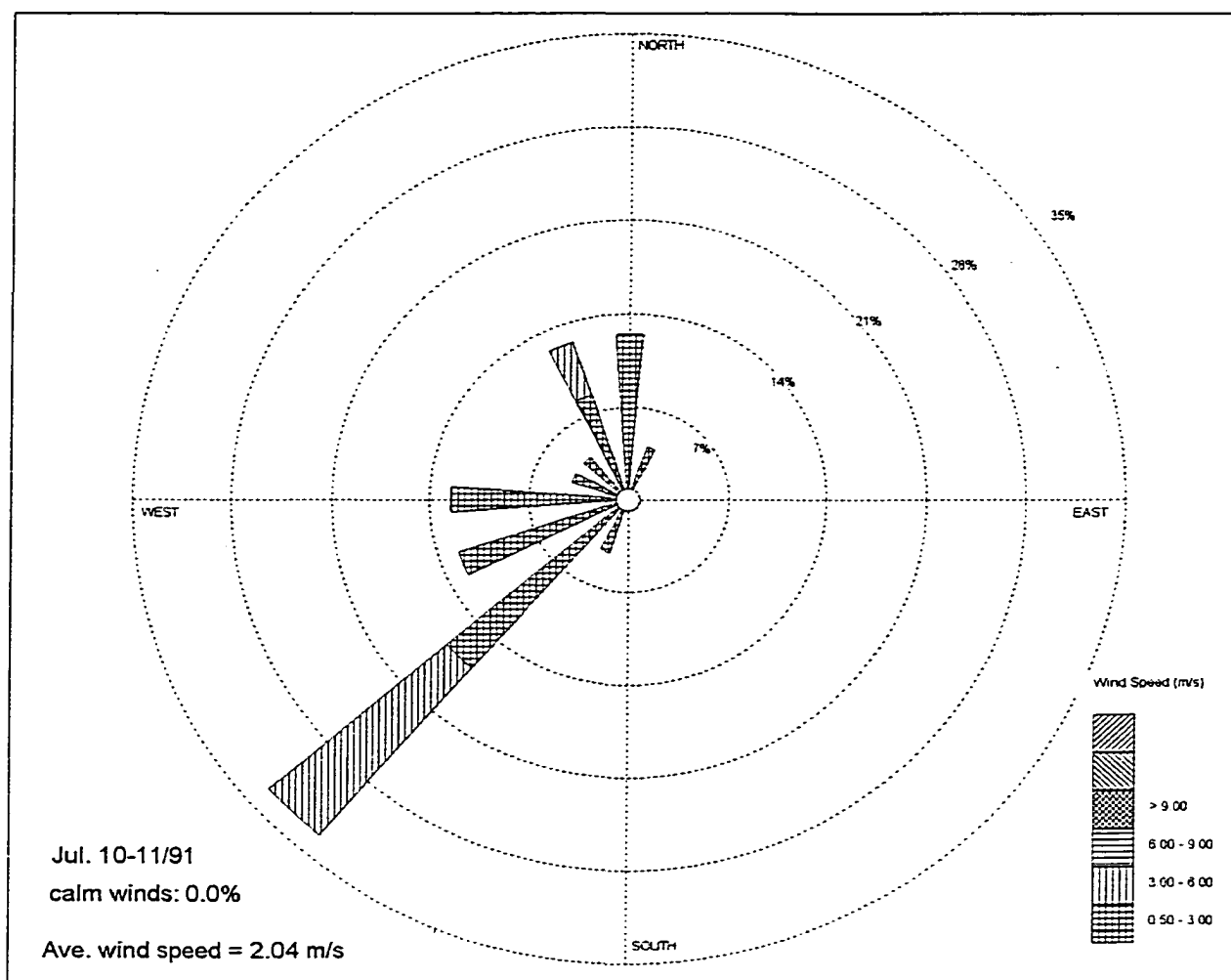
Figure 102.    Wind rose for July 10-11, 1991.

Figure 103. Industrial Source Complex 3 — short term concentration isopleths for July 10-11, 1991.
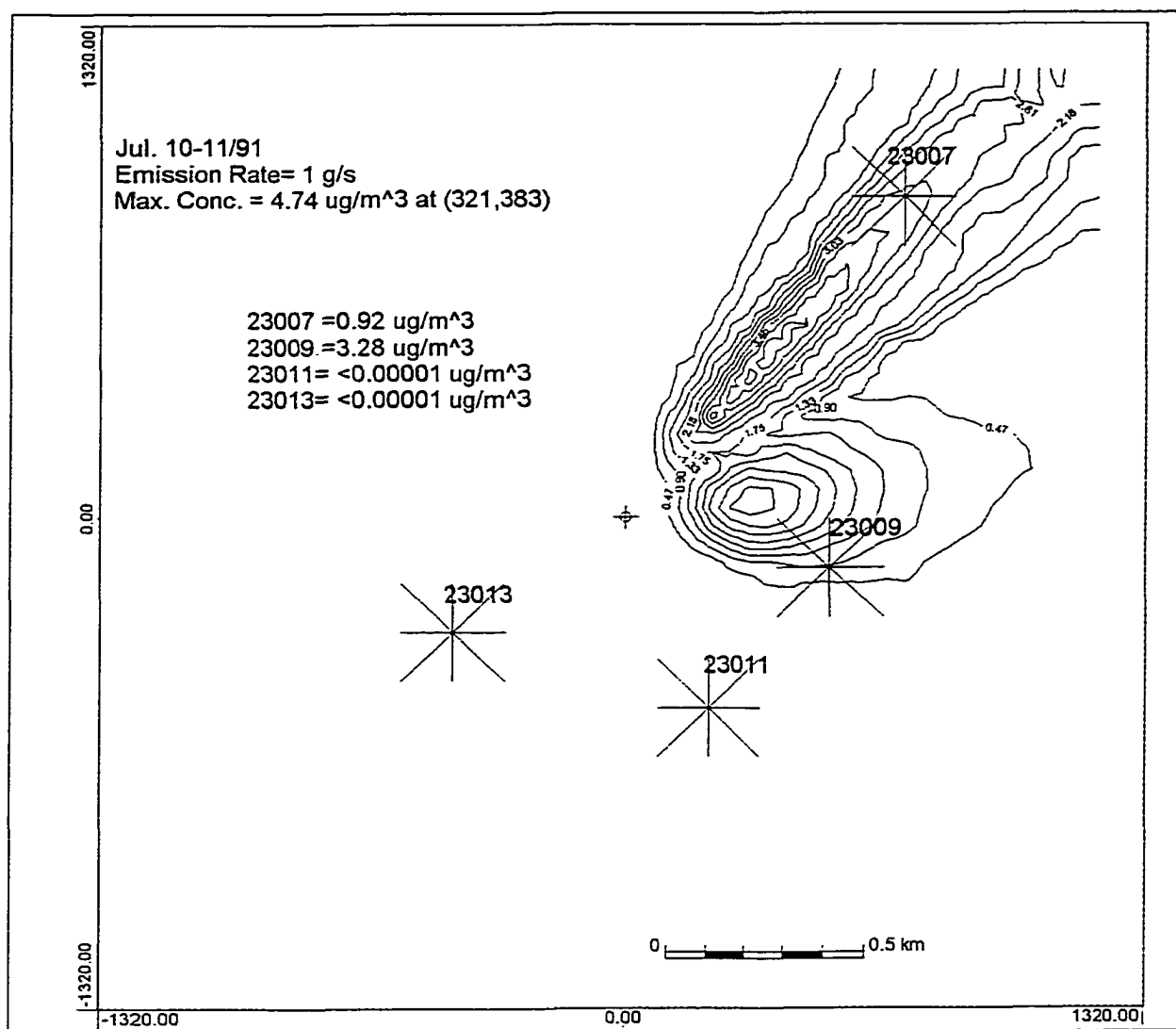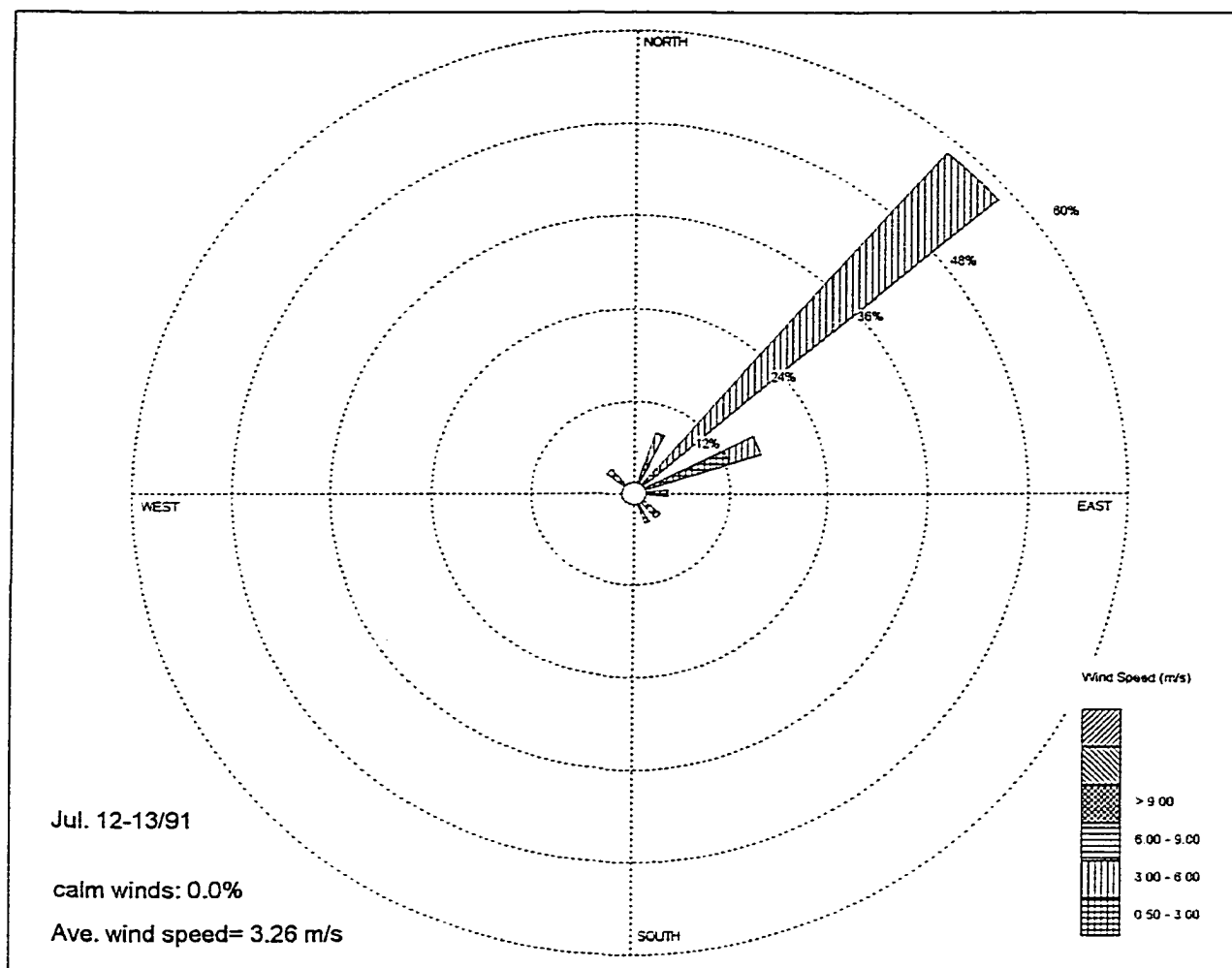
Figure 104.    Wind rose for July 12-13, 1991.
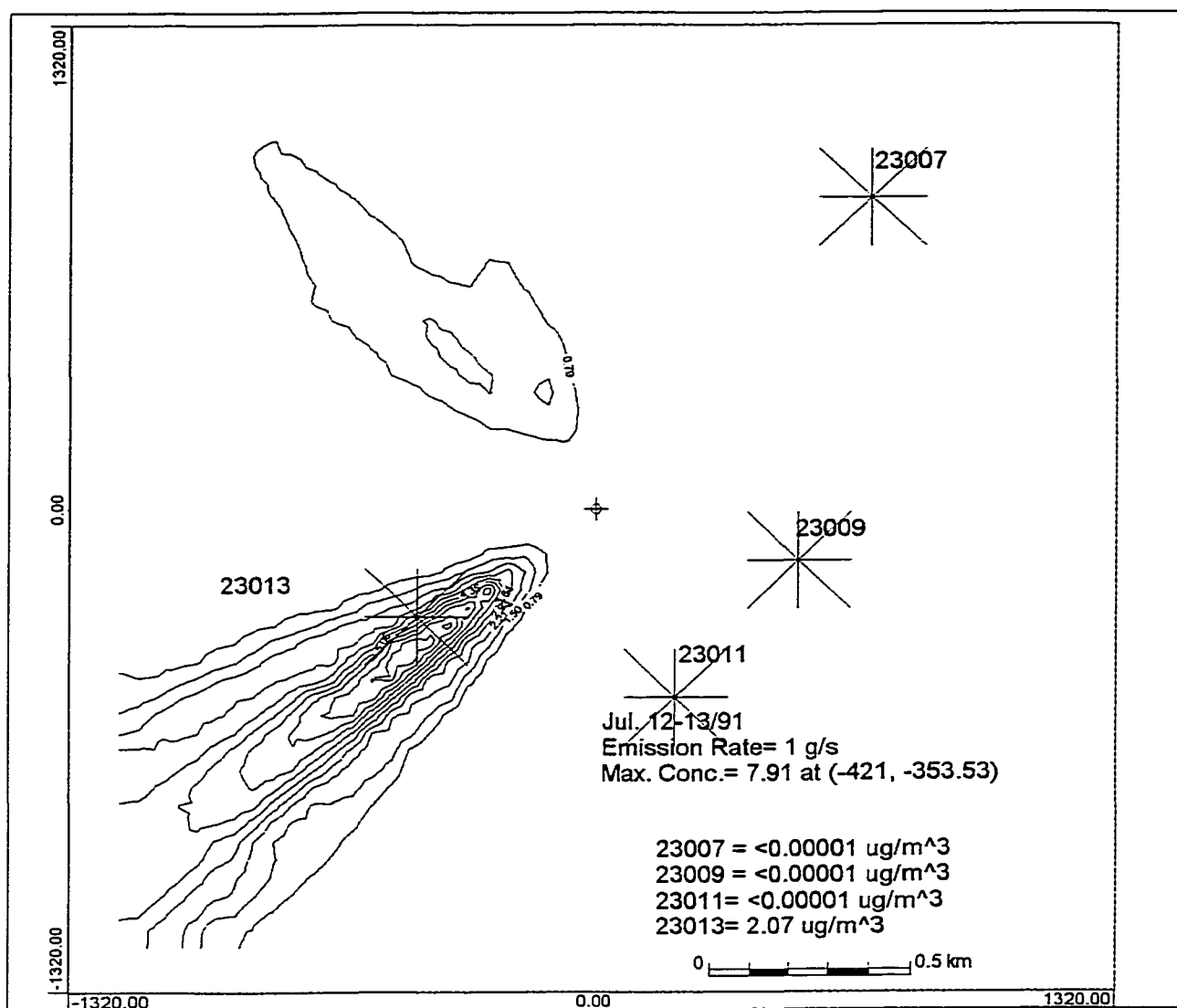
Figure 105. Industrial Source Complex 3 – short term concentration isopleths for July 12-13, 1991.

Jul. 13-14/91

calm winds: 0.0 %

Ave. wind speed 2.98 m/s

Wind Speed (m/s)

> 9.00

6.00 - 9.00

3.00 - 6.00

0.50 - 3.00
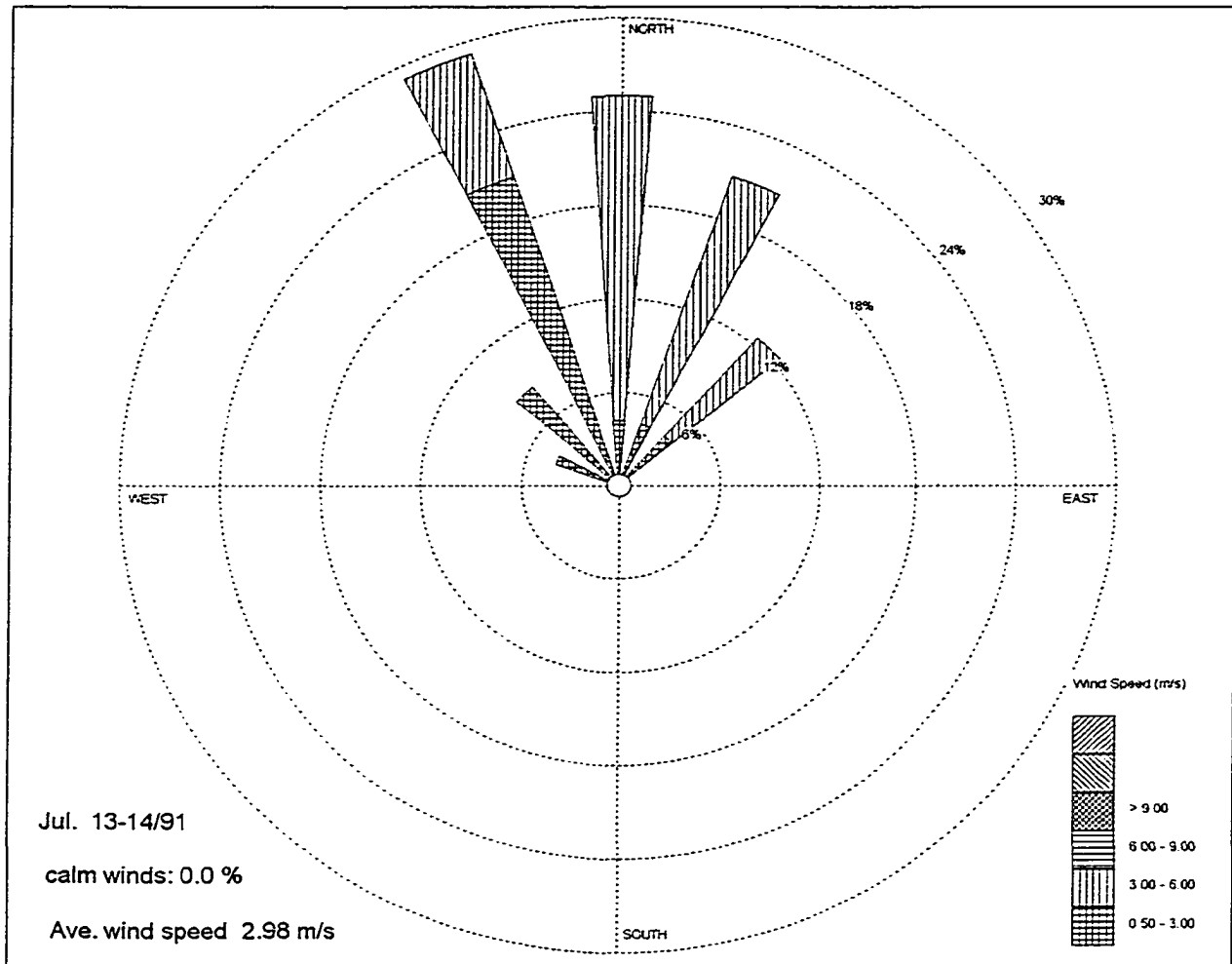
Figure 106.    Wind rose for July 13-14, 1991.

JUl. 13-14/91
Emission Rate= 1 g/s
Max. Conc.= 3.34 ug/m^3 at (-375,-650)

23007 = <0.00001 ug/m^3
23009 = <0.00001 ug/m^3
23011 = <0.00001 ug/m^3
23013= 0.33 ug/m^3

Figure 107.    Industrial Source Complex 3 — short term concentration isopleths for July 13-14, 1991.
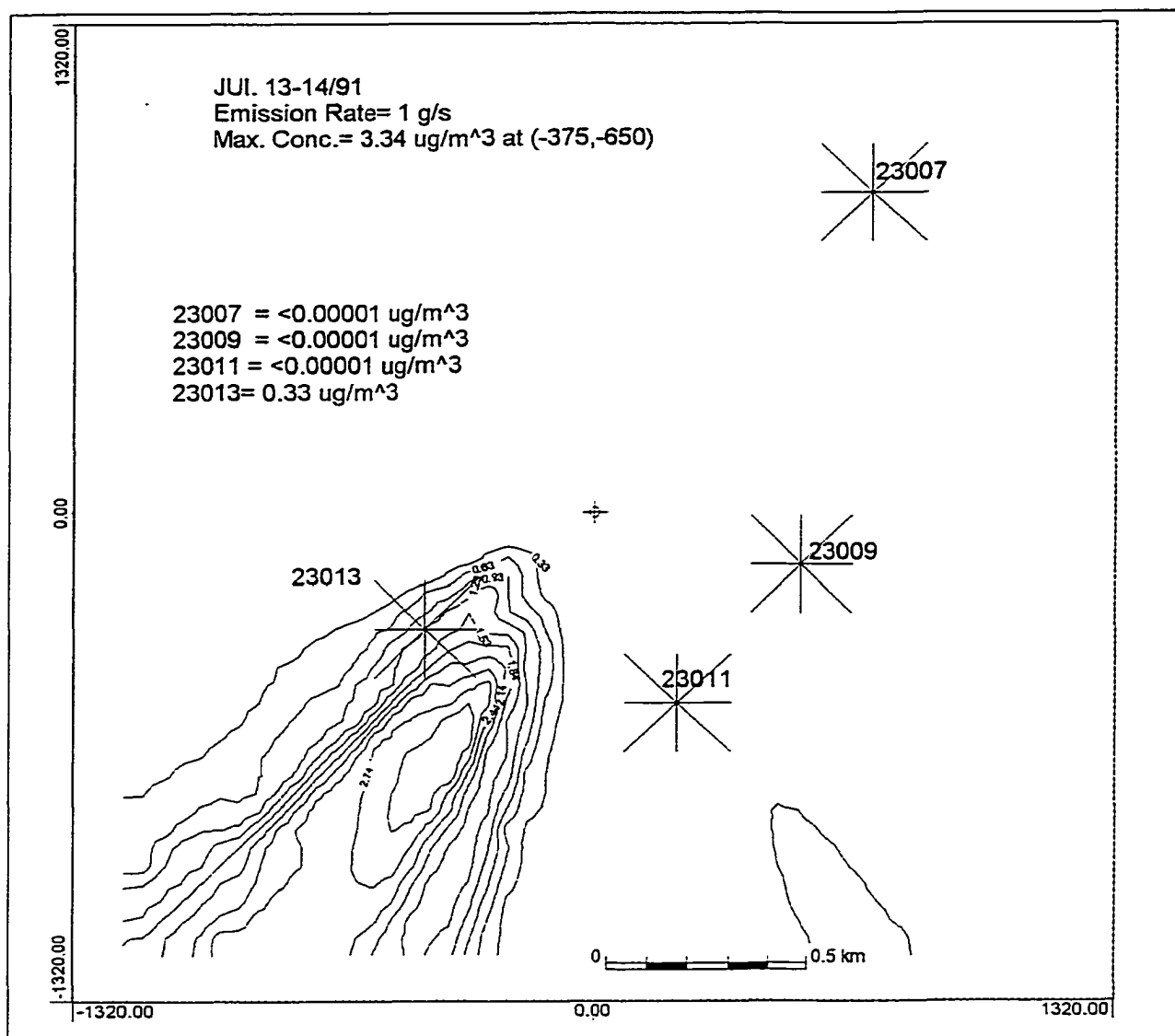
**TABLE CXIX**

OBSERVED AND MODELED POLYCHLORINATED BIPHENYL CONCENTRATIONS
FOR SITE IDENTIFICATION NUMBER 23007

| Actual PCBTOT emission rate (g/s) | Date | Test Designation | Flag | PCBTOT observed (ng/m^3) | PCBTOT calculated from model (ng/m^3) | Rank (observed) | Rank (modeled) |
|---|---|---|---|---|---|---|---|
| 1.37E-06 | 02/16/91 | I-1 | < | 0.2 | **1.62E-03** | 2 | 1 |
| 1.237E-06 | 02/19/91 | I-2 | < | 0.2 | **2.37E-03** | 1 | 1 |
| 1.402E-06 | 02/20/91 | I-3 | < | 0.2 | **7.43E-04** | 1 | 1 |
| 1.457E-06 | 02/24/91 | II-2 | | 0.7 | **1.57E-03** | 2 | 1 |
| 1.328E-06 | 02/25/91 | II-3 | < | 0.2 | 1.33E-08 | 2 | 2 |
| 1.677E-06 | 02/26/91 | II-4 | | 1.1 | 1.68E-08 | 2 | 2 |
| 1.378E-06 | 07/10/91 | V-2 | | 1.6 | 1.27E-03 | 1 | 2 |
| 1.067E-06 | 07/12/91 | V-3 | | 2.3 | 1.07E-08 | 2 | 2 |
| 1.394E-06 | 07/13/91 | V-4 | | 3.6 | 1.39E-08 | 3 | 2 |

**TABLE CXX**

OBSERVED AND MODELED POLYCHLORINATED BIPHENYL CONCENTRATIONS
FOR SITE IDENTIFICATION NUMBER 23009

| Actual PCBTOT emission rate (g/s) | Date | Test Designation | Flag | PCBTOT observed (ng/m^3) | PCBTOT calculated from model (ng/m^3) | Rank (observed) | Rank (modeled) |
|---|---|---|---|---|---|---|---|
| 1.37E-06 | 02/16/91 | I-1 | | **2.6** | 1.37E-08 | 1 | 2 |
| 1.237E-06 | 02/19/91 | I-2 | < | 0.2 | 6.93E-04 | 1 | 2 |
| 1.402E-06 | 02/20/91 | I-3 | < | 0.2 | 1.40E-08 | 1 | 2 |
| 1.457E-06 | 02/24/91 | II-2 | | 1.9 | 1.46E-08 | 1 | 4 |
| 1.328E-06 | 02/25/91 | II-3 | < | 0.2 | 1.33E-08 | 2 | 2 |
| 1.677E-06 | 02/26/91 | II-4 | <T | 0.7 | **2.25E-03** | 4 | 1 |
| 1.378E-06 | 07/10/91 | V-2 | | 1.5 | **4.52E-03** | 2 | 1 |
| 1.067E-06 | 07/12/91 | V-3 | | 1.5 | 1.07E-08 | 4 | 2 |
| 1.394E-06 | 07/13/91 | V-4 | | 3.4 | 1.39E-08 | 4 | 2 |

**TABLE CXXI**

OBSERVED AND MODELED POLYCHLORINATED BIPHENYL CONCENTRATIONS
FOR SITE IDENTIFICATION NUMBER 23011

| Actual PCBTOT emission rate (g/s) | Date | Test Designation | Flag | PCBTOT observed (ng/m^3) | PCBTOT calculated from model (ng/m^3) | Rank (observed) | Rank (modeled) |
|---|---|---|---|---|---|---|---|
| 1.37E-06 | 02/16/91 | I-1 | < | 0.2 | 1.37E-08 | 2 | 2 |
| 1.237E-06 | 02/19/91 | I-2 | < | 0.2 | 1.24E-08 | 1 | 3 |
| 1.402E-06 | 02/20/91 | I-3 | < | 0.2 | 1.40E-08 | 1 | 2 |
| 1.457E-06 | 02/24/91 | II-2 | | 2.3 | 1.17E-04 | 3 | 3 |
| 1.328E-06 | 02/25/91 | II-3 | | 0.4 | 1.33E-08 | 1 | 2 |
| 1.677E-06 | 02/26/91 | II-4 | | 5 | 1.68E-08 | 1 | 2 |
| 1.378E-06 | 07/10/91 | V-2 | | 1 | 1.38E-08 | 4 | 3 |
| 1.067E-06 | 07/12/91 | V-3 | < | 0.2 | 1.07E-08 | 1 | 2 |
| 1.394E-06 | 07/13/91 | V-4 | | 4.3 | 1.39E-08 | 1 | 2 |

**TABLE CXXII**

OBSERVED AND MODELED POLYCHLORINATED BIPHENYL CONCENTRATIONS
FOR SITE IDENTIFICATION NUMBER 23013

| Actual PCBTOT emission rate (g/s) | Date | Test Designation | Flag | PCBTOT observed (ng/m^3) | PCBTOT calculated from model (ng/m^3) | Rank (observed) | Rank (modeled) |
|---|---|---|---|---|---|---|---|
| 1.37E-06 | 02/16/91 | I-1 | < | 0.2 | 1.37E-08 | 2 | 2 |
| 1.237E-06 | 02/19/91 | I-2 | < | 0.2 | 1.24E-08 | 1 | 3 |
| 1.402E-06 | 02/20/91 | I-3 | < | 0.2 | 1.40E-08 | 1 | 2 |
| 1.457E-06 | 02/24/91 | II-2 | < | 0.2 | 2.33E-04 | 4 | 2 |
| 1.328E-06 | 02/25/91 | II-3 | < | 0.2 | **1.73E-05** | 2 | 1 |
| 1.677E-06 | 02/26/91 | II-4 | | 4.8 | 1.68E-08 | 2 | 2 |
| 1.378E-06 | 07/10/91 | V-2 | | 1 | 1.38E-08 | 3 | 3 |
| 1.067E-06 | 07/12/91 | V-3 | | 1.9 | **2.21E-03** | 3 | 1 |
| 1.394E-06 | 07/13/91 | V-4 | | 3.7 | **4.60E-04** | 2 | 1 |

## 4.8.2 Receptor Modeling

Historically, receptor modeling has usually been applied to particulates, metals, and VOCs [196, 274]. More recently, advances have been made allowing receptor modeling to be used for PAH from combustion sources [275] and other organic aerosols [276]. Simcik, et al. applied receptor modeling techniques to look at source/sink relationships for PAH in the Chicago area [277], but did not discuss the corresponding PCB data. The literature review for this project did not identify any previous use of receptor modeling for PCBs in ambient air samples. One of the primary needs for carrying out receptor modeling is a reasonable number of good, quality source profiles. While these may exist for PCBs, they do not appear to be publicly available. Another unique aspect of this project was the availability of good quality data, for different sources from the source testing (Table CXXIII) and on-site monitoring. Source profiles were developed for 5 on-site sources: Incinerator Stack (stack), Containment Building (contbldg), Dome (dome), Thomas Quonset water treatment building (Thomas), and the Shredder area (shredr). Data for sources were not available electronically and were manually entered into Excel for only a few samples of each source type. Only limited homolog data were available for sources because of the DL used and limited number of samples. The source profile for the incinerator stack using different treatments of ND data is shown in Figure 108. The source profiles for the five sources that were used in this research are shown in Table CXXIV. The source profiles in Table CXXIV are compared in Figure 109.

Receptor modeling could only be applied to samples with PCBTOT above the QL (366 out of 1584 air samples) and at least one homolog observed. There were 312 of the 366

air samples with at least one homolog detected. There are $2^k$ possible equations for the receptor model for each sample, where k=5 sources and $2^5$=32. Therefore, there are a total of 312*32=9984 possible models. The sources were fit using SAS$^{tm}$ based on least square fit with the intercept = 0. Forward, Backward and Stepwise model selection procedures were compared on a small subset, and found to give the same answer for the "best" model (highest $r^2$ value was usually the best). The precision of the data was also accounted for using weighting, in order to prevent higher concentrations from having too great an influence. After this step, only non-negative contributions were retained as "valid" models. Next, the critical values (at 0.95, 0.9 and 0.5) for the analysis of variance (ANOVA) F test were calculated for each sample. Models with $F_{calculated} > F_{critical}$ were retained as valid models. In some cases, multiple models were still retained. (The models reduced by selecting only those with an $r^2$, which is within 0.05 of the maximum $r^2$.) The final model for each sample was then calculated based on the average of each source contribution. The model selection steps are summarized in Table CXXV below. The summary statistics for the source contributions (absolute and relative mass fractions) calculated are provided in Table CXXVI below. In all cases, the Thomas water treatment building had the highest mean and maximum values, and appears to be the leading source. Because the data in Table CXXVI are summary statistics, they do not necessarily represent the relative contribution for each sample.

The observed RM, and ADM results are compared for the 35 samples taken during Source Testing in Table CXXVII. Valid receptor models were produced for 8 of the 35 samples (6 of 35 for 20% precision weighting). For these samples, the <u>maximum</u>

contribution for the incinerator stack calculated by RM was approximately 10% (Table CXXVIII).

It is recognized that this RM was not the definitive study. The results were mainly used as qualitative reinforcement for the conclusions in other Sections. Some possible sources of error in using RM here include the following.

- Stack profile was based upon Series I & II data, because Series V homolog data were not initially available; subsequent to running the model, however, the homolog profile became available. Using the Series V data might have made a difference in the RM results.

- Source profiles used for RM were based on the limited data available electronically, initially representing the average for a few samples early in the program. Data for additional on-site samples are now available in printed format. Using all of the data for each source to determine an "average" profile or to produce source profiles that change with time may have given different results.

- The PCBDI-PCBPNT were the most often reported PCB homologs. Having mono-PCB homolog information may have helped with assigning source contributions.

- The model did not see all sources in all samples. This may have been due either to fluctuations in the source emissions or to the relatively high detection limits used.

**TABLE CXXIII**

POLYCHLORINATED BIPHENYL HOMOLOG DATA FOR INCINERATOR STACK

| | ND | mean value | std. dev. | rel. mass fraction including mono | mean value no mono | rel. mass fraction no mono |
|---|---|---|---|---|---|---|
| | | ng/dscm | | | ng/dscm | |
| MONOPCB | | 3.11 | 4.26 | 0.01 | | |
| PCBDI | | 22.80 | 12.25 | 0.05 | 22.80 | 0.06 |
| PCBTRI | | **145.12** | 98.31 | 0.35 | **145.12** | **0.35** |
| PCBTET | | 132.20 | 29.62 | 0.32 | 132.20 | 0.32 |
| PCBPNT | | 58.54 | 61.03 | 0.14 | 58.54 | 0.14 |
| PCBHEX | | 32.12 | 32.48 | 0.08 | 32.12 | 0.08 |
| PCBHEPT | | 13.91 | 13.72 | 0.03 | 13.91 | 0.03 |
| PCBOCT | | 3.05 | 4.52 | 0.01 | 3.05 | 0.01 |
| PCBNON | | 2.97 | 4.15 | 0.01 | 2.97 | 0.01 |
| PCBDEC | | 3.28 | 3.92 | 0.01 | 3.28 | 0.01 |
| sum MONO-DEC PCBs | | 417.11 | 54.22 | 1.00 | | |
| sum DI-DEC PCBs | | 414.00 | 52.52 | 0.99 | 414.00 | 1.00 |
| difference | | 3.11 | 4.26 | | | |
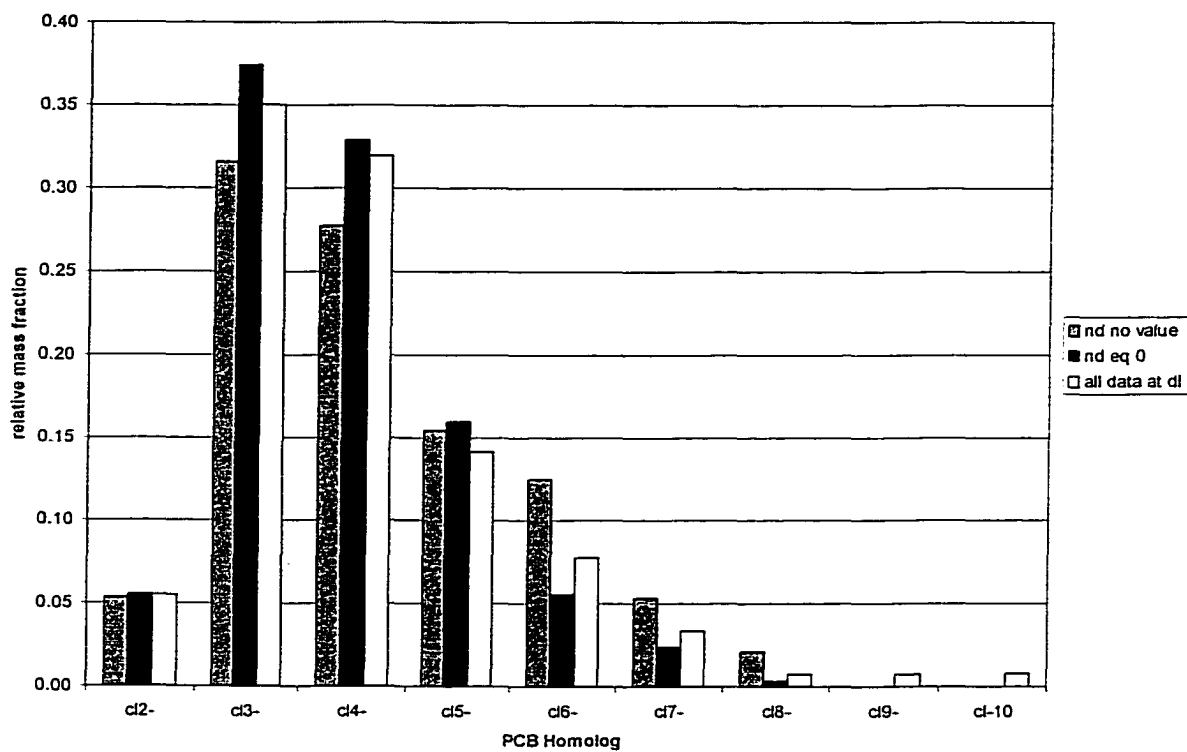
Figure 108.   Incinerator stack polychlorinated biphenyl homolog profiles based on different treatment of non-detect data.

**TABLE CXXIV**

POLYCHLORINATED BIPHENYL SOURCE PROFILES
USED FOR RECEPTOR MODELING

| ANALYTE_ | Incinerator Stack | Containment Building | Dome | Thomas Water Treatment Building | Shredder Area |
|---|---|---|---|---|---|
| PCBDI | 0.00842 | 0.0348 | 0.0227 | 0.0176 | 0.0438 |
| PCBTRI | 0.0573 | 0.0429 | 0.0504 | 0.0346 | 0.0370 |
| PCBTET | 0.0316 | 0.0152 | 0.0269 | 0.0387 | 0.0192 |
| PCBPNT | 0.00264 | 0.00491 | 0 | 0.00458 | 0 |
| PCBHEX | 0 | 0.00223 | 0 | 0.00359 | 0 |
| PCBHEPT | 0 | 0 | 0 | 0.000817 | 0 |
| PCBOCT | 0 | 0 | 0 | 0 | 0 |
| PCBNON | 0 | 0 | 0 | 0 | 0 |
| PCBDEC | 0 | 0 | 0 | 0 | 0 |
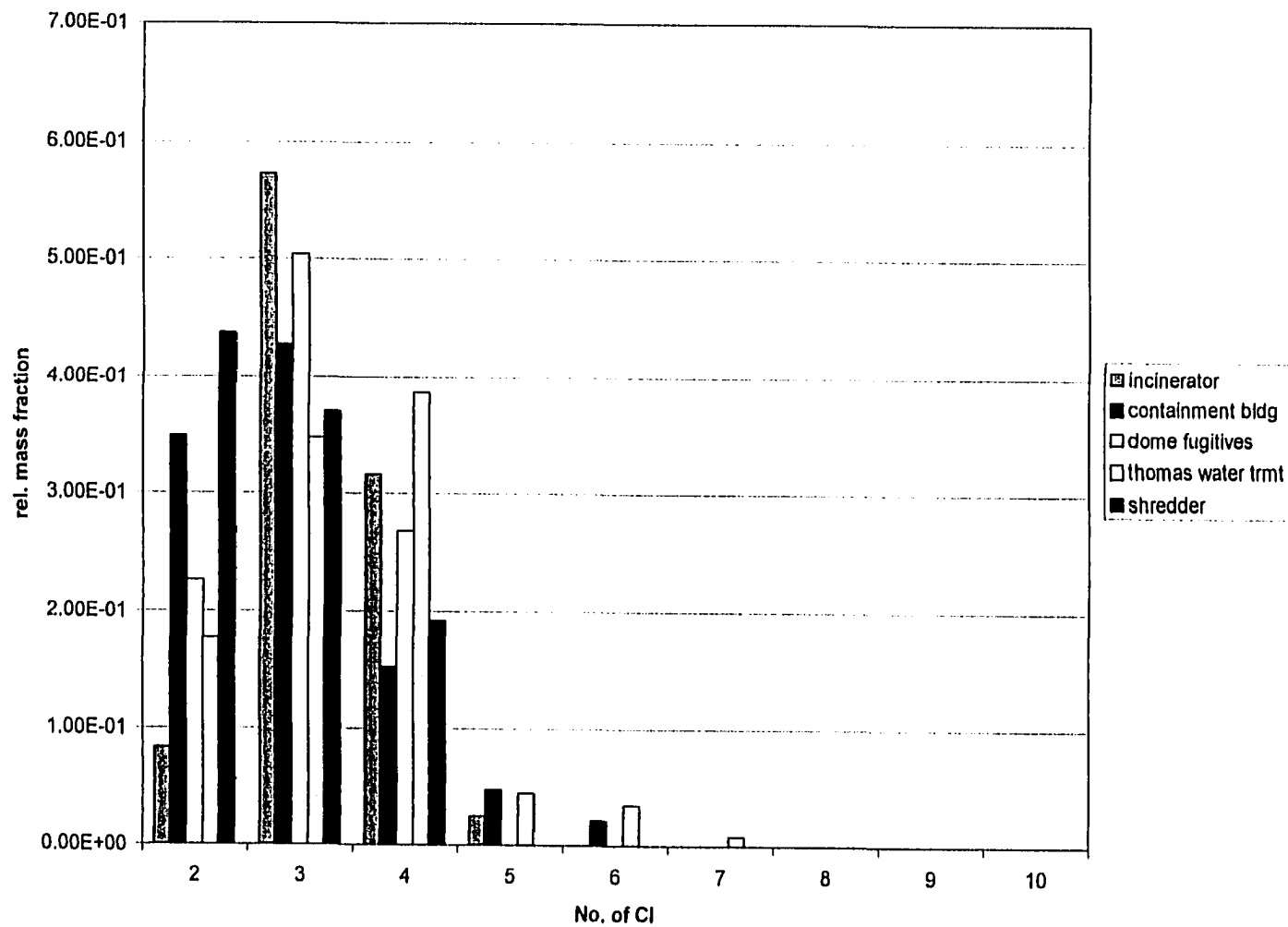
Figure 109.　Source profiles used for receptor modeling.

**TABLE CXXV**

SUMMARY OF RECEPTOR MODELING STEPS

| | No weighting | weighting for 10% precision | weighting for 20% precision |
|---|---|---|---|
| n for all off site samples | 1584 | 1584 | 1584 |
| n for PCBTOT quantified | 366 | 366 | 366 |
| n for 1 or more homolog quantified | 312 | 312 | 312 |
| n of source profiles ($k$) | 5 | 5 | 5 |
| n of possible source profiles = 312*2^k=312*32 | 9984 | 9984 | 9984 |
| n of models with fit | 9672 | 9672 | 9672 |
| n of models with non negative values | 2315 | 2250 | 2250 |
| n of models with valid F | 2164 | 2063 | 2027 |
| n of models > Fcrit 0.95 | | | |
| n of models> Fcrit 0.9 | | | |
| n of models > Fcrit 0.5 | 1620 | 1256 | 1097 |
| n of models with adjrsq differ <0.05 | 571 | 444 | 385 |
| n of unique sample n acceptable models | 224 | 217 | 191 |

**Note:**

F = the F statistic

Fcrit = Critical value of the F statistic

## TABLE CXXVI

## SUMMARY STATISTICS FOR SOURCE CONTRIBUTIONS
## IN AIR SAMPLES (VALUES IN ng/m³)

| Variable | n | n missing | n Contrib-ution > 0 | Mean Value (From SAS) | Std. Dev. | MIN. | MAX. | Median |
|---|---|---|---|---|---|---|---|---|
| STACK | 224 | 0 | 113 | 1.14E+00 | 2.77E+00 | 0.00E+00 | 3.39E+01 | 4.45E-02 |
| CONTBLDG | 224 | 0 | 117 | 1.85E+00 | 3.83E+00 | 0.00E+00 | 3.16E+01 | 1.69E-02 |
| DOME | 224 | 0 | 55 | 5.43E-01 | 1.41E+00 | 0.00E+00 | 9.96E+00 | 0.00E+00 |
| THOMAS | 224 | 0 | 101 | 1.70E+00 | 4.31E+00 | 0.00E+00 | 5.45E+01 | 0.00E+00 |
| SHREDR | 224 | 0 | 67 | 8.08E-01 | 3.17E+00 | 0.00E+00 | 3.56E+01 | 0.00E+00 |
| stack_fract | 224 | 0 | | 2.23E-01 | 3.69E-01 | 0.00E+00 | 1.30E+00 | 9.69E-03 |
| contbldg_fract | 224 | 0 | | 2.06E-01 | 3.42E-01 | 0.00E+00 | 1.19E+00 | 6.64E-03 |
| dome_fract | 217 | 7 | | 4.10E-02 | 1.15E-01 | 0.00E+00 | 7.24E-01 | 0.00E+00 |
| thomas_fract | 224 | 0 | | 3.39E-01 | 4.67E-01 | 0.00E+00 | 1.27E+00 | 0.00E+00 |
| shredr_fract | 224 | 0 | | 1.28E-01 | 2.92E-01 | 0.00E+00 | 1.20E+00 | 0.00E+00 |
| _RSQ_ | 224 | 0 | | 6.80E-01 | 2.26E-01 | 1.06E-01 | 9.97E-01 | 7.53E-01 |
| _ADJRSQ_ | 224 | 0 | | 6.35E-01 | 2.51E-01 | 6.23E-03 | 9.96E-01 | 7.02E-01 |
| Weighting 10% | | | | | | | | |
| STACK1 | 217 | 7 | 117 | 9.10E-01 | 2.44E+00 | 0.00E+00 | 2.75E+01 | 0.00E+00 |
| CONTBLD1 | 217 | 7 | 113 | 1.56E+00 | 3.36E+00 | 0.00E+00 | 2.33E+01 | 0.00E+00 |
| DOME1 | 217 | 7 | 55 | 4.07E-01 | 1.38E+00 | 0.00E+00 | 1.46E+01 | 0.00E+00 |
| THOMAS1 | 217 | 7 | 94 | 4.10E-01 | 7.60E-01 | 0.00E+00 | 8.22E+00 | 0.00E+00 |
| SHREDR1 | 217 | 7 | 67 | 7.09E-01 | 3.35E+00 | 0.00E+00 | 3.45E+01 | 0.00E+00 |
| stack1_fract | 217 | 7 | | 1.62E-01 | 2.63E-01 | 0.00E+00 | 1.05E+00 | 0.00E+00 |
| contbld1_fract | 217 | 7 | | 1.69E-01 | 2.84E-01 | 0.00E+00 | 9.98E-01 | 0.00E+00 |
| | | | | | | | | |
| thomas1_frac | 217 | 7 | | 1.20E-01 | 1.90E-01 | 0.00E+00 | 9.34E-01 | 0.00E+00 |
| shredr1_fract | 217 | 7 | | 8.33E-02 | 1.75E-01 | 0.00E+00 | 7.88E-01 | 0.00E+00 |
| RSQ1 | 217 | 7 | | 4.73E-01 | 3.02E-01 | 7.15E-02 | 9.94E-01 | 4.45E-01 |
| ADJRSQ1 | 217 | 7 | | 4.07E-01 | 3.34E-01 | 0.00E+00 | 9.92E-01 | 3.76E-01 |
| Weighting 20% | | | | | | | | |
| STACK2 | 191 | 33 | 112 | 8.47E-01 | 2.39E+00 | 0.00E+00 | 2.20E+01 | 0.00E+00 |
| CONTBLD2 | 191 | 33 | 115 | 1.17E+00 | 2.58E+00 | 0.00E+00 | 1.88E+01 | 0.00E+00 |
| DOME2 | 191 | 33 | 55 | 5.79E-01 | 1.73E+00 | 0.00E+00 | 1.46E+01 | 0.00E+00 |
| THOMAS2 | 191 | 33 | 71 | 1.77E-01 | 4.15E-01 | 0.00E+00 | 4.59E+00 | 0.00E+00 |
| SHREDR2 | 191 | 33 | 65 | 9.78E-01 | 4.59E+00 | 0.00E+00 | 5.16E+01 | 0.00E+00 |
| stack2_fract | 191 | 33 | | 1.34E-01 | 2.10E-01 | 0.00E+00 | 9.81E-01 | 0.00E+00 |
| contbld2_fract | 191 | 33 | | 1.34E-01 | 2.37E-01 | 0.00E+00 | 9.22E-01 | 0.00E+00 |
| dome2_fract | 191 | 33 | | 5.97E-02 | 1.53E-01 | 0.00E+00 | 7.28E-01 | 0.00E+00 |
| thomas2_frac | 191 | 33 | | 5.95E-02 | 1.12E-01 | 0.00E+00 | 5.22E-01 | 0.00E+00 |
| shredr2_fract | 191 | 33 | | 8.29E-02 | 1.65E-01 | 0.00E+00 | 8.39E-01 | 0.00E+00 |
| RSQ2 | 191 | 33 | | 4.22E-01 | 3.18E-01 | 5.93E-02 | 9.91E-01 | 3.28E-01 |

**Notes:**
fract =        relative fraction
RSQ =          $r^2$
ADJRSQ =       adjusted $r^2$

## TABLE CXXVII

OBSERVED, RECEPTOR MODELED AND INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM MODELED
PCBTOT CONCENTRATIONS FOR AMBIENT AIR SAMPLES DURING SOURCE TESTING

| sample date (mm/dd/yy) | SITE_ID2 | flag | PCBTOT Observed (ng/m^3) | STACK1 (ng/m^3) | CONT BLD1 (ng/m^3) | DOME1 (ng/m^3) | THOMAS1 (ng/m^3) | SHREDR1 (ng/m^3) | ISC3ST calculated concentration (ng/m^3) |
|---|---|---|---|---|---|---|---|---|---|
| 02/17/91 | 23007 | < | 0.20 | | | | | | 1.62E-03 |
| 02/20/91 | 23007 | < | 0.20 | | | | | | 2.37E-03 |
| 02/21/91 | 23007 | < | 0.20 | | | | | | 7.43E-04 |
| 02/25/91 | 23007 | <T | 0.70 | | | | | | 1.57E-03 |
| 02/26/91 | 23007 | < | 0.20 | | | | | | 1.33E-08 |
| 02/27/91 | 23007 | 0 | 1.10 | 0.00 | 0.00 | 0.00 | 0.82 | 0.00 | 1.68E-08 |
| 07/11/91 | 23007 | | 1.60 | | | | | | 1.27E-03 |
| 07/12/91 | 23007 | | 2.30 | | | | | | 1.07E-08 |
| 07/13/91 | 23007 | 0 | 3.60 | 0.00 | 0.41 | 0.00 | 0.00 | 0.49 | 1.39E-08 |

**TABLE CXXVII (Continued)**

OBSERVED, RECEPTOR MODELED AND INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM MODELED,
PCBTOT CONCENTRATIONS FOR AMBIENT AIR SAMPLES DURING SOURCE TESTING

| sample date (mm/dd/yy) | SITE_ ID2 | flag | PCBTOT Observed (ng/m^3) | STACK1 (ng/m^3) | CONT BLD1 (ng/m^3) | DOME1 (ng/m^3) | THOMAS1 (ng/m^3) | SHREDR1 (ng/m^3) | ISC3ST calculated concentration (ng/m^3) |
|---|---|---|---|---|---|---|---|---|---|
| 02/17/91 | 23009 | 0 | 2.60 | 0.00 | 0.00 | 0.00 | 0.98 | 0.00 | 1.37E-08 |
| 02/20/91 | 23009 | < | 0.20 | | | | | | 6.93E-04 |
| 02/21/91 | 23009 | < | 0.20 | | | | | | 1.40E-08 |
| 02/25/91 | 23009 | | 1.90 | | | | | | 1.46E-08 |
| 02/26/91 | 23009 | < | 0.20 | | | | | | 1.33E-08 |
| 02/27/91 | 23009 | <T | 0.70 | | | | | | **2.25E-03** |
| 07/11/91 | 23009 | | 1.50 | | | | | | **4.52E-03** |
| 07/12/91 | 23009 | | 1.50 | | | | | | 1.07E-08 |
| 07/13/91 | 23009 | 0 | 3.40 | 0.00 | 0.41 | 0.00 | 0.00 | 0.48 | 1.39E-08 |

TABLE CXXVII (Continued)

OBSERVED, RECEPTOR MODELED AND INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM MODELED,
PCBTOT CONCENTRATIONS FOR AMBIENT AIR SAMPLES DURING SOURCE TESTING

| sample date (mm/dd/yy) | SITE_ ID2 | flag | PCBTOT Observed (ng/m^3) | STACK1 (ng/m^3) | CONT BLD1 (ng/m^3) | DOME1 (ng/m^3) | THOMAS1 (ng/m^3) | SHREDR1 (ng/m^3) | ISC3ST calculated concentration (ng/m^3) |
|---|---|---|---|---|---|---|---|---|---|
| 02/17/91 | 23011 | < | 0.20 | | | | | | 1.37E-08 |
| 02/20/91 | 23011 | < | 0.20 | | | | | | 1.24E-08 |
| 02/21/91 | 23011 | < | 0.20 | | | | | | 1.40E-08 |
| 02/25/91 | 23011 | <T | 0.40 | | | | | | 1.17E-04 |
| 02/26/91 | 23011 | 0 | 5.00 | 0.00 | 0.00 | 0.00 | 1.01 | 0.00 | 1.33E-08 |
| 02/27/91 | 23011 | <T | 1.00 | | | | | | 1.68E-08 |
| 07/11/91 | 23011 | < | 0.20 | | | | | | 1.38E-08 |
| 07/12/91 | 23011 | | no sample | no sample | no sample | no sample | no sample | no sample | 1.07E-08 |
| 07/13/91 | 23011 | 0 | 4.30 | 0.60 | 0.00 | 0.53 | 0.00 | 0.00 | 1.39E-08 |

**TABLE CXXVII (Concluded)**

OBSERVED, RECEPTOR MODELED AND INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM MODELED,
PCBTOT CONCENTRATIONS FOR AMBIENT AIR SAMPLES DURING SOURCE TESTING

| sample date (mm/dd/yy) | SITE_ ID2 | flag | PCBTOT Observed (ng/m^3) | STACK1 (ng/m^3) | CONT BLD1 (ng/m^3) | DOME1 (ng/m^3) | THOMAS1 (ng/m^3) | SHREDR1 (ng/m^3) | ISC3ST calculated concentration (ng/m^3) |
|---|---|---|---|---|---|---|---|---|---|
| 02/17/91 | 23013 | < | 0.20 | | | | | | 1.37E-08 |
| 02/20/91 | 23013 | < | 0.20 | | | | | | 1.24E-08 |
| 02/21/91 | 23013 | < | 0.20 | | | | | | 1.40E-08 |
| 02/25/91 | 23013 | < | 0.20 | | | | | | 2.33E-04 |
| 02/26/91 | 23013 | < | 0.20 | | | | | | **1.73E-05** |
| 02/27/91 | 23013 | 0 | 4.80 | 0.00 | 0.00 | 0.00 | 1.04 | 0.00 | 1.68E-08 |
| 07/11/91 | 23013 | <T | 1.00 | | | | | | 1.38E-08 |
| 07/12/91 | 23013 | | 1.90 | | | | | | **2.21E-03** |
| 07/13/91 | 23013 | 0 | 3.70 | 0.00 | 0.41 | 0.00 | 0.00 | 0.49 | **4.60E-04** |

## TABLE CXXVIII

### SUMMARY STATISTICS FOR OBSERVED, INDUSTRIAL SOURCE COMPLEX 3 – SHORT TERM AND RECEPTOR MODELED FOR SOURCE TESTING DATES

| | | PCBTOT Observed (ng/m^3) | STACK1 (ng/m^3) | CONT BLD1 (ng/m^3) | DOME1 (ng/m^3) | THOMAS1 (ng/m^3) | SHREDR1 (ng/m^3) | ISC3ST calculated concentration (ng/m^3) |
|---|---|---|---|---|---|---|---|---|
| n PCB Air samples | 35 | 35 | 8 | 8 | 8 | 8 | 8 | 36 |
| n flagged | 21 | 21 | | | | | | |
| n not flagged | 14 | 14 | | | | | | |
| n with valid model | 8 | | | | | | | |
| mean | | 1.32 | 0.07 | 0.15 | 0.07 | 0.48 | 0.18 | 5.02E-04 |
| MIN. | | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.07E-08 |
| MAX. | | 5.00 | 0.60 | 0.41 | 0.53 | 1.04 | 0.49 | 4.52E-03 |
| med. | | 0.70 | 0.00 | 0.00 | 0.00 | 0.41 | 0.00 | 1.40E-08 |
| mode | | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.33E-08 |
| std. dev. | | 1.49 | 0.21 | 0.21 | 0.19 | 0.52 | 0.25 | 9.99E-04 |

### 4.8.3  Additional Modeling

In previous sections of this thesis, it was shown that on-site PCB concentrations were much higher than those observed in the incinerator stack. Based on this and other findings in this thesis, it was proposed that fugitive emissions from site activities other than the incinerator appeared to be more important contributors to the concentrations of PCBs observed off-site. In this Section 4.8.3, additional modeling was carried out for on-site fugitive emissions to develop estimates of annual mass emissions from Site fugitives (using the PCBTOT air results for on-site monitoring) and to compare these annual emissions to the estimated incinerator stack annual emissions. The dispersion of the fugitive air emissions was then evaluated using the simple Gaussian dispersion equation and compared to observed values. Finally, the annual mass emissions from the storage of PCB wastes in the Containment Building over the 1987-1992 time period are estimated.

#### 4.8.3.1  Simple Box Model

In Table CIX of Section 4.7.3, the PCBTOT results for ambient air samples for fugitive emissions collected on-site at ground level (94 samples, 74 sampling periods) during Phase 3 are shown. Nearly all of these on-site concentrations were higher (in many cases, much higher) than those found in the incinerator stack, which was ~20 m above ground level (i.e., on-site ambient air sample conc. of daily average of 865.9 ng/acm (n=76) vs. average stack emission conc. of 179.1 ng/acm (n=9)). However, no direct comparison can be made between emissions rates (in mass/time) for site fugitive and stack emissions with the concentration data (in mass/volume). Therefore, a simple single box model [42] was applied to obtain estimates of the emissions rates for the Site fugitive emissions. The box model is

based upon conservation of mass within the box. A diagrammatic representation of the simple box model is shown in Figure 110. Table CXXIX contains information on the length ($x$), width ($y$), various mixing heights ($z$), face areas, and volumes used for calculations with the box model. The calculated flow rates for various box values are shown in Table CXXX. The summary information for the daily wind speed and temperature for the December 1, 1990 through January 31, 1993 period and the on-site sampling dates are shown in Table CXXXI. The on-site data appear to be representative of the meteorological conditions over the course of the project. The on-site ambient air monitoring averaged air concentrations for wind speed and temperature groupings are shown in Tables CXXXII and CXXXIII, respectively.

The mass emission rates in mass/time from the site "box" were calculated as follows: average wind velocity ($v$) (or WS) (m/s) * area of box face (A) for assumed mixing height ($z$) ($m^2$) * average concentration (C) ($ng/m^3$) = emission rate (Q) (the values here are in ng/s or g/s). The annual emission rate was then estimated from the 1-second emission rate. The results obtained from these calculations are shown in Tables CXXXIV through CXXXVI. The calculated emissions rates for the incinerator stack are shown in Table CXXXVII. In Table CXXXVIII, the vertical dispersion coefficients (roughly equivalent to mixing height over the Site) are calculated and suggest a mixing height of 10-20 m is a reasonable, conservative estimate for the Site dimensions. The results in Table CXXXVI indicate that for a mixing height of 10 m (500 m might be a more typical mixing height across a city or large tract of land [102]), a PCBTOT mass of 79-105 **kg/yr** was being emitted from the Site fugitives, compared to an estimated <u>maximum</u> of approximately 53 **g/yr** from the stack

(Table CXXXVII). Therefore, the on-site fugitive emissions rate is a <u>minimum</u> of 1500 X greater than the incinerator stack. This factor will become even larger as the assumed mixing height is increased. Unfortunately, no multi-height sampling or atmospheric soundings were carried out at the Site to determine the actual mixing heights or vertical concentration gradients for the Site. Despite this, it was felt that these calculations are certainly sufficient to show that the Site was a major source of PCB emissions to the surrounding environment and these fugitive site emissions were independent of, and much greater than, the incinerator stack emissions.
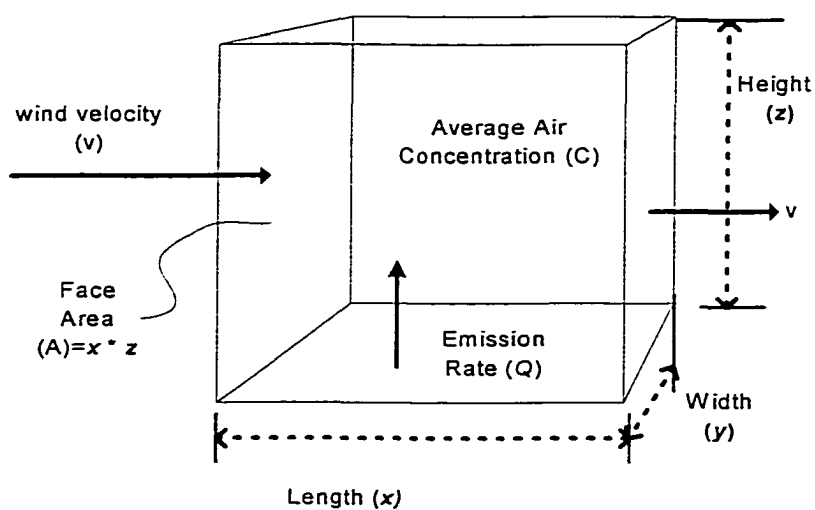
Figure 110.   Diagram of the single box model. The parameters are as follows: v is the wind velocity (m/s), C is average concentration (ng/m$^3$) in the box (can vary with time), x and y are horizontal dimensions (in m) for the box (the Site dimensions in this case), z is the mixing height (in m) (which can be time varying), and Q is the emission rate (in g/m$^2$/s).

**TABLE CXXIX**

MIXING HEIGHT VALUES EVALUATED FOR BOX MODEL

| Site Width (N side) (m) | Site Length (E side) (m) | Site Area (sq. m) | Mixing Height (m) | Box Face Area (m²) | Box Volume (m³) |
|---|---|---|---|---|---|
| 122 | 67 | 8174 | 10 | 1220 | 81740 |
| 122 | 67 | 8174 | 20 | 2440 | 163480 |
| 122 | 67 | 8174 | 100 | 12200 | 817400 |
| 122 | 67 | 8174 | 200 | 24400 | 1634800 |
| 122 | 67 | 8174 | 500 | 61000 | 4087000 |
| 122 | 67 | 8174 | 1000 | 122000 | 8174000 |
| 122 | 67 | 8174 | 2000 | 244000 | 16348000 |

**Notes:**

A mixing height of 10-20 m is suggested by vertical dispersion coefficient calculations.

Mixing height = 500 m suggested as an "average" value by Wania et al. [102]

**TABLE CXXX**

BOX VOLUME FLOW RATES (CUBIC METERS PER SECOND)
CALCULATED FOR MIXING HEIGHTS

| wind speed (m/s) | Height (m) of "Box" (m) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 10 | 20 | 100 | 200 | 500 | 1000 | 2000 |
| 1 | 1220 | 2440 | 12200 | 24400 | 61000 | 122000 | 244000 |
| 2 | 2440 | 4880 | 24400 | 48800 | 122000 | 244000 | 488000 |
| 3 | 3660 | 7320 | 36600 | 73200 | 183000 | 366000 | 732000 |
| 5 | 6100 | 12200 | 61000 | 122000 | 305000 | 610000 | 1220000 |
| 6 | 7320 | 14640 | 73200 | 146400 | 366000 | 732000 | 1464000 |
| 9 | 10980 | 21960 | 109800 | 219600 | 549000 | 1098000 | 2196000 |
| 10 | 12200 | 24400 | 122000 | 244000 | 610000 | 1220000 | 2440000 |
| 15 | 18300 | 36600 | 183000 | 366000 | 915000 | 1830000 | 3660000 |

**TABLE CXXXI**

SUMMARY OF PHASE 3 AND ON-SITE SAMPLING DATES METEOROLOGICAL DATA

| | Phase 3 MAX. Temp. (°C) | On-site Temp. MIN. (°C) | Phase 3 MAX. Temp. (°C) | On-Site Temp MAX. (°C) | Phase 3 Ave. Temp. (°C) | On-site Temp. Ave. (°C) | Phase 3 Wind Speed MIN. (m/s) | On-site Wind Speed MIN. (m/s) | Phase 3 Wind Speed MAX. (m/s) | On-site Wind Speed MAX. (m/s) | Phase 3 Wind Speed Ave. (m/s) | On-site Wind Speed Ave. (m/s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| n =0 | 21 | 0 | 4 | 0 | 1 | 0 | 222 | 20 | 6 | 0 | 6 | 0 |
| n <0 | 258 | 25 | 85 | 8 | 180 | 15 | 0 | 0 | 0 | 0 | 0 | 0 |
| n >0 | 517 | 50 | 706 | 67 | 614 | 60 | 576 | 55 | 790 | 75 | 790 | 75 |
| n | 94 | 75 | 94 | 75 | 94 | 75 | 94 | 75 | 94 | 75 | 94 | 75 |
| mean | 4.67 | 4.5 | 12.08 | 11.9 | 8.23 | 7.8 | 1.23 | 1.25 | 6.47 | 6.22 | 3.54 | 3.54 |
| std. dev. | 9.19 | 9.1 | 10.23 | 10.5 | 9.60 | 9.7 | 1.35 | 1.30 | 2.86 | 2.28 | 1.78 | 1.68 |
| median | 3.55 | 3.2 | 11.15 | 10.7 | 7.17 | 6.3 | 0.83 | 1.11 | 6.11 | 5.83 | 3.25 | 3.21 |
| mode | 0.00 | -2.2 | 1.00 | 3.9 | 4.55 | -0.6 | 0.00 | 0.00 | 5.56 | 4.72 | 3.51 | 4.38 |
| MIN. | -18.90 | -18.1 | -18.90 | -11.4 | -18.90 | -14.6 | error | 0.00 | error | 1.94 | error | 0.59 |
| MAX. | 24.40 | 24.4 | 30.80 | 29.1 | 27.02 | 26.4 | 7.50 | 6.11 | 35.00 | 11.94 | 12.20 | 8.11 |
| 95% CI | 1.86 | 2.1 | 2.07 | 2.4 | 1.94 | 2.2 | 0.27 | 0.29 | 0.58 | 0.52 | 0.36 | 0.38 |
| 99th percentile | 21.10 | 24.4 | 29.60 | 29.0 | 24.96 | 26.4 | 5.83 | 4.88 | 13.37 | 11.94 | 8.36 | 7.52 |
| 95th percentile | 18.60 | 19.3 | 27.30 | 28.3 | 22.50 | 23.8 | 3.99 | 3.61 | 11.39 | 10.64 | 7.04 | 7.13 |
| 90th percentile | 16.97 | 17.9 | 25.60 | 27.3 | 21.00 | 22.1 | 2.97 | 2.94 | 10.00 | 9.33 | 6.09 | 6.22 |
| 75th percentile | 12.78 | 11.8 | 21.80 | 21.1 | 17.40 | 15.5 | 1.94 | 1.94 | 7.78 | 7.50 | 4.48 | 4.37 |
| 50th percentile | 3.55 | 3.2 | 11.15 | 10.7 | 7.17 | 6.3 | 0.83 | 1.11 | 6.11 | 5.83 | 3.25 | 3.21 |
| 25th percentile | -1.80 | -1.9 | 3.33 | 3.7 | 0.59 | 1.2 | 0.00 | 0.00 | 4.44 | 4.72 | 2.26 | 2.52 |

## TABLE CXXXII

AVERAGE ON-SITE TOTAL POLYCHLORINATED BIPHENYL
CONCENTRATION BY WIND SPEED GROUPING

| Wind speed grouping (m/s) | Average wind speed for grouping (m/s) | Average temperature for grouping (°C) | Average on-site PCBTOT concentration (ng/m³) |
|---|---|---|---|
| <3 | 2.22 | 9.7 | 930 |
| 3-6 | 4.02 | 10.8 | 680 |
| >6 | 7.04 | 4.0 | 380 |

## TABLE CXXXIII

AVERAGE ON-SITE TOTAL POLYCHLORINATED BIPHENYL
CONCENTRATION BY AVERAGE TEMPERATURE GROUPING

| Temperature grouping (°C) | Average wind speed for grouping (m/s) | Average on-site PCBTOT concentration (ng/m³) |
|---|---|---|
| <0 | 3.37 | 190 |
| 0-15 | 3.87 | 910 |
| >15 | 2.96 | 1110 |

**TABLE CXXXIV**

SITE MASS EMISSION RATE (GRAMS PER SECOND)
CALCULATED FOR BOX MODEL

| Ave. temp. (°C) | Ave. On-site PCBTOT conc. (ng/m³) | Ave. wind speed (m/s) | mixing height z for box (m) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 10 | 20 | 100 | 200 | 500 | 1000 | 2000 |
| 9.7 | 930 | 2.22 | 2.52E-03 | 5.04E-03 | 2.52E-02 | 5.04E-02 | 1.26E-01 | 2.52E-01 | 5.04E-01 |
| 10.8 | 680 | 4.022 | 3.34E-03 | 6.67E-03 | 3.34E-02 | 6.67E-02 | 1.67E-01 | 3.34E-01 | 6.67E-01 |
| 4 | 380 | 7.04 | 3.26E-03 | 6.53E-03 | 3.26E-02 | 6.53E-02 | 1.63E-01 | 3.26E-01 | 6.53E-01 |

**TABLE CXXXV**

SITE MASS EMISSION RATE (GRAMS PER DAY) CALCULATED FOR BOX MODEL

| Ave. temp (°C) | Ave. On-site PCBTOT conc. (ng/m³) | Ave. wind speed (m/s) | mixing height z for box (m) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 10 | 20 | 100 | 200 | 500 | 1000 | 2000 |
| 9.7 | 930 | 2.22 | 218 | 435 | 2176 | 4353 | 10881 | 21763 | 43525 |
| 10.8 | 680 | 4.022 | 288 | 577 | 2883 | 5766 | 14414 | 28829 | 57657 |
| 4 | 380 | 7.04 | 282 | 564 | 2820 | 5640 | 14099 | 28199 | 56398 |

**TABLE CXXXVI**

SITE MASS EMISSION RATE (KILOGRAMS PER YEAR)
CALCULATED FOR BOX MODEL

| Ave. On-site PCBTOT conc. (ng/m³) | Ave. wind speed (m/s) | mixing height z for box (m) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 100 | 200 | 500 | 1000 | 2000 |
| 930 | 2.22 | 79 | 159 | 794 | 1589 | 3972 | 7943 | 15887 |
| 680 | 4.022 | 105 | 210 | 1052 | 2104 | 5261 | 10522 | 21045 |
| 380 | 7.04 | 103 | 206 | 1029 | 2059 | 5146 | 10293 | 20585 |

**TABLE CXXXVII**

EMISSION RATES (GRAMS PER SECOND AND GRAMS PER YEAR)
CALCULATED FOR INCINERATOR STACK

|  | Incinerator Stack PCBTOT Conc. (ng/acm) | Incinerator Stack PCBTOT Conc. (ng/dscm) | PCBTOT emission rate (g/s) | PCBTOT emission rate (g/yr) |
|---|---|---|---|---|
| n | 9 | 9 | 9 | 9 |
| mean | 179.06 | 416.92 | 1.37E-06 | 43.1 |
| MIN. | 145.04 | 350.62 | 1.07E-06 | 33.6 |
| MAX. | 217.17 | 496.00 | 1.68E-06 | 52.9 |
| mode | none | none | none | #N/A |
| std. dev. | 22.00 | 53.99 | 1.64E-07 | 5.2 |
| 95th percentile | 209.66 | 490.76 | 1.59E-06 | 50.1 |
| kurtosis | 0.00 | -1.53 | 2.01 | 2.01 |
| skewness | 0.12 | 0.51 | 0.02 | 0.02 |

**TABLE CXXXVIII**

## CALCULATED VALUES FOR DISPERSION COEFFICIENTS
## FOR DIFFERENT DISTANCES FROM SITE

| Stability Class | $x$ (km) | $\sigma_y$ (m) | $\sigma_z$ (m) |
|---|---|---|---|
| A | 0.067 | 19.5 | to |
| | 0.122 | 33.1 | 5.0 |
| | 0.39 | 92.3 | 59.8 |
| | 0.54 | 122.8 | 123.4 |
| | 0.6 | 134.7 | 157.1 |
| | 0.9 | 192.1 | 418.7 |
| | 1 | 210.5 | 551.1 |
| | 1.1 | 228.6 | 714.3 |
| | 1.25 | 255.2 | 1031.3 |
| | 1.4 | 284.7 | 1462.3 |
| | 2 | 379.4 | 5460.7 |
| | 2.1 | 394.8 | 6780.7 |
| | | | |
| Stability Class | $x$ (km) | $\sigma_y$ (m) | $\sigma_z$ (m) |
| C | 0.067 | 8.8 | 5.1 |
| | 0.122 | 15.2 | 8.8 |
| | 0.39 | 44.1 | 25.6 |
| | 0.54 | 59.3 | 34.6 |
| | 0.6 | 65.3 | 38.1 |
| | 0.9 | 94.5 | 55.2 |
| | 1 | 103.9 | 60.8 |
| | 1.1 | 113.2 | 66.4 |
| | 1.25 | 127.0 | 74.6 |
| | 1.4 | 140.5 | 82.7 |
| | 2 | 191.9 | 114.4 |
| | 2.1 | 200.1 | 119.6 |
| | | | |
| Stability Class | $x$ (km) | $\sigma_y$ (m) | $\sigma_z$ (m) |
| F | 0.067 | 2.9 | 2.3 |
| | 0.122 | 4.9 | 3.5 |
| | 0.39 | 14.4 | 7.4 |
| | 0.54 | 19.4 | 9.0 |
| | 0.6 | 21.3 | 9.6 |
| | 0.9 | 30.9 | 12.3 |
| | 1 | 34.0 | 13.0 |
| | 1.1 | 37.0 | 13.7 |
| | 1.25 | 41.6 | 14.6 |
| | 1.4 | 46.0 | 15.4 |
| | 2 | 62.9 | 17.5 |
| | 2.1 | 65.6 | 17.6 |

#### 4.8.3.2 Dispersion from Site

The dispersion of the observed on-site concentrations of PCBs was examined to see if these concentrations might account for more of the observed off-site concentrations than those found from the incinerator stack in Section 4.8.1. For this work, the Generalized Gaussian Dispersion Equation for a Continuous Point Source (Equation 17, below) can be used [37, 42, 194, 195, 278]:

$$C_{at\,x} = \frac{Q}{2\pi v \sigma_y \sigma_z V} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{h_e - z}{\sigma_z}\right)\right] \qquad (17)$$

Where $C_{at\,x}$ = average concentration (g/m$^3$) at distance $x$, $Q$ = emission rate (g/s), $\sigma_y$ = horizontal dispersion coefficient at distance $x$, $\sigma_z$ = vertical dispersion coefficient at distance $x$, v = velocity, exp = exponent, $y$ = horizontal receptor distance from center line at distance $x$, $h_e$ = plume release height at origin, and z = vertical receptor height.

For the case of dispersion of the ground level plume from on-site emissions, Equation 17 reduces to Equation 18, the equation for Ground-Level Centerline Concentrations from Ground-Level Plumes:

$$C_{at\,x} = \frac{Q}{\pi v \sigma_y \sigma_z} \qquad (18)$$

Where z=0, y=0, and $h_e$=0.

An examination of Equation 18 shows that the concentration term ($C_{at\ x}$) is maximized for high Q, low wind velocity, and low values for the dispersion coefficients (stable conditions). For minimum concentrations, Q is low, wind velocity is high, and dispersion coefficients are high (unstable conditions). For ground level releases, Equation 18 may not always accurately reflect the turbulence due to the rapid change in velocity with height close to the surface. Turner [194] has proposed a virtual upwind point source modification to Equation 18 to account for ground level emissions of substances from area sources [278]. In this research, calculations were performed using Equation 18 with and without the virtual point source. Additional discussion of dispersion modeling for ground level plumes can be found in Zanetti [42], Turner [194], and Seinfeld [37].

The values of the dispersion coefficients are a function of distance from the source and stability class. They can be obtained from so-called "Turner Plots" [195], or calculated using Equation 19 for Rural Pasquill Dispersion Coefficients, which was first published by McMullen [195]:

$$\sigma = \exp\left[I + J * \ln(x) + \left\{K\{\ln(x)\}^2\right\}\right] \qquad (19)$$

where the values for I, J and K are constants used for obtaining values for $\sigma_y$ or $\sigma_z$ and are a function of the stability class. Stability class is a qualitative assessment of atmospheric mixing and is classified for values of A through F, as given in look-up tables in various references [194, 195].

Equation 19 was used to calculate the dispersion coefficients for the distances of interest and stability classes in this research (the length and width of the Site and distance from the Site to the off-site air monitoring stations). The calculated values for the dispersion coefficients for combinations of distance and stability classes are shown in Table CXXVIII above. Note that the closest air sampling site was located at $x = 390$ m (Site ID 23009 and 23011), while the farthest air sampling site was located at $x = 1100$ m (Site ID 23007).

The dispersion calculations were performed using Equation 18 for $x=390$ m (sampling sites 23009 and 23011) and $x=1100$ m (sampling site 23007) for wind speeds <3, 3-6, >6 m/second, stability classes A and F, with and without a correction for virtual point source. The determination of the virtual point source distance for ground level plumes is a function of the Site's longest dimension. Further details on the derivation of the virtual point source distance are given in [278]. There is no common agreement on the averaging time on which the dispersion coefficients are based, except that it is in the range of 10 minutes to 1 hour [195]. The observed air samples are based on sampling over approximately 24 hours. Therefore, the calculated concentrations using dispersion Equation 18 must be converted to 24-hour averaged results. The correction factors derived by empirical studies are 0.14 (for a 10 minute average time) and 0.17 (for a 1 hour average). These corrected concentrations were also calculated. The results for these dispersion calculations are summarized below in Tables CXXXIX through CXLI.

The data for the observed PCBTOT at the air sampling station and the dispersion calculated concentrations are shown below in Table CXLII. The values calculated using the

dispersion Equation 18 for the on-site fugitive emissions are much closer to the observed results than the ISC3ST modeling results discussed in Section 4.8.1 for the stack incinerator emissions, which supports the hypothesis that site fugitives are the main source of PCBs observed at the off-site sampling locations.

# TABLE CXXXIX

## CALCULATED CONCENTRATIONS FROM DISPERSION,
## WIND SPEED LESS THAN 3 METERS PER SECOND

| Pt source location | Stability Class | Mixing hgt (m) | Emission rate Q (g/s) | Mean v (m/s) | Dist. from site (km) | $\sigma_y$ (m) | $\sigma_z$ (m) | Calc. conc. location x, y=0, z=0 (g/m3) | Calc. conc. (ng/m³) | Calc. 24 hr ave. conc. (based on 10 min. ave.) (ng/m³) | Calc. 24 hr ave. conc. (based on 1 hr ave.) (ng/m³) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| property line | A | 10 | 2.52E-03 | 2.22 | 0.39 | 92.3 | 59.8 | 2.06E-07 | 205.8 | 28.8 | 35.0 |
| virtual pt source | A | 10 | 2.52E-03 | 2.22 | 0.54 | 122.8 | 123.4 | 7.49E-08 | 74.9 | 10.5 | 12.7 |
| property line | A | 20 | 5.04E-03 | 2.22 | 0.39 | 92.3 | 59.8 | 4.12E-07 | 411.7 | 57.6 | 70.0 |
| virtual pt source | A | 20 | 5.04E-03 | 2.22 | 0.54 | 122.8 | 123.4 | 1.50E-07 | 149.7 | 21.0 | 25.5 |
| property line | A | 500 | 1.26E-01 | 2.22 | 0.39 | 92.3 | 59.8 | 1.03E-05 | 10291.5 | 1440.8 | 1749.6 |
| virtual pt source | A | 500 | 1.26E-01 | 2.22 | 0.54 | 122.8 | 123.4 | 3.74E-06 | 3743.1 | 524.0 | 636.3 |
| | | | . | | | | | | | | |
| property line | F | 10 | 0.00252 | 2.22 | 0.39 | 14.4 | 7.4 | 1.07E-05 | 10732.6 | 1502.6 | 1824.5 |
| virtual pt source | F | 10 | 0.00252 | 2.22 | 0.54 | 19.4 | 9.0 | 6.48E-06 | 6482.4 | 907.5 | 1102.0 |
| property line | F | 20 | 0.00504 | 2.22 | 0.39 | 14.4 | 7.4 | 2.15E-05 | 21465.3 | 3005.1 | 3649.1 |
| virtual pt source | F | 20 | 0.00504 | 2.22 | 0.54 | 19.4 | 9.0 | 1.30E-05 | 12964.9 | 1815.1 | 2204.0 |
| property line | F | 500 | 0.126 | 2.22 | 0.39 | 14.4 | 7.4 | 5.37E-04 | 536631.9 | 75128.5 | 91227.4 |
| virtual pt source | F | 500 | 0.126 | 2.22 | 0.54 | 19.4 | 9.0 | 3.24E-04 | 324121.6 | 45377.0 | 55100.7 |

441

## TABLE CXXXIX (Concluded)

## CALCULATED CONCENTRATIONS FROM DISPERSION,
## WIND SPEED LESS THAN 3 METERS PER SECOND

| Pt source location | Stability Class | Mixing hgt (m) | Emission rate Q (g/s) | Mean v (m/s) | Dist. from site (km) | $\sigma_y$ | $\sigma_z$ | Calc. conc. location x, y=0, z=0 (g/m³) | Calc. conc. (ng/m³) | Calc. 24 hr ave. conc. based on 10 min. average | Calc. 24 hr ave. conc. based on 1 hr average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| property line | A | 10 | 0.00252 | 2.22 | 1 | 210.5 | 551.1 | 9.79E-09 | 9.8 | 1.4 | 1.7 |
| virtual pt source | A | 10 | 0.00252 | 2.22 | 1.4 | 284.7 | 1462.3 | 2.73E-09 | 2.7 | 0.4 | 0.5 |
| property line | A | 20 | 0.00504 | 2.22 | 1 | 210.5 | 551.1 | 1.96E-08 | 19.6 | 2.7 | 3.3 |
| virtual pt source | A | 20 | 0.00504 | 2.22 | 1.4 | 284.7 | 1462.3 | 5.45E-09 | 5.5 | 0.8 | 0.9 |
| property line | A | 500 | 0.126 | 2.22 | 1 | 210.5 | 551.1 | 4.89E-07 | 489.3 | 68.5 | 83.2 |
| virtual pt source | A | 500 | 0.126 | 2.22 | 1.4 | 284.7 | 1462.3 | 1.36E-07 | 136.3 | 19.1 | 23.2 |
|  |  |  |  |  |  |  |  |  |  |  |  |
| property line | F | 10 | 0.00252 | 2.22 | 1 | 34.0 | 13.0 | 2.56E-06 | 2563.8 | 358.9 | 435.9 |
| virtual pt source | F | 10 | 0.00252 | 2.22 | 1.4 | 46.0 | 15.4 | 1.60E-06 | 1599.9 | 224.0 | 272.0 |
| property line | F | 20 | 0.00504 | 2.22 | 1 | 34.0 | 13.0 | 5.13E-06 | 5127.7 | 717.9 | 871.7 |
| virtual pt source | F | 20 | 0.00504 | 2.22 | 1.4 | 46.0 | 15.4 | 3.20E-06 | 3199.8 | 448.0 | 544.0 |
| property line | F | 500 | 0.126 | 2.22 | 1 | 34.0 | 13.0 | 1.28E-04 | 128192.1 | 17946.9 | 21792.7 |
| virtual pt source | F | 500 | 0.126 | 2.22 | 1.4 | 46.0 | 15.4 | 8.00E-05 | 79996.1 | 11199.5 | 13599.3 |

# TABLE CXL

## DISPERSION CALCULATIONS OF CONCENTRATIONS, WIND SPEED THREE TO SIX METERS PER SECOND

| Pt source location | Stability Class | Mixing hgt (m) | Emission rate Q (g/s) | Mean v (m/s) | Dist. from site (km) | $\sigma_y$ | $\sigma_z$ | Calc. conc. location $x$, $y=0$, $z=0$ (g/m³) | Calc. conc. (ng/m³) | Calc. 24 hr ave. conc. based on 10 min. average | Calc. 24 hr ave. conc. based on 1 hr average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| property line | A | 10 | 3.34E-03 | 4.02 | 0.39 | 92.3 | 59.8 | 1.51E-07 | 150.7 | 21.1 | 25.6 |
| virtual pt source | A | 10 | 3.34E-03 | 4.02 | 0.54 | 122.8 | 123.4 | 5.48E-08 | 54.8 | 7.7 | 9.3 |
| property line | A | 20 | 6.67E-03 | 4.02 | 0.39 | 92.3 | 59.8 | 3.01E-07 | 300.9 | 42.1 | 51.1 |
| virtual pt source | A | 20 | 6.67E-03 | 4.02 | 0.54 | 122.8 | 123.4 | 1.09E-07 | 109.4 | 15.3 | 18.6 |
| property line | A | 500 | 1.67E-01 | 4.02 | 0.39 | 92.3 | 59.8 | 7.53E-06 | 7532.7 | 1054.6 | 1280.6 |
| virtual pt source | A | 500 | 1.67E-01 | 4.02 | 0.54 | 122.8 | 123.4 | 2.74E-06 | 2739.7 | 383.6 | 465.7 |
|  |  |  |  |  |  |  |  |  |  |  |  |
| property line | F | 10 | 0.00334 | 4.02 | 0.39 | 14.4 | 7.4 | 7.86E-06 | 7855.6 | 1099.8 | 1335.5 |
| virtual pt source | F | 10 | 0.00334 | 4.02 | 0.54 | 19.4 | 9.0 | 4.74E-06 | 4744.7 | 664.3 | 806.6 |
| property line | F | 20 | 0.00667 | 4.02 | 0.39 | 14.4 | 7.4 | 1.57E-05 | 15687.7 | 2196.3 | 2666.9 |
| virtual pt source | F | 20 | 0.00667 | 4.02 | 0.54 | 19.4 | 9.0 | 9.48E-06 | 9475.2 | 1326.5 | 1610.8 |
| property line | F | 500 | 0.167 | 4.02 | 0.39 | 14.4 | 7.4 | 3.93E-04 | 392780.0 | 54989.2 | 66772.6 |
| virtual pt source | F | 500 | 0.167 | 4.02 | 0.54 | 19.4 | 9.0 | 2.37E-04 | 237236.1 | 33213.1 | 40330.1 |

# TABLE CXL (Concluded)

## DISPERSION CALCULATIONS OF CONCENTRATIONS, WIND SPEED THREE TO SIX METERS PER SECOND

| Pt source location | Stability Class | Mixing hgt (m) | Emission rate Q (g/s) | Mean v (m/s) | Dist. from site (km) | $\sigma_y$ | $\sigma_z$ | Calc. conc. location $x$, $y=0$, $z=0$ (g/m³) | Calc. conc. (ng/m³) | Calc. 24 hr ave. Conc. based on 10 min. average | Calc. 24 hr ave. conc. based on 1 hr average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| property line | A | 10 | 0.00334 | 4.02 | 1 | 210.5 | 551.1 | 7.16E-09 | 7.2 | 1.0 | 1.2 |
| virtual pt source | A | 10 | 0.00334 | 4.02 | 1.4 | 284.7 | 1462.3 | 2.00E-09 | 2.0 | 0.3 | 0.3 |
| property line | A | 20 | 0.00667 | 4.02 | 1 | 210.5 | 551.1 | 1.43E-08 | 14.3 | 2.0 | 2.4 |
| virtual pt source | A | 20 | 0.00667 | 4.02 | 1.4 | 284.7 | 1462.3 | 3.99E-09 | 4.0 | 0.6 | 0.7 |
| property line | A | 500 | 0.167 | 4.02 | 1 | 210.5 | 551.1 | 3.58E-07 | 358.1 | 50.1 | 60.9 |
| virtual pt source | A | 500 | 0.167 | 4.02 | 1.4 | 284.7 | 1462.3 | 9.98E-08 | 99.8 | 14.0 | 17.0 |
| | | | | | | | | | | | |
| property line | F | 10 | 0.00334 | 4.02 | 1 | 34.0 | 13.0 | 1.88E-06 | 1876.6 | 262.7 | 319.0 |
| virtual pt source | F | 10 | 0.00334 | 4.02 | 1.4 | 46.0 | 15.4 | 1.17E-06 | 1171.0 | 163.9 | 199.1 |
| property line | F | 20 | 0.00667 | 4.02 | 1 | 34.0 | 13.0 | 3.75E-06 | 3747.5 | 524.7 | 637.1 |
| virtual pt source | F | 20 | 0.00667 | 4.02 | 1.4 | 46.0 | 15.4 | 2.34E-06 | 2338.6 | 327.4 | 397.6 |
| property line | F | 500 | 0.167 | 4.02 | 1 | 34.0 | 13.0 | 9.38E-05 | 93828.4 | 13136.0 | 15950.8 |
| virtual pt source | F | 500 | 0.167 | 4.02 | 1.4 | 46.0 | 15.4 | 5.86E-05 | 58552.0 | 8197.3 | 9953.8 |

# TABLE CXLI

## DISPERSION CALCULATIONS OF CONCENTRATIONS, WIND SPEED GREATER THAN 6 METERS PER SECOND

| Pt source location | Stability Class | Mixing hgt (m) | Emission rate Q (g/s) | Mean v (m/s) | Dist. from site (km) | $\sigma_y$ | $\sigma_z$ | Calc. conc. location x, y=0, z=0 (g/m³) | Calc. conc. (ng/m³) | Calc. 24 hr ave. conc. based on 10 min. average | Calc. 24 hr ave. conc. based on 1 hr average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Property line | A | 10 | 3.26E-03 | 7.04 | 0.39 | 92.3 | 59.8 | 8.40E-08 | 84.0 | 11.8 | 14.3 |
| virtual pt source | A | 10 | 3.26E-03 | 7.04 | 0.54 | 122.8 | 123.4 | 3.05E-08 | 30.5 | 4.3 | 5.2 |
| Property line | A | 20 | 6.53E-03 | 7.04 | 0.39 | 92.3 | 59.8 | 1.68E-07 | 168.2 | 23.5 | 28.6 |
| virtual pt source | A | 20 | 6.53E-03 | 7.04 | 0.54 | 122.8 | 123.4 | 6.12E-08 | 61.2 | 8.6 | 10.4 |
| Property line | A | 500 | 1.63E-01 | 7.04 | 0.39 | 92.3 | 59.8 | 4.20E-06 | 4198.3 | 587.8 | 713.7 |
| virtual pt source | A | 500 | 1.63E-01 | 7.04 | 0.54 | 122.8 | 123.4 | 1.53E-06 | 1527.0 | 213.8 | 259.6 |
|  |  |  |  |  |  |  |  |  |  |  |  |
| Property line | F | 10 | 3.26E-03 | 7.04 | 0.39 | 14.4 | 7.4 | 4.38E-06 | 4378.3 | 613.0 | 744.3 |
| virtual pt source | F | 10 | 3.26E-03 | 7.04 | 0.54 | 19.4 | 9.0 | 2.64E-06 | 2644.5 | 370.2 | 449.6 |
| Property line | F | 20 | 6.53E-03 | 7.04 | 0.39 | 14.4 | 7.4 | 8.77E-06 | 8770.0 | 1227.8 | 1490.9 |
| virtual pt source | F | 20 | 6.53E-03 | 7.04 | 0.54 | 19.4 | 9.0 | 5.30E-06 | 5297.0 | 741.6 | 900.5 |
| Property line | F | 500 | 1.63E-01 | 7.04 | 0.39 | 14.4 | 7.4 | 2.19E-04 | 218914.2 | 30648.0 | 37215.4 |
| virtual pt source | F | 500 | 1.63E-01 | 7.04 | 0.54 | 19.4 | 9.0 | 1.32E-04 | 132222.5 | 18511.2 | 22477.8 |

**TABLE CXLI (Concluded)**

DISPERSION CALCULATIONS OF CONCENTRATIONS,
WIND SPEED GREATER THAN 6 METERS PER SECOND

| Pt source location | Stability Class | Mixing hgt (m) | Emission rate Q (g/s) | Mean v (m/s) | Dist. from site (km) | $\sigma_y$ | $\sigma_z$ | Calc. conc. location $x$, $y=0, z=0$ (g/m³) | Calc. conc. (ng/m³) | Calc. 24 hr ave. conc. based on 10 min. average | Calc. 24 hr ave. conc. based on 1 hr average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Property line | A | 10 | 3.26E-03 | 7.04 | 1 | 210.5 | 551.1 | 3.99E-09 | 4.0 | 0.6 | 0.7 |
| virtual pt source | A | 10 | 3.26E-03 | 7.04 | 1.4 | 284.7 | 1462.3 | 1.11E-09 | 1.1 | 0.2 | 0.2 |
| Property line | A | 20 | 6.53E-03 | 7.04 | 1 | 210.5 | 551.1 | 8.00E-09 | 8.0 | 1.1 | 1.4 |
| virtual pt source | A | 20 | 6.53E-03 | 7.04 | 1.4 | 284.7 | 1462.3 | 2.23E-09 | 2.2 | 0.3 | 0.4 |
| Property line | A | 500 | 1.63E-01 | 7.04 | 1 | 210.5 | 551.1 | 2.00E-07 | 199.6 | 27.9 | 33.9 |
| virtual pt source | A | 500 | 1.63E-01 | 7.04 | 1.4 | 284.7 | 1462.3 | 5.56E-08 | 55.6 | 7.8 | 9.5 |
|  |  |  |  |  |  |  |  |  |  |  |  |
| Property line | F | 10 | 3.26E-03 | 7.04 | 1 | 34.0 | 13.0 | 1.05E-06 | 1045.9 | 146.4 | 177.8 |
| virtual pt source | F | 10 | 3.26E-03 | 7.04 | 1.4 | 46.0 | 15.4 | 6.53E-07 | 652.7 | 91.4 | 111.0 |
| Property line | F | 20 | 6.53E-03 | 7.04 | 1 | 34.0 | 13.0 | 2.10E-06 | 2095.0 | 293.3 | 356.2 |
| virtual pt source | F | 20 | 6.53E-03 | 7.04 | 1.4 | 46.0 | 15.4 | 1.31E-06 | 1307.3 | 183.0 | 222.2 |
| Property line | F | 500 | 1.63E-01 | 7.04 | 1 | 34.0 | 13.0 | 5.23E-05 | 52294.8 | 7321.3 | 8890.1 |
| virtual pt source | F | 500 | 1.63E-01 | 7.04 | 1.4 | 46.0 | 15.4 | 3.26E-05 | 32633.7 | 4568.7 | 5547.7 |

**TABLE CXLII**

COMPARISON OF DISPERSION MODELING OF
SITE FUGITIVES TO OBSEVED DATA

| | 23007 | 23009 | 23011 | 23013 | ALL DATA |
|---|---|---|---|---|---|
| x (km) | 1.1 | 0.4 | 0.4 | 0.6 | |
| n | 396 | 391 | 397 | 400 | 1584 |
| n not blank | 45 | 46 | 48 | 45 | 184 |
| n=0 | 0 | 0 | 0 | 0 | 0 |
| n blank | 1188 | 1193 | 1187 | 1184 | 4752 |
| mean | 1.6 | 1.6 | 1.4 | 0.7 | 1.3 |
| std. dev. | 3.09 | 3.98 | 5.40 | 1.56 | 3.8 |
| 95% CI | 0.9 | 1.2 | 1.5 | 0.5 | 0.6 |
| mode | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| median | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| MIN. | 0.2 | 0 | 0.2 | 0.2 | 0 |
| MAX. | 22.3 | 37 | 83.2 | 18 | 83.2 |
| range | 22.1 | 37 | 83 | 17.8 | 83.2 |
| 99th percentile | 16.2 | 20.5 | 12.9 | 8.6 | 14 |
| 95th percentile | 9 | 7.3 | 5.46 | 2.9 | 6.2 |
| 90th percentile | 5 | 4.4 | 3.3 | 1.61 | 3.3 |
| 75th percentile | 1.5 | 1.1 | 0.8 | 0.4 | 0.9 |
| 50th percentile | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| 25th percentile | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| 10th percentile | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| kurtosis | 13 | 36 | 158 | 53 | 178 |
| skewness | 3 | 5 | 12 | 6 | 11 |
| MH=10m, WS < 3 m/s, stability=A | 9.8 (1.4, 1.7) | 205.8 (28.2, 35.0) | 205.8 (28.2, 35.0) | | |
| MH=10m, WS < 3 m/s, stability=F class | 2563 (358.9, 435.9) | 10732 (1502.6, 1824.5) | 10732 (1502.6, 1824.5) | | |
| MH=10m, WS 3-6 m/s, stability=A | 7.2 (1.0, 1.2) | 150.7 (21.1, 25.6) | 150.7 (21.1, 25.6) | | |
| MH=10m, WS 3-6 m/s, stability=F | 1876 (262.7, 319.0) | 7866 (1099, 1335) | 7866 (1099, 1335) | | |
| MH=10m, WS >6 m/s, stability=A | 4.0 (0.6, 0.7) | 84 (11.8, 14.3) | 84 (11.8, 14.3) | | |
| MH=10m, WS >6 m/s, stability=F | 1045 (146.4, 177.8) | 4378 (613, 744.3) | 4378 (613, 744.3) | | |

**Note:**

( , ) = value for 24 hour average concentration based on 10 minute average, value for 24 hour ave. concentration based on one hour average

MH = mixing height

Stability class F does not exist for WS >3 m/s; values are provided for comparison only

### 4.8.3.3 Storage Building Emissions

In addition to the ambient air on-site samples for PCBs, there were a number of air samples taken inside the PCB containment building. Table CXLIII summarizes the data obtained over the May, 1987 through June, 1992 period, and is subdivided for some additional periods. During this time, concentrations approaching 100,000 ng/m$^3$ were observed. For the May, 1987 to May, 1991 period, the containment building ventilation was operated intermittently with a fan that reportedly provided up to eight air changes per day under normal conditions; however, it is believed that higher ventilation rates were possible (Peter Buekema, P&R personal communication). In addition, passive venting could occur. Therefore, calculations for emissions from the containment building, based upon air concentrations, were performed using a range of 1-24 air changes per day. After May, 1991, the CFU was installed and operating at 15,000 cfm. These calculations are summarized in Table CXLIV. The average emissions during this time were calculated to be 0.92 kg/year (MIN. 0.002, MAX. 4.6) for 24 air changes per day (1 per hour).

Similar results might be expected for other storage sites, especially those storing high concentration liquid PCBs. However, very little work on PCB emissions from discrete storage sites has been reported in the literature. In one study, Hsu and Holsen estimated that PCB mass loading to the metropolitan Chicago air shed ranged from 90-400 kg/year, which calculations were based on air sampling and meteorological data [279]. One can see that it would not take too many storage sites like the SV Site to approach the Chicago air shed loading. This estimated mass loading from fugitive PCB emissions from the SV Site emphasizes the importance of identifying and reducing PCB emissions from sources that are

controllable. In the case of PCB storage sites, control could include installation of an air pollution control system, such as a CFU, or the destruction (not just continued storage or land disposal) of the PCB material.

**TABLE CXLIII**

AIR MONITORING SUMMARY FOR CONTAINMENT BUILDING,
MAY, 1987 TO MAY, 1992

| | ALL DATA (May 1987-May 1992) | May 1987-Jan. 1990 | May 1987-June 1990 | June 1990 Only | Phase 3 Only (June 1991-May 1992) | Average Temp. (°C) |
|---|---|---|---|---|---|---|
| n | 44 | 31 | 35 | 4 | 9 | 43 |
| ave | 19760 | 23437 | 23625 | 25084 | 4730 | 10 |
| std. dev. | 24905 | 28169 | 26481 | 3010 | 5838 | 10 |
| median | 9247 | 10056 | 11484 | 25187 | 2065 | 13 |
| mode | None | None | None | None | None | 17 |
| MIN. | 36.00 | 36.00 | 36.00 | 21316.90 | 805.00 | -9.41 |
| MAX. | 99737.00 | 99737.00 | 99737.00 | 28646.00 | 18960.40 | 24.77 |
| 95% CI | 7359 | 9916 | 8773 | 2950 | 3814 | 3 |
| 99th percentile | 97949 | 98454 | 98299 | 28553 | 18032 | 24 |
| 95th percentile | 82442 | 94208 | 93703 | 28183 | 14320 | 24 |
| 90th percentile | 44256 | 55176 | 52676 | 27720 | 9679 | 20 |
| 75th percentile | 24245 | 26206 | 26678 | 26332 | 6515 | 17 |
| 50th percentile | 9247 | 10056 | 11484 | 25187 | 2065 | 13 |
| 25th percentile | 2637 | 4555 | 5048 | 23940 | 1321 | 2 |
| kurtosis | 4.67 | 2.87 | 3.34 | 1.22 | 5.05 | -0.93 |
| skewness | 2.20 | 1.90 | 1.94 | -0.20 | 2.19 | -0.47 |

# TABLE CXLIV

## CALCULATED AIR EMISSIONS FOR BUILDING VIA PASSIVE OR LOW LEVEL ACTIVE VENTILATION (1-24 AIR CHANGES PER DAY)

| n=44 bldg volume= 5300 m$^3$ | Concentration (ng/m$^3$) | g/bldg volume | g/yr for air changes/day | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 4 | 6 | 8 | 24 |
| ave | 19760 | 0.104728 | 38 | 76 | 153 | 229 | 306 | 917 |
| Min | 36 | 0.000191 | 0.1 | 0.1 | 0.3 | 0.4 | 0.6 | 2 |
| max | 99737 | 0.528606 | 193 | 386 | 772 | 1158 | 1544 | 4631 |
| 99th percentile | 97949 | 0.51913 | 189 | 379 | 758 | 1137 | 1516 | 4548 |
| 95th percentile | 82442.4 | 0.436945 | 159 | 319 | 638 | 957 | 1276 | 3828 |
| 90th percentile | 44256.4 | 0.234559 | 86 | 171 | 342 | 514 | 685 | 2055 |
| 75th percentile | 24244.8 | 0.128497 | 47 | 94 | 188 | 281 | 375 | 1126 |
| 50th percentile | 9247 | 0.049009 | 18 | 36 | 72 | 107 | 143 | 429 |
| 25th percentile | 2636.7 | 0.013975 | 5 | 10 | 20 | 31 | 41 | 122 |

## 4.9    Modeling for Polychlorinated Dibenzo-p-dioxins/Dibenzofurans Ambient Air Data

Although the major focus of the work in this thesis is on the PCB results, it was felt that some limited air modeling (similar to that described in Section 4.8) for PCDD/DF would be beneficial. In order to carry out this modeling, the source testing data for PCDD/DF was utilized further. A brief discussion of the PCDD/DF emission data is provided below.

The PCDD/DF congener specific emission information from the source testing is provided in Table CXLV. The PCDD/DF emissions information (concentration and emission rates, in I-TEQ) is summarized in Table CXLVI. Summary statistics for the ITEQ emissions data is provided in Table CXLVII. In Figure 111, the PCB feed rate and PCDD/DF concentration are plotted for each source test. There appears to be a direct relation, with higher PCB feed rates showing higher I-TEQ concentrations. However, further analysis of the data indicates that it was actually TSP concentration that was correlated with PCDD/DF concentration (Figure 112). When PCB feed rate and TSP concentration are plotted on the same graph (Figure 113), there is a relationship, with higher PCB feed rate resulting in higher TSP concentrations. Linear regression analysis was carried out for PCB feed rate and TSP (Figure 114), PCB feed rate and ITEQ (Figure 115), and ITEQ and TSP concentrations (Figure 116). The strongest correlation was observed for TSP and ITEQ ($r^2 > 0.8$). The PCB feed rate and TSP concentrations were correlated ($r^2 > 0.5$). Probably the higher PCB feed rates resulted in higher concentration of NaCl in the scrubber effluent and that NaCl was then being carried through the APCS. Analysis of a particulate filter under

similar operating conditions in May, 1991 showed that over 50% of the TSP mass was due to NaCl.

To address this issue, ENSCO was required to make several modifications to the APCS and operational procedures. These changes were tested and shown to have resulted in much lower TSP before the Series V Source Testing took place. The TSP and PCDD/DF I-TEQ concentrations observed in Series V were much lower than for Series II, primarily because of these changes. It is interesting to note that higher PCB DRE appeared to be correlated with higher I-TEQ concentrations for the first 6 source test runs (Figure 117). This relationship disappeared in the Series V tests (after the APCS modifications).

# TABLE CXLV

## SOURCE TESTING DATA FOR 2, 3, 7, 8 POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN COMPOUNDS[a]

| Date (mm/dd/yy) | Source Test ID | PCB feed rate (kg/hr) | flag | 2,3,7,8-Cl4-dibenzofuran | flag | 2,3,7,8-Cl4-dibenzo-p-dioxin | flag | 1,2,3,7,8-Cl5-dibenzofuran | flag | 2,3,4,7,8-Cl5-dibenzofuran | flag | 1,2,3,7,8-Cl5-dibenzo-p-dioxin | flag | 1,2,3,4,7,8-Cl6-dibenzofuran | flag | 1,2,3,6,7,8-Cl6-dibenzofuran | flag | 2,3,4,6,7,8-Cl6-dibenzofuran | flag | 1,2,3,7,8,9-Cl6-dibenzofuran |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I-TEF | | | | 0.1 | | 1 | | 0.01 | | 0.5 | | 0.5 | | 0.1 | | 0.1 | | 0.1 | | 0.1 |
| 2/16/91 | I-1 | 26.07 | < | 0.219 | < | 0.07 | < | 0.017 | < | 0.015 | < | 0.02 | < | 0.005 | < | 0.005 | < | 0.016 | < | 0.005 |
| 2/19/91 | I-2 | 22.24 | < | 0.004 | < | 0.08 | < | 3E-04 | < | 0.02 | < | 0.02 | < | 0.006 | < | 0.006 | < | 0.019 | < | 0.006 |
| 2/20/91 | I-3 | 18.31 | < | 0.004 | < | 0.09 | < | 3E-04 | < | 0.02 | < | 0.025 | < | 0.007 | < | 0.007 | < | 0.021 | < | 0.007 |
| 2/24/91 | II-2 | 197.4 | < | 0.023 | < | 0.08 | < | 0.002 | < | 0.025 | < | 0.025 | | 0.031 | | 0.023 | < | 0.021 | | 0.035 |
| 2/25/91 | II-3 | 212.9 | < | 0.09 | < | 0.09 | | 0.004 | < | 0.18 | < | 0.025 | | 0.194 | | 0.049 | | 0.09 | | 0.12 |
| 2/26/91 | II-4 | 233.8 | < | 0.077 | < | 0.09 | < | 0.004 | < | 0.195 | < | 0.025 | < | 0.188 | < | 0.341 | < | 0.214 | < | 0.239 |
| 7/11/91 | V-2 | 241.92 | | 0.063 | | 0.0279 | | 0.004 | | 0.207 | | 0.0384 | | 0.23 | | 0 | | 0 | | 0 |
| 7/12/91 | V-3 | 160.56 | | 0.036 | | 0.0203 | | 0.001 | | 0.123 | | 0.0155 | | 0.0605 | | 0 | | 0 | | 0 |
| 7/13/91 | V-4 | 154.8 | | 0.03 | | 0.017 | | 0.002 | | 0.098 | | 0.016 | | 0.0876 | | 0 | | 0 | | 0 |

Note:

a    Values in I-TEQ ng/dscm

TABLE CXLV (Concluded)

## SOURCE TESTING DATA FOR 2, 3, 7, 8 POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURAN COMPOUNDS [a]

| Source Test ID | flag | 1, 2, 3, 4, 7, 8-Cl6-dibenzo-p-dioxin | flag | 1, 2, 3, 6, 7, 8-Cl6-dibenzo-p-dioxin | flag | 1, 2, 3, 7, 8, 9-Cl6-dibenzo-p-dioxin | flag | 1,2,3, 4, 6, 7, 8-Cl7-dibenzofuran | flag | 1,2,3,4,7,8,9-Cl7-dibenzofuran | flag | 1,2,3,4,6,7,8-Cl7-dibenzo-p-dioxin | flag | 1,2,3,4,6,7,8,9-Cl8-dibenzofuran | flag | 1,2,3,4,6,7,8,9-Cl8-dibenzo-p-dioxin | I-TEQ calculated (ND at DL) (ng/dscm) | Reported in Project Report | Conc. in Stack Test Report | Flowrate (dscm/s) | emission rate (ng I-TEQ/s) | TSP conc. (mg/dscm) | PCB DRE (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.1 | | 0.1 | | 0.1 | | 0.01 | | 0.01 | | 0.001 | | 0.001 | | 0.001 | | | | | | | |
| I-1 | < | 0.007 | < | 0.007 | < | 0.006 | < | 0.0003 | < | 0.0005 | < | 0.00056 | < | 0.00003 | < | 0.00003 | 0.393 | 0.136 | 0.411 | 3.6944 | 1.45236 | 16 | 99.99998109 |
| I-2 | < | 0.008 | < | 0.008 | < | 0.007 | < | 0.0003 | < | 0.0006 | < | 0.00064 | < | 0.00003 | < | 0.00004 | 0.186 | 0.121 | 0.185 | 3.5278 | 0.655849 | 0.6 | 99.99997997 |
| I-3 | < | 0.009 | < | 0.009 | < | 0.008 | < | 0.0004 | < | 0.0006 | < | 0.00073 | < | 0.00003 | < | 0.00004 | 0.209 | 0.138 | 0.208 | 3.5833 | 0.749275 | 2.9 | 99.99997250 |
| II-2 | < | 0.009 | < | 0.009 | < | 0.008 | < | 0.0017 | < | 0.0006 | < | 0.00072 | | 0.28223 | < | 0.01054 | 0.587 | 0.455 | 0.598 | 3.5 | 2.053765 | 41 | 99.99999735 |
| II-3 | < | 0.01 | < | 0.009 | < | 0.008 | | 0.0563 | | 0.0342 | < | 0.00075 | | 0.03548 | | 0.0019 | 0.997 | 0.696 | 0.998 | 3.3889 | 3.379163 | 59.9 | 99.99999776 |
| II-4 | < | 0.01 | < | 0.009 | < | 0.008 | < | 0.1403 | < | 0.0432 | < | .00075 | | 0.0591 | | 0.00438 | 1.648 | 1.651 | 1.651 | 3.472 | 5.722674 | 91.8 | 99.99999742 |
| V-2 | | 0.0212 | | 0 | | 0 | | 0.12646 | | 0.0219 | | 0.000175 | | 0.03034 | | 0.002392 | 0.773 | 0.536 | 0.53 | 2.9 | 2.240352 | 23 | 99.99999795 |
| V-3 | | 0.00689 | | 0 | | 0 | | 0.02044 | | 0.00423 | | 0.000128 | | 0.0046 | | 0.000416 | 0.2934 | 0.167 | 0.205 | 2.83 | 0.829399 | 16.6 | 99.99999761 |
| V-4 | | 0.00771 | | 0 | | 0 | | 0.037 | | 0.0091 | | 0.000197 | | 0.02484 | | 0.000936 | 0.330 | 0.271 | 0.256 | 2.81 | 0.926679 | 44 | 99.99999491 |

**Note:**

[a]    Values in I-TEQ ng/dscm

**TABLE CXLVI**

SUMMARY OF INTERNATIONAL TOXIC EQUIVALENCY EMISSIONS CONCENTRATION
AND RATES FROM SOURCE TESTING

| Date (mm/dd/yy) | Run ID | PCB feed rate (kg/hr) | PCB DRE (%) | I-TEQ (ng/dscm) calculated ND = 0 | I-TEQ (ng/dscm) calculated ND=DL | I-TEQ conc. (ng/dscm) Reported in Project Report | I-TEQ conc. (ng/dscm) Reported in Stack Test Report | Flow rate (dscm/s) | Emission rate ITEQ (ng/s) ND=0 | Emission rate ITEQ (ng/s) ND=DL | TSP conc. (mg/dscm) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/16/91 | I-1 | 26.07 | 99.9999811 | 0.250 | 0.393 | 0.136 | 0.411 | 3.694 | 0.924 | 1.452 | 16 |
| 2/19/91 | I-2 | 22.24 | 99.99998 | 0.008 | 0.186 | 0.121 | 0.185 | 3.528 | 0.026 | 0.656 | 0.6 |
| 2/20/91 | I-3 | 18.31 | 99.9999725 | 0.010 | 0.209 | 0.138 | 0.208 | 3.583 | 0.036 | 0.742 | 2.9 |
| 2/24/91 | II-2 | 197.4 | 99.9999973 | 0.012 | 0.587 | 0.455 | 0.598 | 3.500 | 0.042 | 2.054 | 41 |
| 2/25/91 | II-3 | 212.9 | 99.9999978 | 0.024 | 0.997 | 0.696 | 0.998 | 3.389 | 0.081 | 3.379 | 59.9 |
| 2/26/91 | II-4 | 233.8 | 99.9999974 | 0.090 | 1.648 | 1.651 | 1.651 | 3.472 | 0.313 | 5.723 | 91.8 |
| 7/11/91 | V-2 | 241.92 | 99.9999979 | 0.221 | 0.773 | 0.536 | 0.530 | 2.900 | 0.640 | 2.240 | 23 |
| 7/12/91 | V-3 | 160.56 | 99.9999976 | 0.184 | 0.293 | 0.167 | 0.205 | 2.830 | 0.519 | 0.829 | 16.6 |
| 7/13/91 | V-4 | 154.8 | 99.9999949 | 0.100 | 0.330 | 0.271 | 0.256 | 2.810 | 0.281 | 0.927 | 44.1 |

# TABLE CXLVII

### SUMMARY STATISTICS FOR 2, 3, 7, 8 POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN EMISSIONS FOR SOURCE TEST

|  | I-TEQ (ng/dscm) Calculated ND = 0 | I-TEQ calculated ND at DL (ng/dscm) | ITEQ conc. Reported in Project Report (ng/dscm) | Conc. in Stack Test Report (ng/dscm) | TSP conc. (mg/dscm) | MAX. emission rate (ng I-TEQ/s) |
|---|---|---|---|---|---|---|
| MEAN | 0.1 | 0.602 | 0.463444 | 0.56 | 32.9 | 2.001 |
| Std. Dev. | 0.096 | 0.477 | 0.490538 | 0.486 | 29.5 | 1.659 |
| 95% CI | 0.063 | 0.312 | 0.320479 | 0.318 | 19.3 | 1.084 |
| MIN. | 0.008 | 0.186 | 0.121 | 0.185 | 0.6 | 0.656 |
| MAX. | 0.25 | 1.648 | 1.651 | 1.651 | 91.8 | 5.723 |

**Note:**

MAX. emission rate is calculated using I-TEQ concentrations with ND=DL
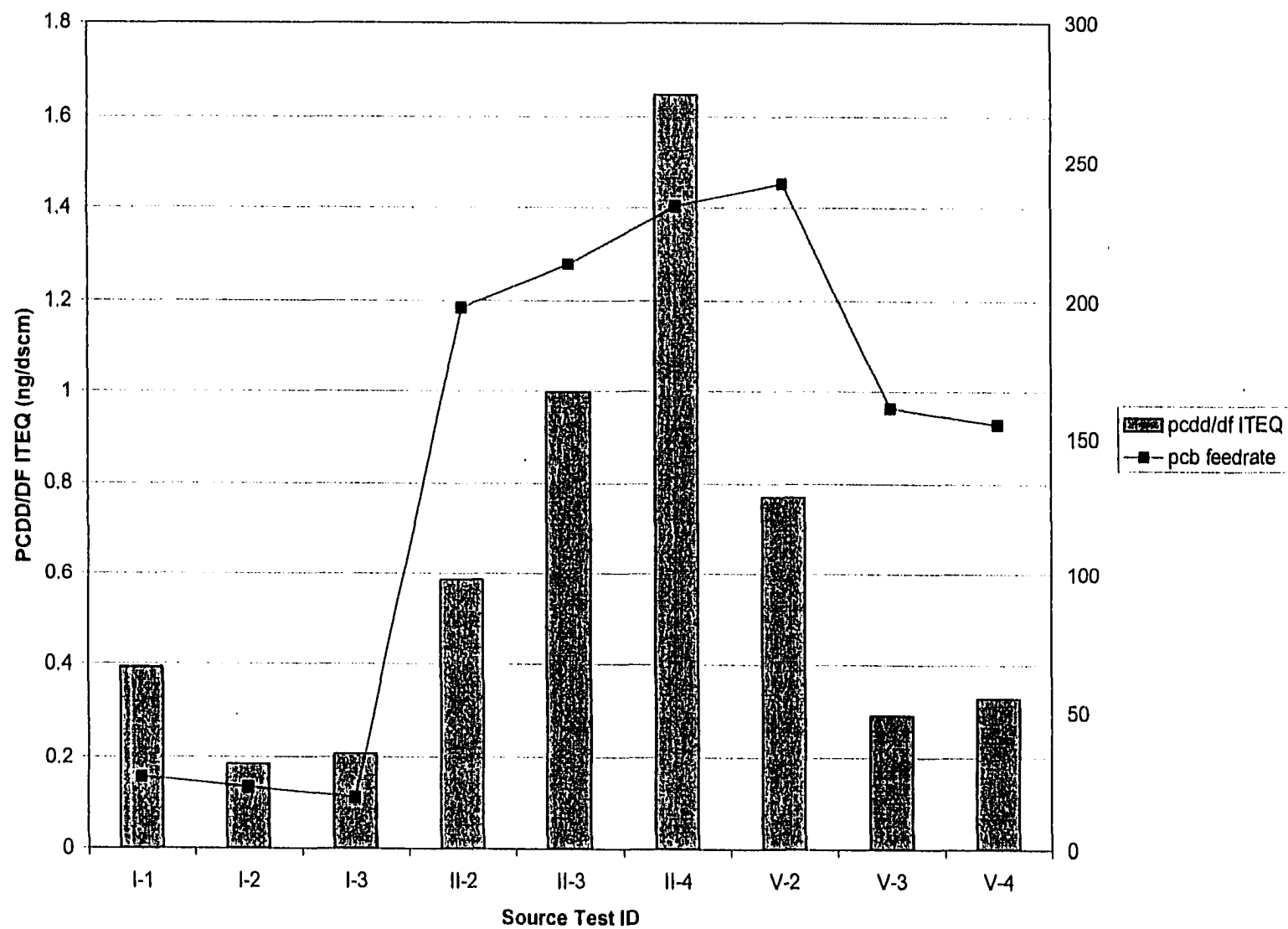
Figure 111. Polychlorinated dibenzo-p-dioxins/dibenzofurans concentration and polychlorinated biphenyl feed rate.
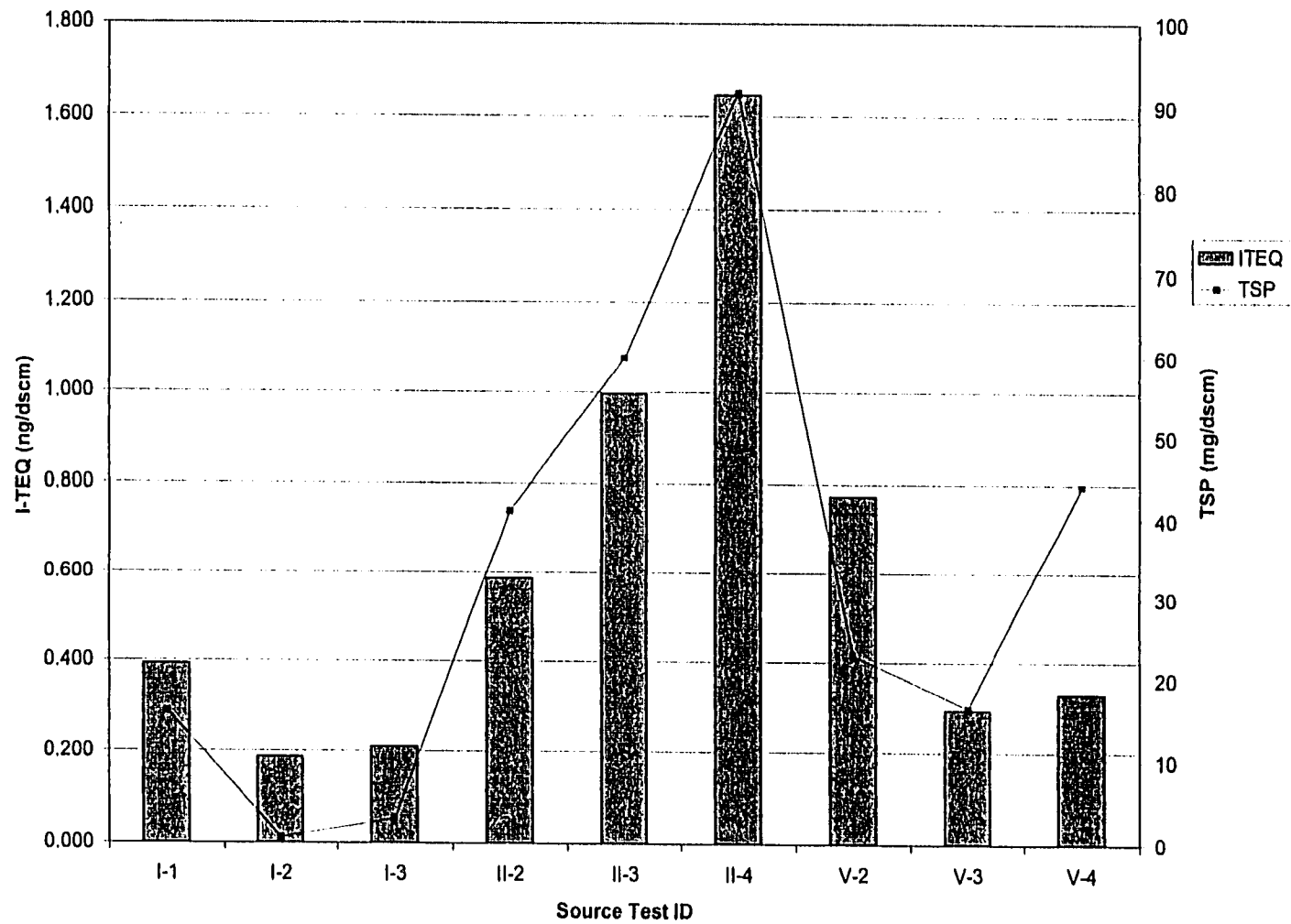
Figure 112.   Polychlorinated dibenzo-p-dioxins/dibenzofurans international toxic equivalency emissions and total suspended particulate concentrations.
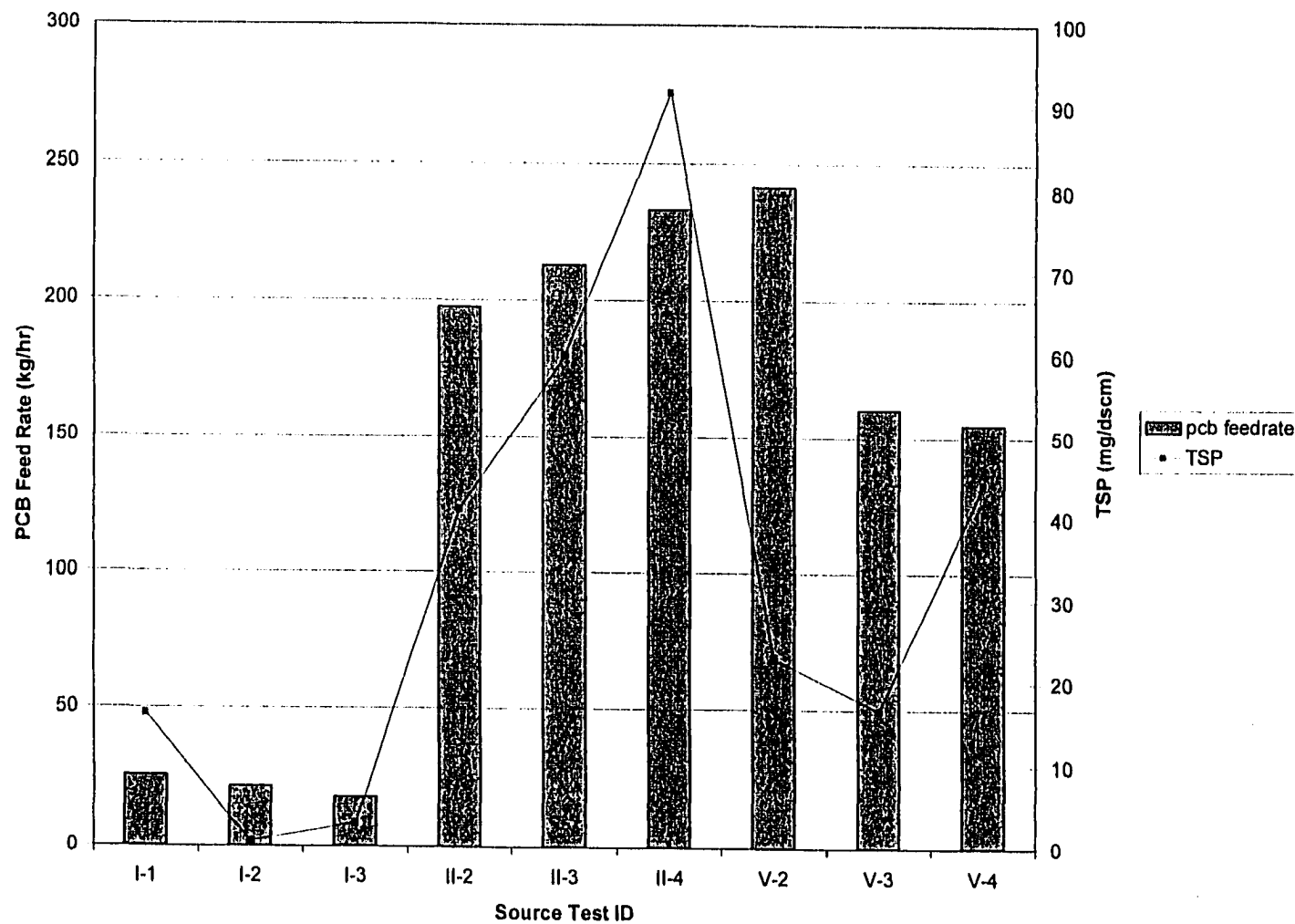
Figure 113.    Polychlorinated biphenyl feed rate and total suspended particulate concentrations.
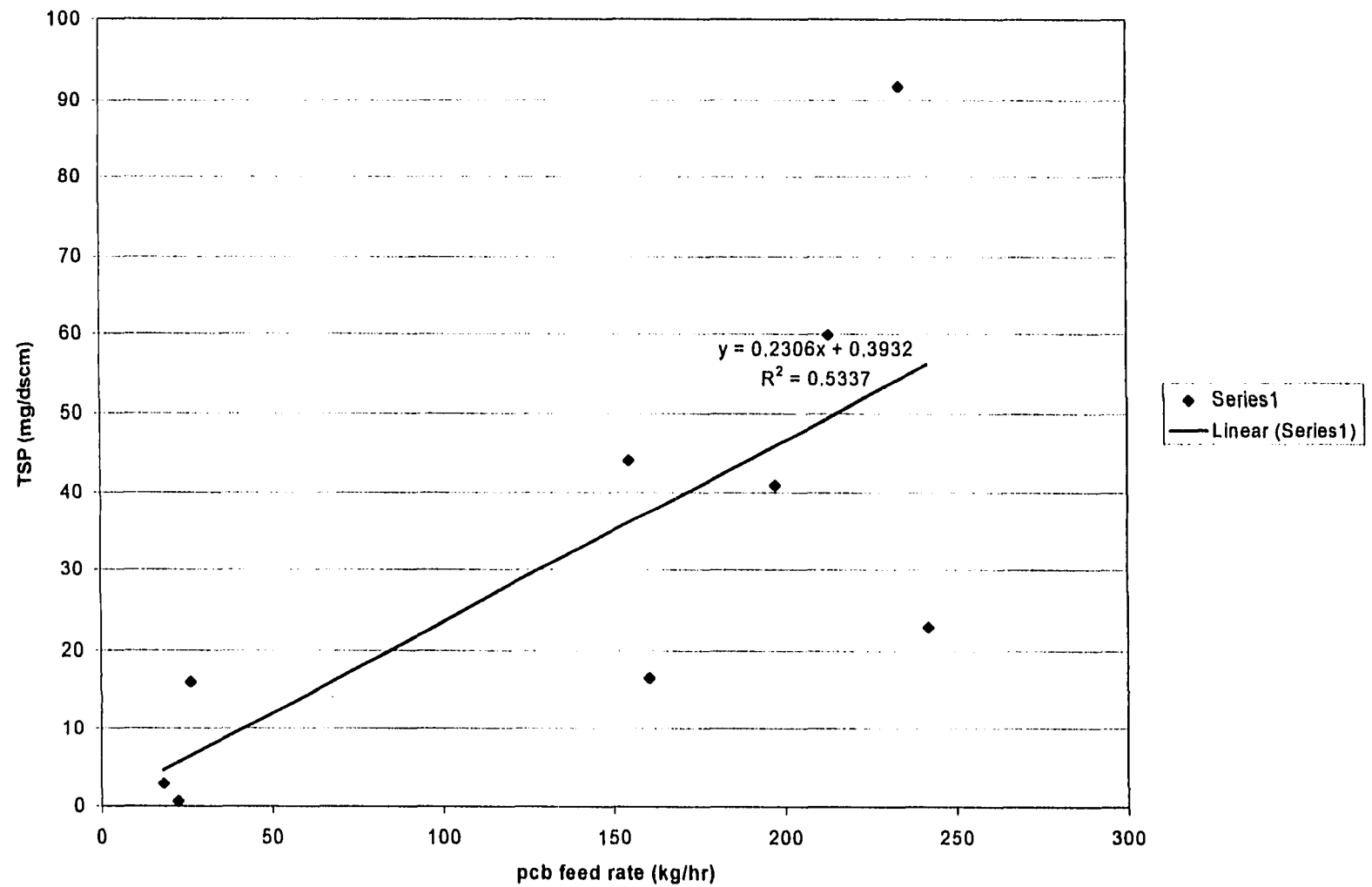
Figure 114. Correlation plot for polychlorinated biphenyl feed rate and total suspended particulate concentration.
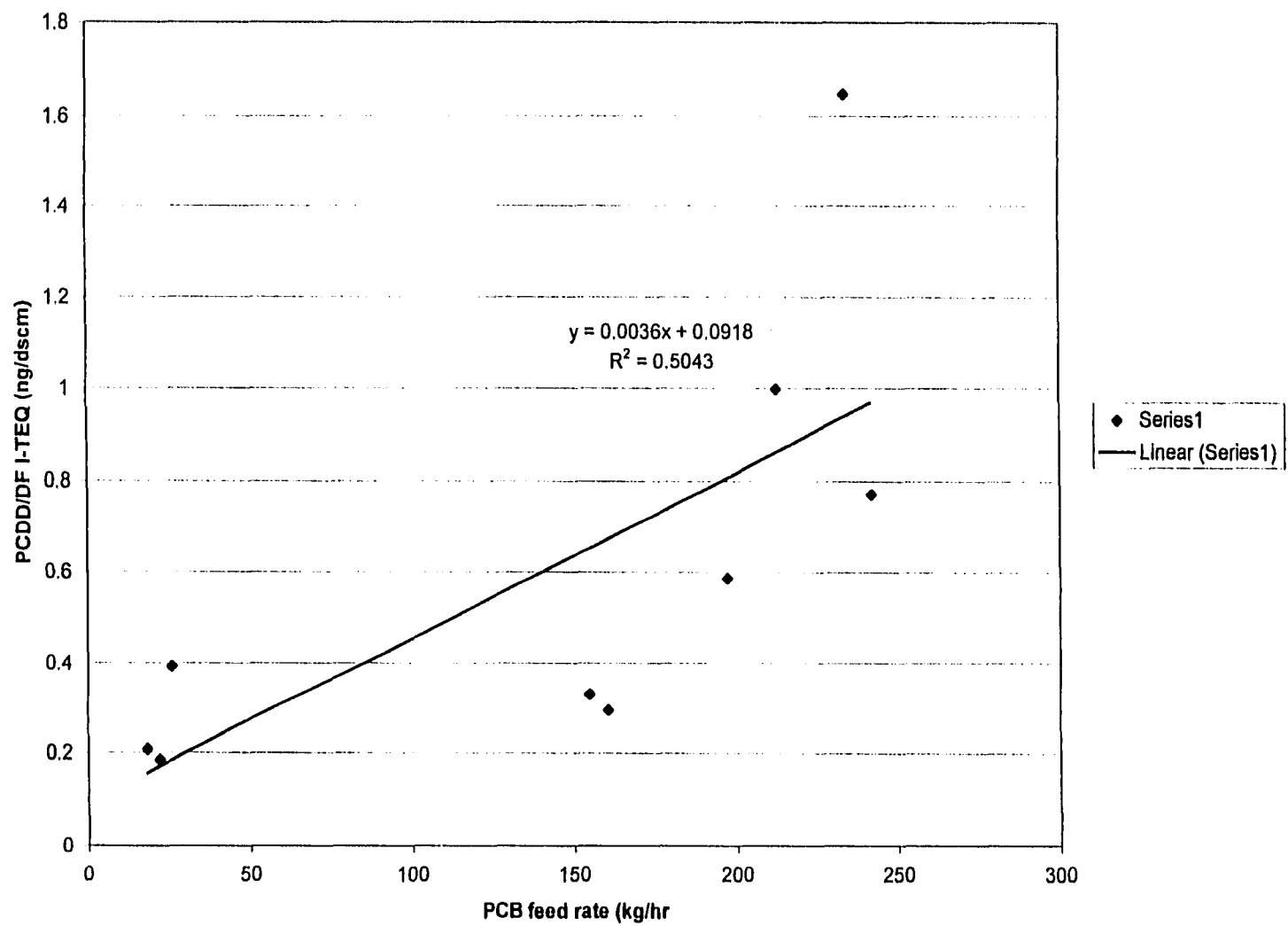
Figure 115. Correlation of polychlorinated biphenyl feed rate and polychlorinated dibenzo-p-dioxins/dibenzofurans international toxic equivalency concentration.
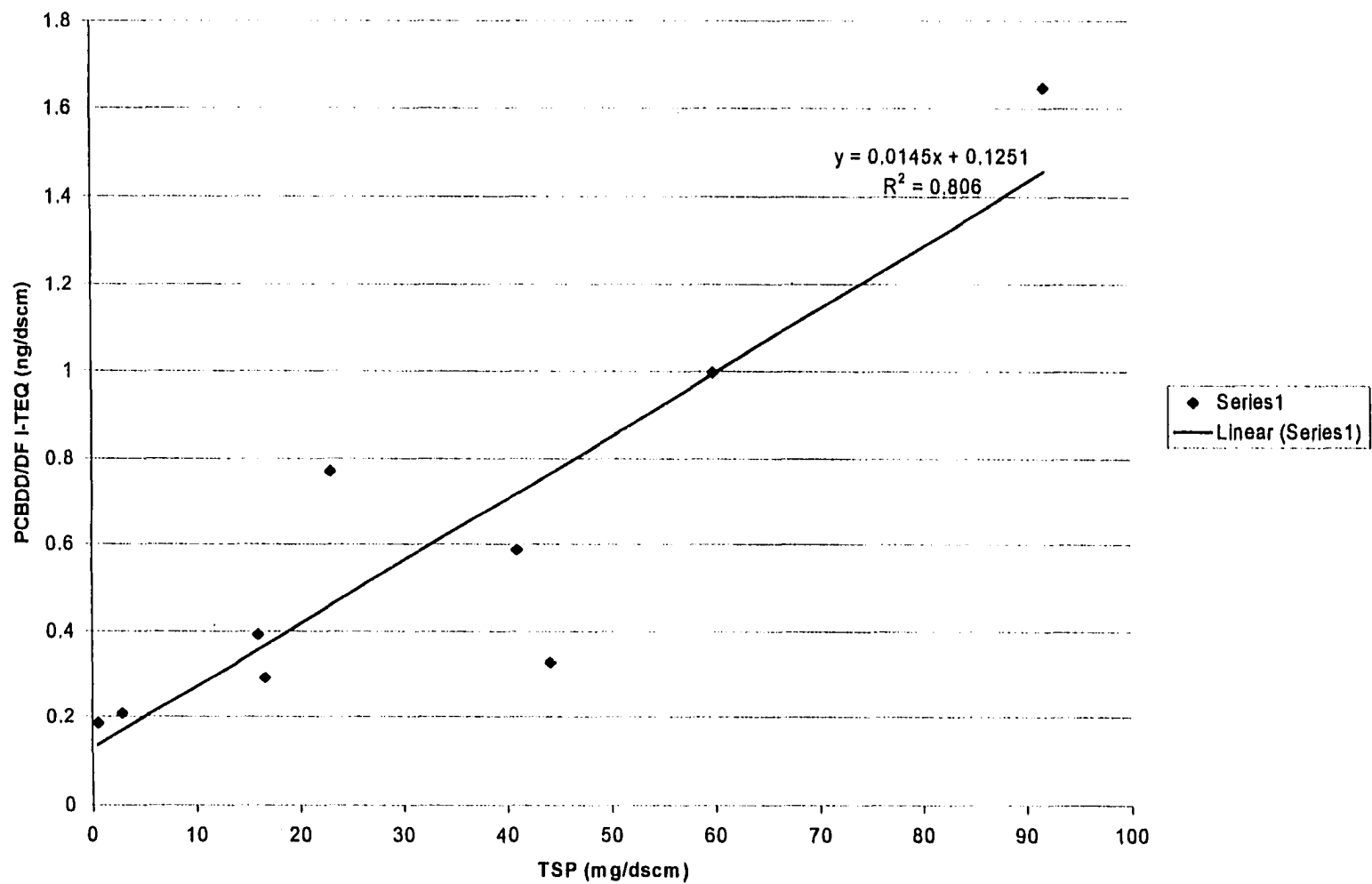
Figure 116. Correlation plot for total suspended particulate concentration and polychlorinated dibenzo-p-dioxins/dibenzofurans international toxic equivalency.
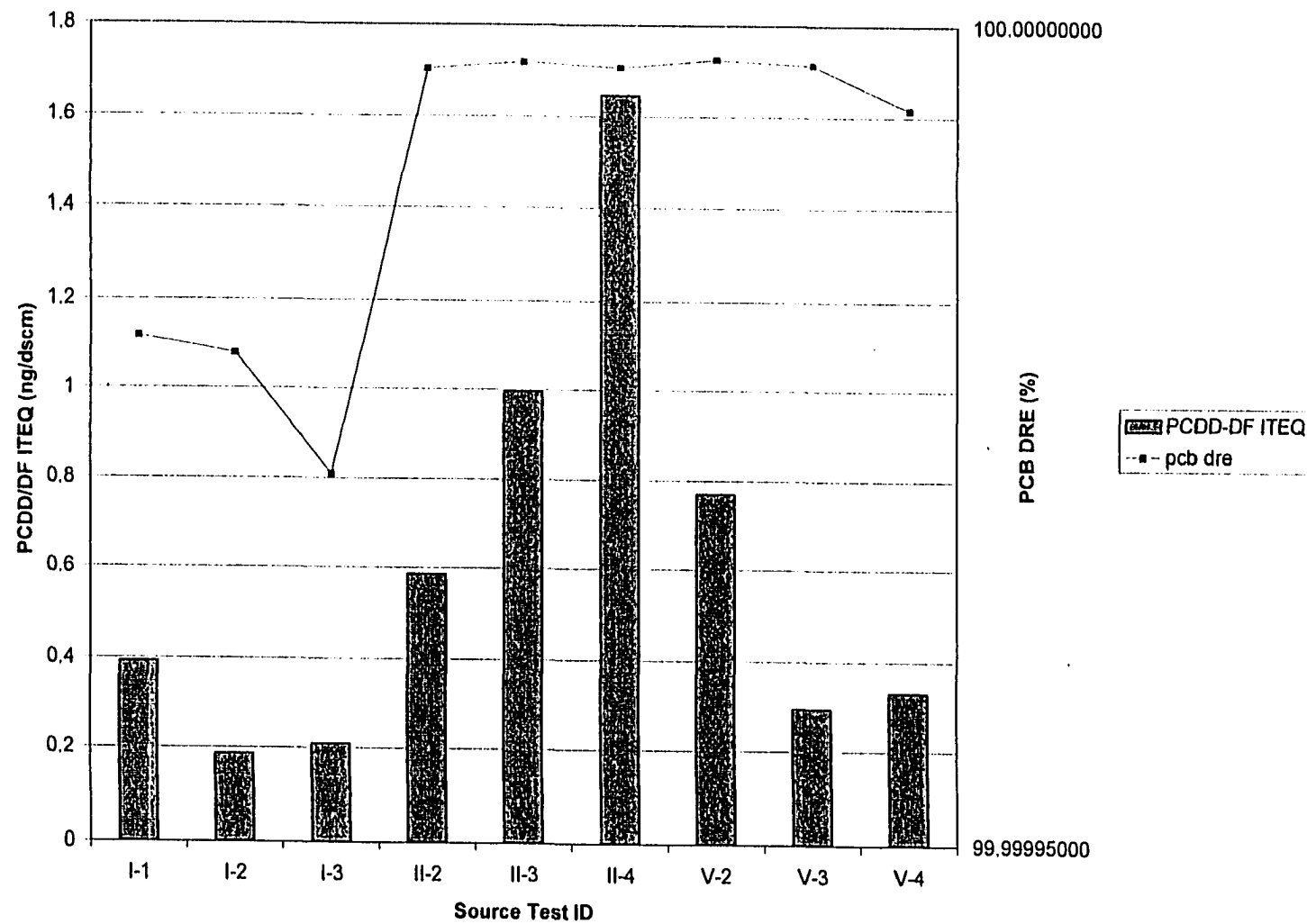
Figure 117. Polychlorinated biphenyl destruction and removal efficiency and polychlorinated dibenzo-p-dioxins/dibenzofurans international toxic equivalency.

### 4.9.1   Air Dispersion Modeling

The ISC3ST modeling results obtained in Section 4.8.1 for the 9 Source Testing dates were also used to calculate ambient air PCDD/DF concentrations for the stack emissions. In contrast to PCBTOT, where emission concentrations do not appear to have any correlation with TSP concentration (Figure 118), PCDD/DF emissions were correlated with TSP concentrations, indicating most of PCDD/DF is probably particulate bound. This indicates that particulate emission information (size fraction, etc.) may be less important in the modeling of PCB than of PCDD/DF. As noted in Section 4.8, no specific particulate size fraction information was available for the ENSCO unit, although the designer has indicated that he expected "most" of the particulate to be submicron [213]. Therefore, ambient air concentrations were calculated by the ISC3ST model, assuming the PCDD/DFs were present in the gaseous phase.

### 4.9.1.1 Worst Case Scenario

The worst case air dispersion modeling results from Section 4.8 were used to calculate the maximum concentrations for PCDD/DF using the maximum emission rate for the 9 Source Tests. The worst case dispersion results are shown in Table CXLVIII. A maximum concentration of 0.12 pg/m I-TEQ was calculated. While this is in the range observed for the ambient air samples during the project, it should be noted that these are background concentrations for this region [125, 149].
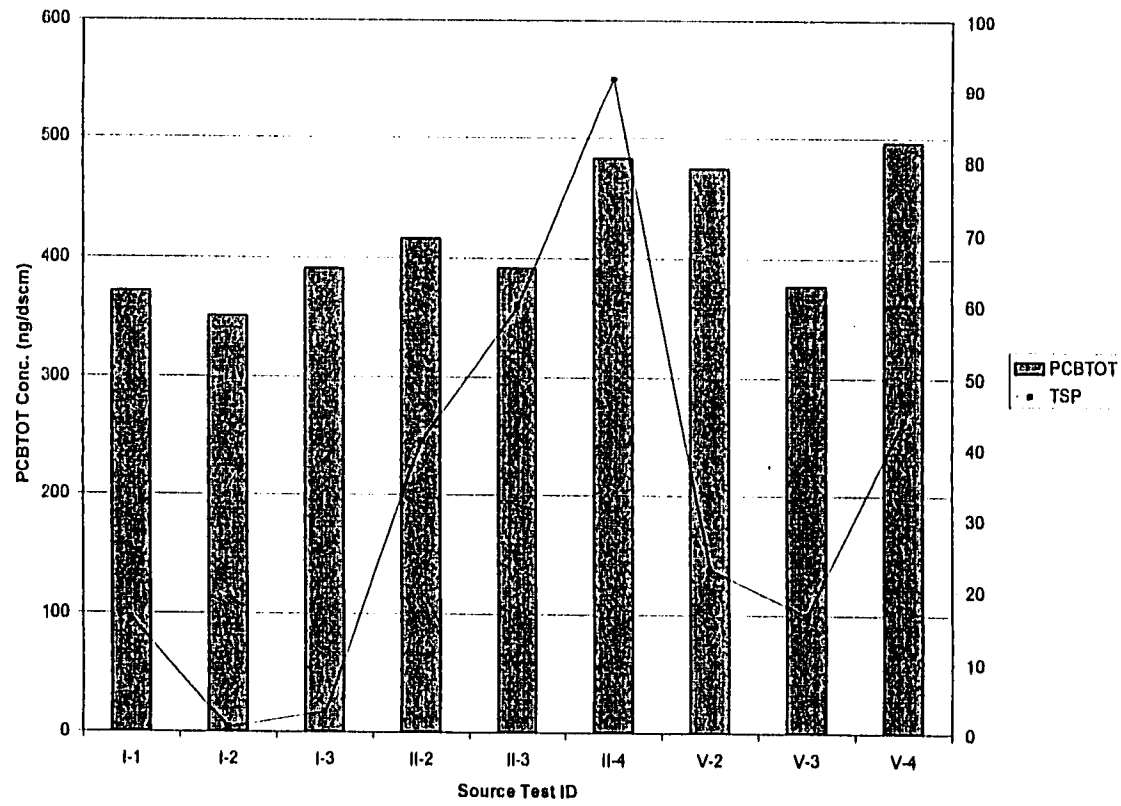
Figure 118. Total polychlorinated biphenyl and total suspended particulate concentrations.

**TABLE CXLVIII**

**WORST CASE AIR DISPERSION MODELING RESULTS FOR
POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURANS**

| model | PCDD/DF emission rate I-TEQ (g/s) | Stack Height (m) | Stack velocity (m/s) | Stack Dia. (m) | Stack T (C) | Ambient T (K) | Receptor Height (m) | MAX. Conc. (ug/m^3) | MAX. Conc. (ng/m^3) | MAX. Conc. I-TEQ (pg/m^3) | x (m) | y (m) | Distance from stack |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| screen3 | 1 | 21.9 | 17.48 | 0.762 | 79.2 | 293 | 0 | 26.05 | 26050 | 26050000 | -- | -- | 247 |
| screen3 | 5.72E-09 | 21.9 | 17.48 | 0.762 | 79.2 | 293 | 0 | 1.49E-07 | 0.000149 | 0.149 | -- | -- | 247 |
| ISC3ST | 1 | 21.9 | 17.48 | 0.762 | 79.2 | screen.met | 0 | 20.85 | 20850 | 20850000 | 225 | 268 | 350 |
| ISC3ST | 5.72E-09 | 21.9 | 17.48 | 0.762 | 79.2 | screen.met | 0 | 1.19E-07 | 0.000119 | 0.119 | 225 | 268 | 350 |

## 4.9.1.2 Industrial Source Complex Modeling for Source Test Data and Dates

The ISC3ST model results (from Section 4.8) for the 9 Source Tests were used to calculate ambient air PCDD/DF concentrations due to the stack emissions. The PCDD/DF emissions data for 2,3,7,8-substituted PCDD/DF congeners in Table CXLVI above were used for the emissions rate. The calculated ambient air concentrations for each of the Source Tests are shown in Table CXLIX. Note that these are 24-hour average calculations. There were ambient air PCDD/DF samples taken during 2 of the periods during which source testing took place, but these air samples were approximately 48-hr. averages. The observed and ISC3 calculated concentrations are shown in Table CL. For the ambient air sampling period ending February 26, 1991, the maximum concentration site calculated by ISC3 and the maximum concentration site observed corresponded (23007), but the modeled concentrations were 18 times lower. For the period ending July 11, 1991, the ISC3 calculated maximum concentration site was 23007 (calculated concentration = 0.002 pg/m$^3$ I-TEQ, observed = 0.0017 pg/m$^3$ I-TEQ), was different from the observed maximum concentration site (23011, observed concentration = 0.012 pg/m$^3$ I-TEQ, calculated concentration = <0.0001 pg/m$^3$).

The ISC3 modeled concentrations for PCDD/DF are within one order of magnitude of the observed concentrations. This is a closer match than for the PCB air results. However, it must be noted that, unlike the PCB ambient air concentrations, which are elevated relative to background, the ambient air PCDD/DF results for the Phase 3 are at background concentrations and are lower than PCDD/DF concentrations sampled in Hamilton during the 1991-92 period [170].

**TABLE CXLIX**

RESULTS FROM INDUSTRIAL SOURCE COMPLEX 3 –
SHORT TERM MODELING FOR SOURCE TEST DATA

| Test Designation | Feed Material | MAX. emission rate (ng I-TEQ/s) | PCDD/DF Actual Emission Rate I-TEQ (g/s) | 23007 modeled I-TEQ (pg/m^3) | 23009 modeled I-TEQ (pg/m^3) | 23011 modeled I-TEQ (pg/m^3) | 23013 modeled I-TEQ (pg/m^3) | MAX. conc. modeled I-TEQ (pg/m^3) | MAX. conc. coordinates (x) | MAX. conc. coordinates (y) |
|---|---|---|---|---|---|---|---|---|---|---|
| I-1 | soils | 1.452 | 1.45E-09 | 0.00171 | 0 | 0 | 0 | 8.42E-09 | 321 | 383 |
| I-2 | soils | 0.656 | 6.56E-10 | 0.00126 | 0.000367 | 0 | 0 | 2.2E-09 | 205 | 564 |
| I-3 | soils | 0.749 | 7.49E-10 | 0.000397 | 0 | 0 | 0 | 1.86E-09 | 460 | 386 |
| II-2 | solids/ liquids | 2.054 | 2.05E-09 | 0.00222 | 0 | 0.000164 | 0.000329 | 6.06E-09 | -766 | -643 |
| II-3 | solids/ liquids | 3.379 | 3.38E-09 | 0 | 0 | 0 | 4.39E-05 | 2.93E-08 | -612 | -514 |
| II-4 | solids/ liquids | 5.723 | 5.72E-09 | 0 | 0.00767 | 0 | 0 | 1.9E-08 | 800 | 0 |
| V-2 | solids/ liquids | 2.24 | 2.24E-09 | 0.00206 | 0.00735 | 0 | 0 | 1.06E-08 | 321 | 383 |
| V-3 | solids/ liquids | 0.829 | 8.29E-10 | 0 | 0 | 0 | 0.00172 | 6.56E-09 | -421 | -353 |
| V-4 | solids/ liquids | 0.927 | 9.27E-10 | 0 | 0 | 0 | 0.000306 | 3.1E-09 | -375 | -650 |

469

## TABLE CL

### COMPARISON OF MODELED AND OBSERVED POLYCHLORINATED DIBENZO-P-DIOXIN/DIBENZOFURAN AIR CONCENTRATIONS

| date (mm/dd/yy) | Test Desig-nation | Ambient air date | 23007 modeled | 23007 observed | 23009 modeled | 23009 observed | 23011 modeled | 23011 observed | 23013 modeled | 23013 observed |
|---|---|---|---|---|---|---|---|---|---|---|
| 02/25/91 | II-3 | 2/26/91 | **0.00111** | **0.0202** | <0.0001 | 0.003507 | 8.22E-05 | no sample | 0.000186 | 0.0182 |
| 07/10/91 | V-2 | 7/11/91 | **0.00206** | 0.00168 | <0.0001 | 0.005761 | 0 | **0.0123** | <0.0001 | 0.00195 |

**Notes:**

**Bolded** text represents maximum value for a sampling period.

Concentrations in pg/m$^3$ I-TEQ

Modeled Conc. is average for two previous days (if available)

## 4.9.2 Receptor Modeling

In most ambient air samples, OCDD is the predominant PCDD/DF observed [160, 162]. However, the "average" source profile for combustion sources is dominated by tetra-hepta-CDFs [141, 160]. The reason for this difference is the subject of debate. Recently Baker and Hites have suggested that a possible reason for the enhancement in OCDD concentrations is the atmospheric reaction of pentachlorophenol (PCP) [160], while others have suggested that it may be due, in part, to the longer environmental half lives for OCDF and OCDD, compared to other PCDD/DF homologs [121]. It was decided to use the OCDF/OCDD ratio in the incinerator stack and ambient air to do some rudimentary analysis (based upon receptor modeling principles) of the ambient air PCDD/DF data.

The source test data for the OCDF/OCDD ratio are summarized in Table CLI below. Frequency histograms plots for the OCDF/OCDD ratios for all data and source tests, with at least one of the OCDF or OCDD detected, are shown in Figure 119 (a) and (b). Additional summary statistics are provided for the source test data in Table CLII. The OCDF/OCDD ratio was also compared to the I-TEQ concentration (Figure 120), PCB feed rate (Figure 121), and TSP concentration (Figure 122). There does not appear to be a relationship between the I-TEQ concentration and OCDF/OCDD ratio, but there is somewhat of a relationship to the PCB feed rate and TSP. At the low PCB feed rates for Series I (soils), neither the OCDF nor OCDD was detected. Once higher PCB feed rates were used (Series II and V), OCDF was observed in all 6 runs, and OCDD was observed in 5 of the 6 runs. Even including all 9 runs, the 95% CI is greater than 6. For the 6 tests in which there which OCDF and/or OCDD were detected, the ratios are all >10. Therefore, the OCDF/OCDD ratio in

ambient air samples was proposed to serve as a rough indicator of the contribution of the incinerator stack to the ambient air concentrations, with ratios of >1 indicating that the incinerator stack was possibly responsible for >10% of the observed air concentrations.

The ambient air OCDF/OCDD ratio was calculated for each of the samples in the ambient air PCDD/DF data. The summary statistics for the OCDF, OCDD and OCDF/OCDD ratio in ambient air are provided in Table CLIII. Frequency data and histogram plots are provided for the OCDF/OCDD ratio in Table CLIV and Figure 123, respectively. Only 2 of the 185 ambient air samples have a OCDF/OCDD ratio of >1, with a maximum of 3.14. If the data for detects only are compared, the mean and median values for ambient air (0.352 and 0.196) suggests that the incinerator (mean and median value = 18) contributes, on average, less than 2.5% of the observed ambient concentrations. It should be noted that this assumes that the OCDF/OCDD ratio is relatively constant in the stack (which does appear to be the case), and that this ratio is related to the concentrations of the other PCDD/DF homologs and congeners (which over the short distance from the site and 1-2 day sampling periods would appear to be a reasonable assumption). This relatively crude receptor modeling analysis supports the conclusion from the air dispersion and receptor modeling analysis of the PCB data, i.e., that the incinerator was not the major contributor to the concentrations observed in ambient air sampling.

The question of how the source profile for the incinerator at Smithville compares to other sites was also investigated briefly. Source test results from a number of other PCB incineration projects were obtained from H. Dodohara of the USEPA TSCA Office. A

preliminary review of these other emissions data showed an inverse of the OCDF/OCDD ratio observed for the ENSCO incinerator, that is more OCDD than OCDF. The reason for this difference is not clear. It is noted here, but was not investigated further as it was outside the scope of this thesis.

Because the main focus of this research was the PCB ambient air data, and the PCDD/DF ambient air data was not very amenable to data analysis, further receptor modeling work was not carried out for the work in this thesis.

## TABLE CLI

POLYCHLORINATED DIBENZO-P-DIOXINS/DIBENZOFURAN SOURCE TEST DATA WITH
OCTACHLORODIBENZOFURAN/OCTACHLORODIBENZO-P-DIOXIN RATIOS

| Date (mm/dd/yy) | Source Test ID | I-TEQ (ng/dscm) ND=0 | I-TEQ (ng/dscm) ND=DL | I-TEQ conc. (ng/dscm) Reported in Project Report | I-TEQ conc. (ng/dscm) Conc. Reported in Stack Test Report | Emission rate I-TEQ (ng/s) ND=0 | Emission rate I-TEQ (ng/s) ND=DL | TSP conc. (mg/dscm) | PCBTOT conc. (ng/dscm) | Ratio OCDF: OCDD | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2/16/91 | I-1 | 0.250 | 0.393 | 0.136 | 0.411 | 0.924 | 1.452 | 16 | 371.47 | 1.00 | OCDD & OCDF ND |
| 2/19/91 | I-2 | 0.008 | 0.186 | 0.121 | 0.185 | 0.026 | 0.656 | 0.6 | 350.62 | 0.75 | OCDD & OCDF ND |
| 2/20/91 | I-3 | 0.010 | 0.209 | 0.138 | 0.208 | 0.036 | 0.749 | 2.9 | 391.3 | 0.75 | OCDD & OCDF ND |
| 2/24/91 | II-2 | 0.012 | 0.587 | 0.455 | 0.598 | 0.042 | 2.054 | 41 | 416.2 | 26.78 | OCDD ND |
| 2/25/91 | II-3 | 0.024 | 0.997 | 0.696 | 0.998 | 0.081 | 3.379 | 59.9 | 391.8 | 18.67 | |
| 2/26/91 | II-4 | 0.090 | 1.648 | 1.651 | 1.651 | 0.313 | 5.723 | 91.8 | 482.9 | 13.49 | |
| 7/11/91 | V-2 | 0.221 | 0.773 | 0.536 | 0.530 | 0.640 | 2.240 | 23 | 475 | 12.68 | |
| 7/12/91 | V-3 | 0.184 | 0.293 | 0.167 | 0.205 | 0.519 | 0.829 | 16.6 | 377 | 11.06 | |
| 7/13/91 | V-4 | 0.100 | 0.330 | 0.271 | 0.256 | 0.281 | 0.927 | 44.1 | 496 | 26.53 | |
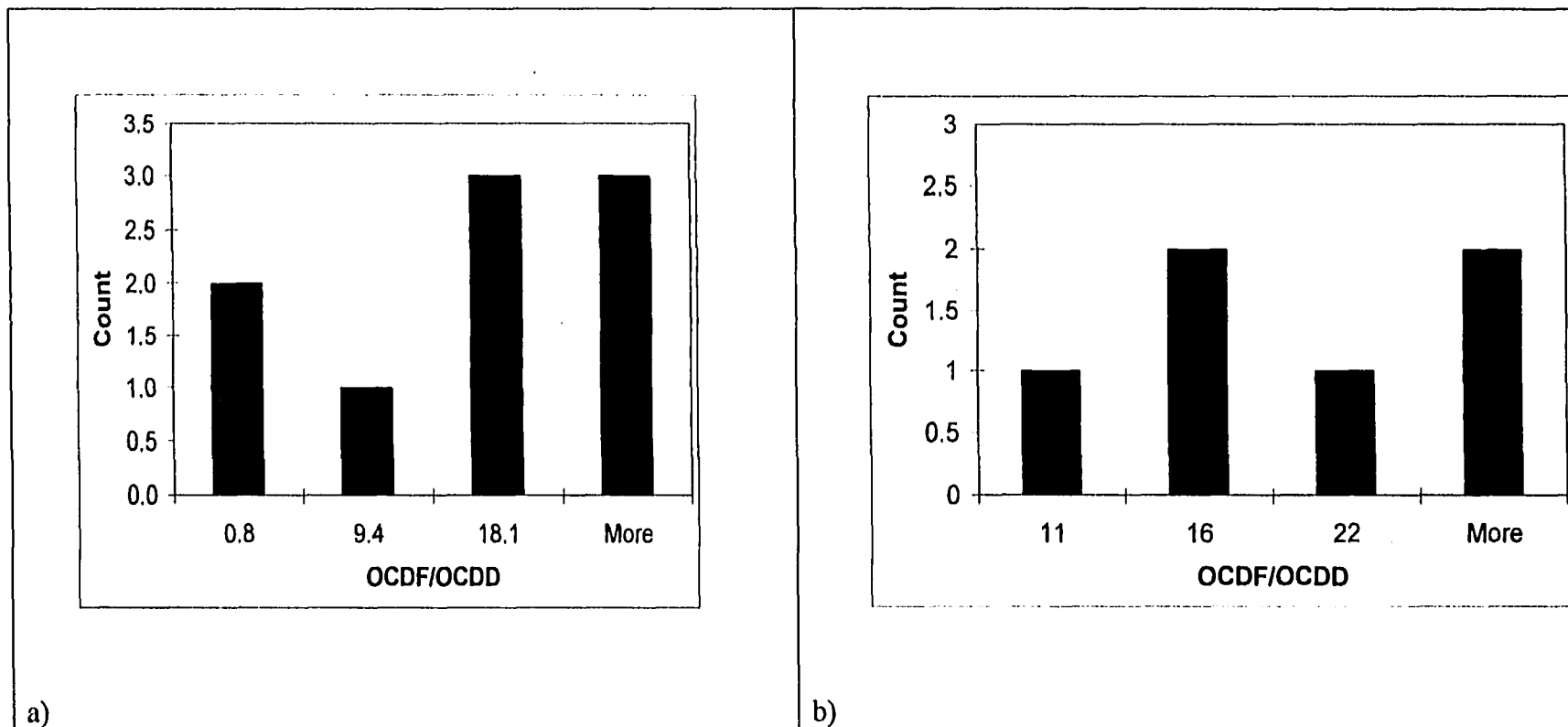
Figure 119.  a) Histogram frequency plot for source test octachlorodibenzofuran/octachlorodibenzo-p-dioxin including non-detect values at detection limit; b) Histogram frequency plot for source test octachlorodibenzofuran/octachlorodibenzo-p-dioxin detected values only.

**TABLE CLII**

SUMMARY STATISTICS FOR
OCTACHLORODIBENZOFURAN/OCTACHLORODIBENZO-P-DIOXIN
RATIO FOR SOURCE TESTS

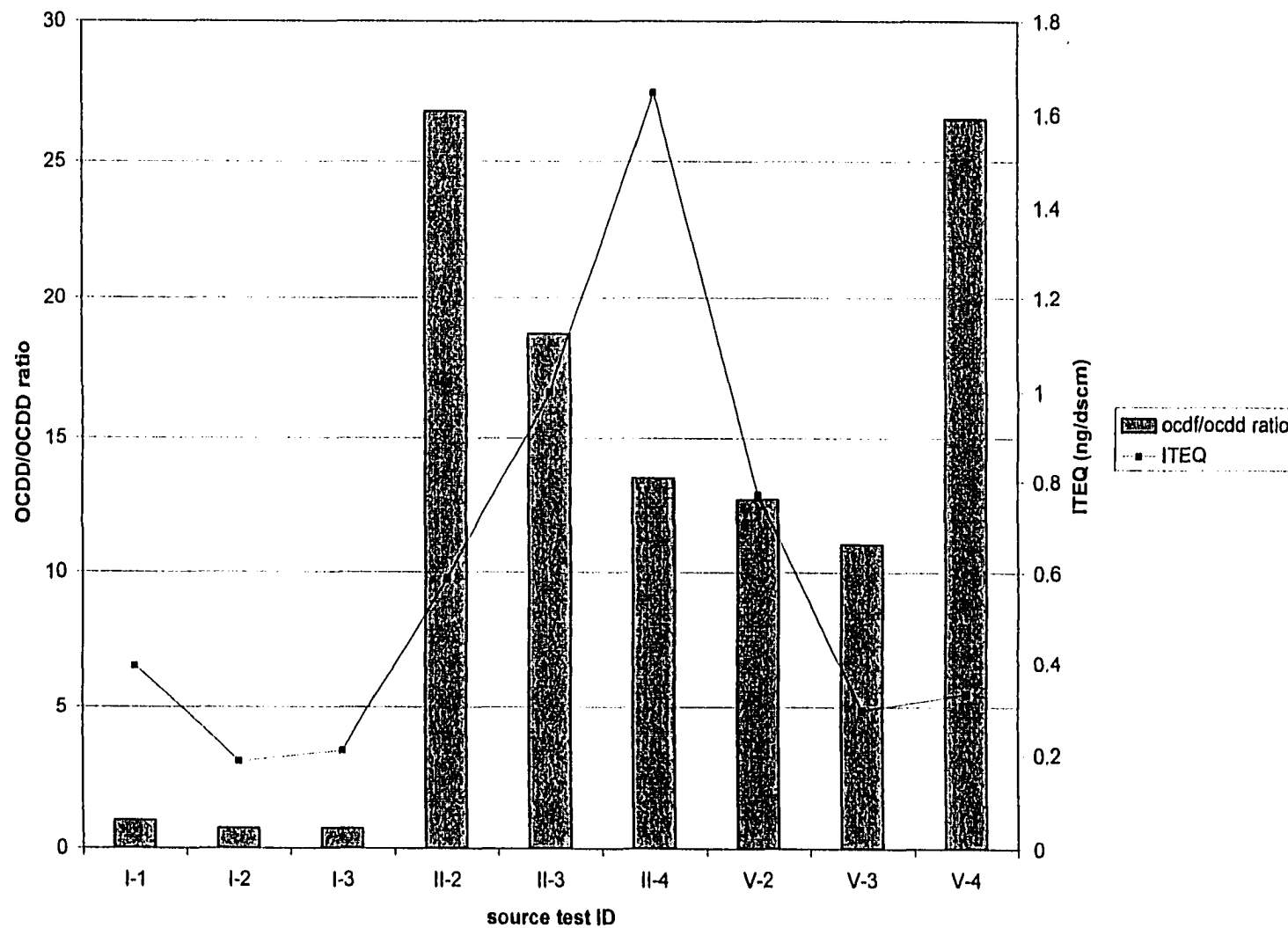| Statistic | ALL Source Tests | Source Tests with OCDF or OCDD detected |
|---|---|---|
| n | 9 | 6 |
| Minimum | 0.75 | 11.06 |
| Maximum | 26.78 | 26.78 |
| Range | 26.03 | 15.72 |
| Sum | 111.72 | 109.22 |
| Median | 12.68 | 16.08 |
| Mean | 12.41 | 18.20 |
| C95% CI | 6.736 | 5.622 |
| 95% CI Upper | 19.15 | 23.83 |
| 95% CI Lower | 5.68 | 12.58 |
| mode | 0.75 | #N/A |
| Std. Dev. | 10.31 | 7.026 |
| Variance | 106.289 | 49.37 |
| Skewness (G1) | 0 | 0 |
| Kurtosis (G2) | -1 | -2 |

**Note:**

ND values at DL

Figure 120. Octachlorodibenzofuran/octachlorodibenzo-p-dioxin ratio and international toxic equivalency concentration by source test.
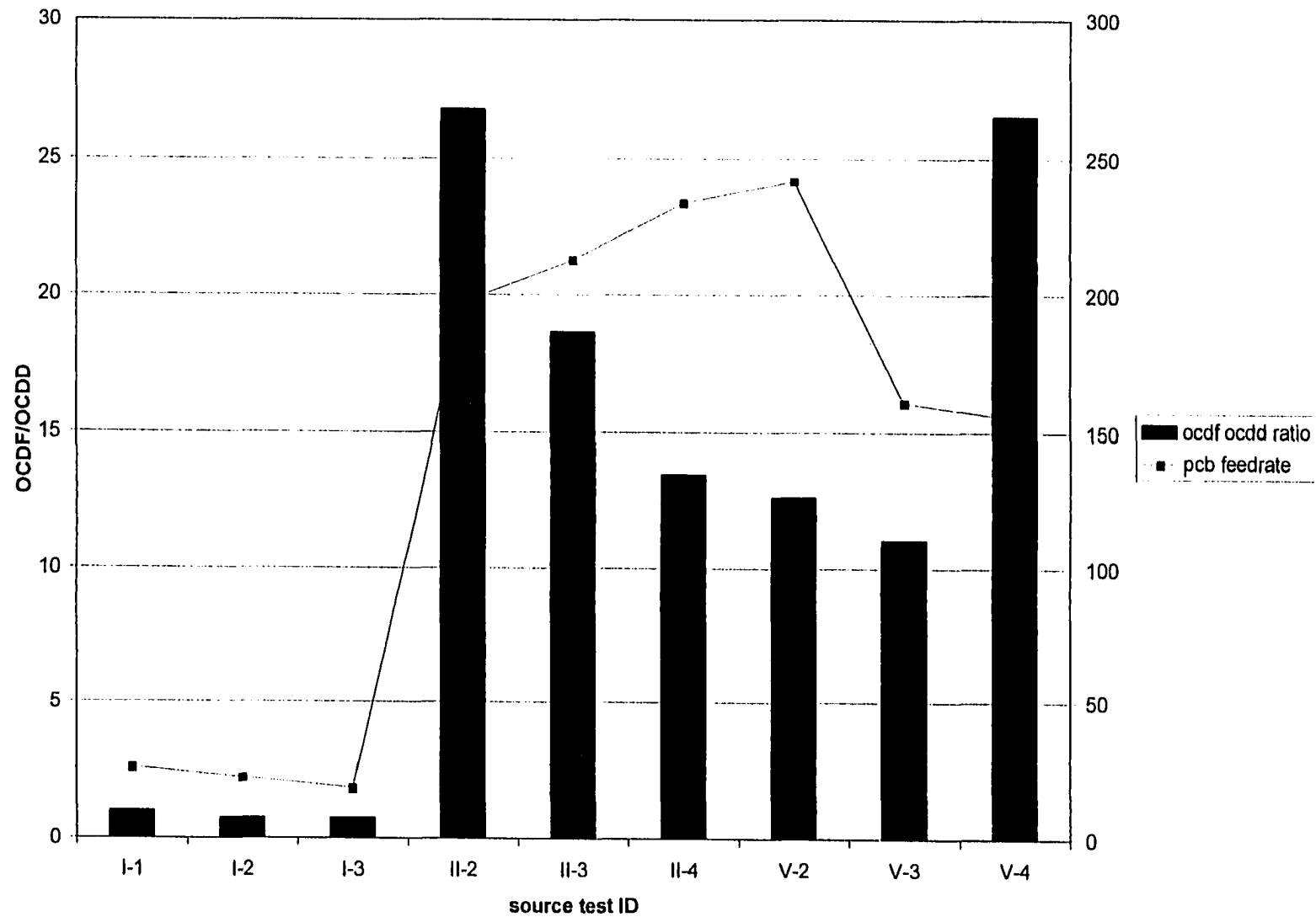
Figure 121. Octachlorodibenzofuran/octachlorodibenzo-p-dioxin ratio and polychlorinated biphenyl feed rate for source tests.
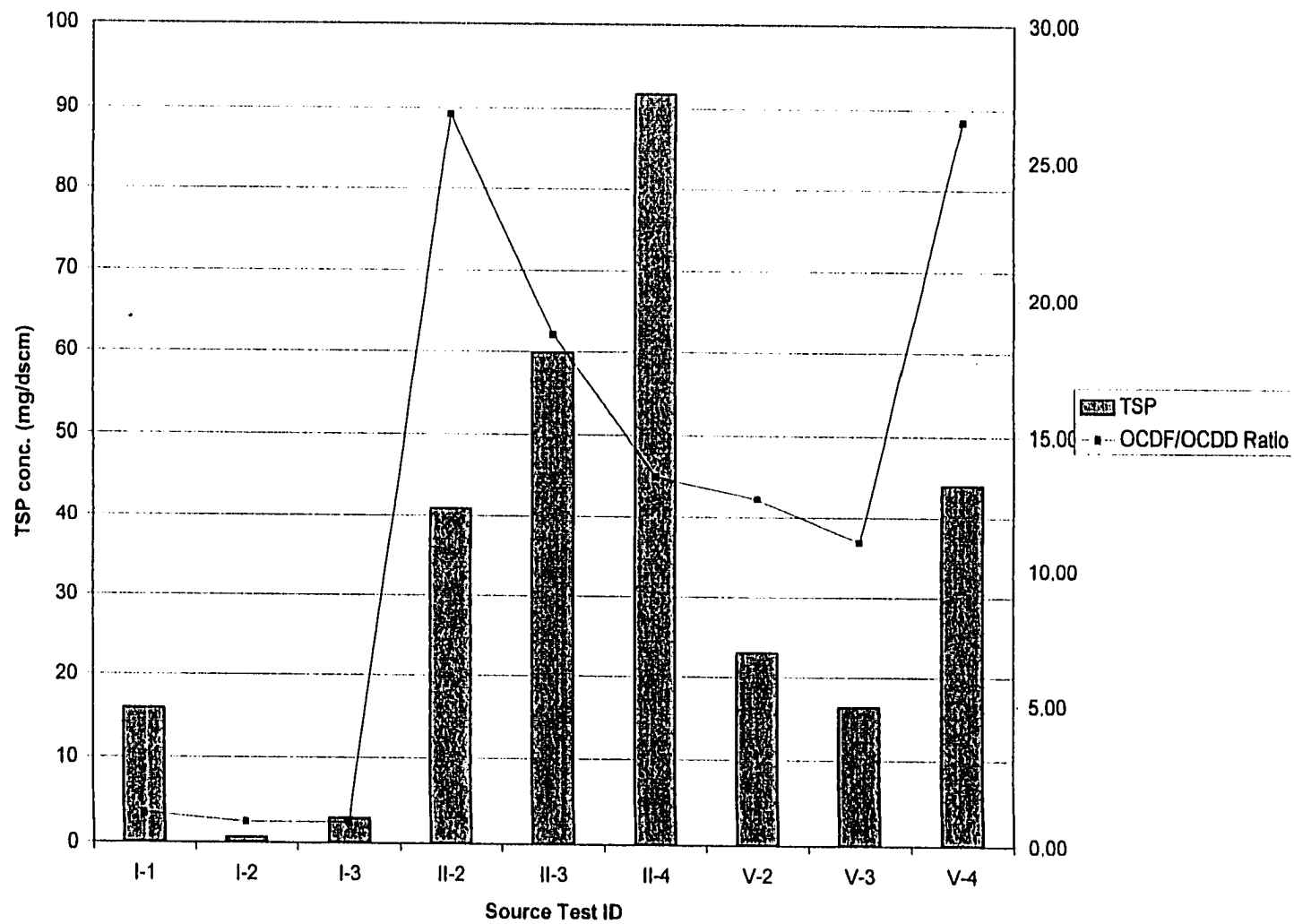
Figure 122. Octachlorodibenzofuran/octachlorodibenzo-p-dioxin ratio and total suspended particulate concentration for source tests.

**TABLE CLIII**

SUMMARY STATISTICS FOR OCTACHLORODIBENZOFURAN AND
OCTACHLORODIBENZO-P-DIOXIN IN AMBIENT AIR SAMPLES

| | OCDF[a] | OCDD[a] | OCDF/ OCDD | OCDF/ OCDD | OCDF/ OCDD | OCDF/ OCDD |
|---|---|---|---|---|---|---|
| **Treatment of ND data** | | | **Both detected** | **OCDF ND=0** | **OCDF = 2E-5** | **ND=blank** |
| n observations | 185 | 185 | 92 | 162 | 185 | 162 |
| n = 0 | 93 | 23 | 0 | 0 | 23 | 0 |
| n > 0 | 92 | 162 | 92 | 162 | 162 | 162 |
| n blank | 0 | 0 | 93 | 0 | 0 | 23 |
| Minimum | 0 | 0 | 5.54E-02 | #DIV/0! | 0.00E+00 | 9.42E-03 |
| Maximum | 0.00356 | 0.00318 | **3.14E+00** | #DIV/0! | 6.61E-01 | **3.14E+00** |
| Range | 0.00356 | 0.00318 | 3.09E+00 | #DIV/0! | 6.61E-01 | 3.13E+00 |
| Sum | 0.0191 | 0.0851 | 3.24E+01 | #DIV/0! | 1.13E+01 | 3.72E+01 |
| Median | 0 | 0.000347 | 1.96E-01 | #DIV/0! | 2.07E-02 | 1.07E-01 |
| Mean | 0.000103 | 0.00046 | 3.52E-01 | #DIV/0! | 6.11E-02 | 2.30E-01 |
| 95% CI Upper | 0.000459 | 0.000926 | 8.67E-01 | #DIV/0! | 1.62E-01 | 6.43E-01 |
| 95% CI Lower | -0.000252 | -5.59E-06 | -1.63E-01 | #DIV/0! | -3.95E-02 | -1.83E-01 |
| Mode | 0 | 0 | 2.14E-01 | #DIV/0! | 0.00E+00 | 2.14E-01 |
| Std. Error | 2.61E-05 | 3.42E-05 | 5.37E-02 | #DIV/0! | 7.40E-03 | 3.25E-02 |
| Std. Dev. | 0.000355 | 0.000466 | 5.15E-01 | #DIV/0! | 1.01E-01 | 4.13E-01 |
| Variance | 1.263E-07 | 2.169E-07 | 2.65E-01 | #DIV/0! | 1.01E-02 | 1.71E-01 |
| CV | 344.46 | 101.21 | 1.46E+02 | #DIV/0! | 1.65E+02 | 1.80E+02 |
| Skewness (G1) | 7 | 3 | 4 | #DIV/0! | 3 | 5 |
| Kurtosis (G2) | 61 | 11 | 17 | #DIV/0! | 13 | 29 |

**Note:**

[a]    Conc. values in pg/m³ (I-TEQ), multiply by 1000 (i.e., 1/0.001) to get actual concentration values for OCDF and OCDD

#DIV/0!    Calculations could not be performed

**TABLE CLIV**

OCTACHLORODIBENZOFURAN/OCTACHLORODIBENZO-P-DIOXIN
RATIO FREQUENCY DISTRIBUTION DATA FOR AMBIENT AIR

| OCDF/OCDD Ratio | Frequency |
|---|---|
| 0 | 23 |
| 0.050836 | 106 |
| 0.101672 | 22 |
| 0.152508 | 9 |
| 0.203344 | 4 |
| 0.254181 | 12 |
| 0.305017 | 5 |
| 0.355853 | 1 |
| 0.406689 | 0 |
| 0.457525 | 1 |
| 0.508361 | 0 |
| 0.559197 | 0 |
| 0.610033 | 0 |
| More | 2 |
| Total n | 185 |

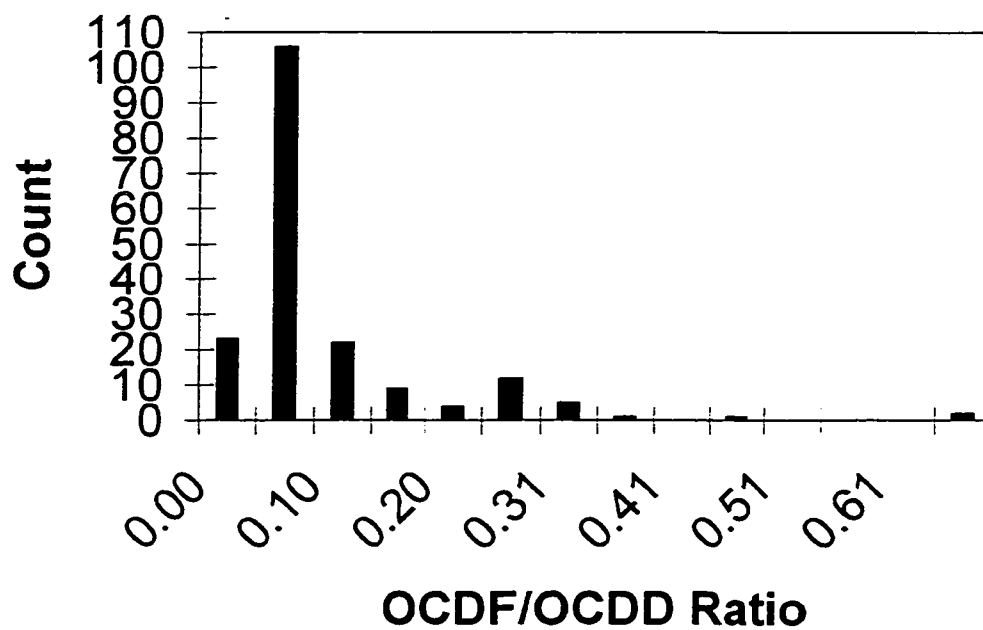**Note:**

OCDF/OCDD Ratio=0 for both compounds ND

Figure 123.    Frequency histogram for octachlorodibenzofuran/octachlorodibenzo-p-dioxin ratio in ambient air polychlorinated dibenzo-p-dioxin/dibenzofuran data.

## 4.10 Conclusions

The work carried out for this thesis has generated a great deal of additional data and information. In this Section 4.10, the major conclusions that come out of the work are summarized.

### 4.10.1 Summary and Conclusions Regarding Data Gathered at Site

The data from the School monitoring station (Site ID= 23013) is different from the other monitoring stations. This could be due to a variety of factors, including distance, wind direction, and topography, none of which cannot be isolated individually. However, the wind sector scoring appears to show that 23013 does not "see" the Site as often as the others. In addition, there are several large buildings, including a grain elevator, that are suspected to have disrupted the air flow between the CWML SV Site and the air samplers.

Despite this difference, some general conclusions can be drawn from looking at the data as a whole:

1) Significant seasonal variations in PCB concentrations were observed. Higher PCB concentrations occurred when temperatures were warmer.

2) Diurnal variations in temperature and relative RH may also be important.

   a. Higher PCB concentrations were observed for the warmer sampling periods.

b.      Although the effect of RH was not considered in this work, the inclusion of RH would be expected to strengthen the relationship between temperature and PCB concentrations.

3)      In general, higher PCB concentrations occurred when wind speeds were lower. However, the lower wind speeds were related to warmer temperatures.

## 4.10.2 <u>Summary and Conclusions Regarding Methodologies Used to Analyze Data</u>

Wind Sector Scoring worked reasonably well for the 24-hour sampling data available for this project. Wind rose and LAR coefficient analyses did not work as well for the 24-hour samples. It is suggested that these analysis methods are better suited to shorter time periods or periods when wind directions do not change more than 45-90°.

The existence of PCB homolog data allowed the use of CC plots to show a linear relationship between concentrations (as Ln $P_{vap}$) and temperature (as 1/T).

## 4.10.3 <u>Summary and Conclusions Regarding Management and Disposal of Polychlorinated Biphenyls Based on Analysis of Data</u>

Based on the data collected and the analytical methodologies used, certain conclusions can be drawn regarding management and disposal practices. A point that this research reiterated is the importance of remembering that PCBs are semivolatile, not non-volatile, compounds.

The air monitoring data indicated that elevated PCB levels observed in the summer months (especially for 1991) were not due to the incineration operations. The data show that properly performed incineration can be safe, and results in the rapid reduction of PCBs in the air around a site. Incinerator "upsets," such as AWFSO or TRV openings, did not appear to have a significant effect on the PCB levels detected at the monitoring locations. Site activities, such spills etc. as noted in the OR, did not result in significant differences in the off-site PCB concentrations. The incinerator operations (and emissions) did not vary with temperature as demonstrated by emissions testing.

The reduction in ambient air levels of PCBs observed in the summer of 1992 (relative to the summer of 1991) was due primarily to the destruction of the high level liquid PCBs that were on-site. Any fugitive emissions from soils, while still probably occurring and of concern, were not as great as those emissions from PCB liquids in storage. The air concentrations of PCBs after the Phase 3 Cleanup were significantly lower (non-detects only observed) compared to levels observed before and during the cleanup process. This indicates that the destruction of the PCB was successful in reducing environmental loadings as was hoped.

The finding of the importance of high concentration PCB liquids is especially significant in light of the fact that the Smithville storage site represented a "state of the art" facility for the storage of liquids and solids containing PCBs. Although use of a more sophisticated containment building might have resulted in lower emissions, there is essentially no such thing as storage with zero PCB emissions with techniques commonly

used today. "Breathing" of storage sites will continue until PCB destruction takes place. This conclusion suggests some possible solutions in the short term for reducing PCB concentrations in urban areas and/or areas with highly elevated (>1-2 ng/m$^3$) levels of PCBs.

The ongoing storage of PCBs, especially liquid PCBs, and delaying destruction of PCBs while waiting for the "holy grail" technology, rather than utilizing currently available destruction technologies, leads to continued loading of PCBs to the environment. This proposition is supported by the results presented in this thesis, which showed a rapid reduction of PCB concentrations even before destruction of all PCBs was completely finished.

## 4.11    Recommendations And Suggestions For Further Work

In the process of analyzing the data for the CWML SV Site, a number of issues/areas for improvement were identified. A series of recommendations are made in this Section 4.11 regarding further analysis of the data at that Site, other PCB remediation sites, and areas for improvements in gathering data at future remediation projects

### 4.11.1 Further Analysis of the Site Data

1)    The ambient air data for Inorganics and PCDD/DF could be analyzed vs. the PCB/CB and meteorology to see if there are any correlations.

2)    The incinerator emissions data could be reviewed in further detail for SVOC, Inorganics and VOC for comparison between analytes and process conditions.

3)   The effect of moisture and/or RH on observed PCB air concentrations could be evaluated. However, it is not clear what RH data is available for Smithville during the time period of the Phase 3 Cleanup.

4)   The effect of RH on fugitive emissions (as represented by the on-site monitoring data) could be investigated.

5)   The preliminary conclusions about the importance of PCB emissions from stored high concentrations compared to soils could be investigated in much more detail.

6)   Evaluate the PAH emissions profile of the incinerator to determine whether PAHs might have been used as a better marker for identifying the incinerator emissions contribution to the ambient air at the monitoring locations.

7)   There is still considerable body of on-site data available for PCBs and PCDD/DF that is not in electronic format. This data could be entered into electronic format by manual data entry, voice entry or scanning and optical character recognition.

8)   Evaluate target analyte list for PCB emission data and compare to the ambient air analyte list to determine if the non-ortho, mono-ortho PCB were

determined. This might allow an estimate of the total TEQ for air samples and the relative contribution from PCB vs. PCDD/DF.

9) The ambient air data for PCB could be reanalyzed using multiple variable regression, looking at combinations of wind direction, wind speed, relative humidity, etc., with an objective of obtaining higher $r^2$ values.

10) Principal component analysis might also provide some insight into factors and combinations of factors responsible for the observed PCB concentrations.

11) The importance of Wet versus Dry Deposition pathways could be examined for the Smithville data set to see if the deposition process was important.

12) The linear regression analyses could be performed again looking in further detail at the effect of outliers, precision, residuals, leverage etc. This might allow better fits to the data and strengthen the conclusions that were made.

13) The PCB homolog data from TAGA monitoring could be compared to the PCB homolog data at the fixed on and off-site monitoring locations. This would allow one to see the profiles for the site are being "averaged out" by the longer monitoring times.

14)   If the original congener analyses results for the ambient air PCB samples could be obtained in electronic format the same analyses in this thesis could be repeated to determine if the conclusions change from those from those based on homolog data.

15)   There is some PCB data from the IADN site near Buffalo (Sturgeon Point) available for the same time period as the Phase 3 Cleanup. The amount of data available could be reviewed and if there are sufficient data available comparisons to the Smithville data made. Because the IADN PCB data is in congener format, it will need to be summed by homologs. It might be interesting to look at dates when air masses were from Smithville can be differentiated from periods when air masses came from other directions data.

16)   The information form collocated samples could be reviewed for differences in concentrations and homolog profiles. The differences between different types of samplers and analytical methods could also be evaluated.

## 4.11.2 Research at Other Sites

1)   Additional sampling is needed on emissions from landfills or other sites where PCBs have been disposed. Information is needed on concentration ranges, temporal/diurnal concentration fluctuations, congener and homolog profiles and phase distribution ("vapor" vs. "particulate").

2)   Additional sampling at locations with in-use PCB transformers (especially ones using Askarel), stored transformers, and general PCB storage sites to determine if there are large differences in air emissions, and if so, what the possible factors controlling the emissions are. The concentrations and congener/homolog profiles should be compared to ambient air monitoring carried out at the same time off-site.

3)   Sampling of PCB air emissions from other types of sites with high level PCB liquids, such as hydraulic oil or compressor oils, is needed to determine if these sites are a significant ongoing source of PCB to air. The concentrations and congener/homolog profiles should be compared to ambient air monitoring carried out at the same time off-site.

### 4.11.3 Improved Techniques Related to Gathering Data

1)   Air sampling for PCB (and other SVOC) should be performed using filters and sorbents. Where possible the analysis should be done for the filter (representing particulate phase) and sorbent (representing vapor phase) separately. If cost is an issue, a subset of 10-20% of the filter and sorbent could be analyzed separately and the rest as combined samples.

2)   More use of TAGA monitoring for PCB is recommended near PCB storage sites. This might allow better source identification, especially sources with mono-penta PCB homologs.

3)   Adding additional sampling locations and parameters, in addition to those operated by IADN and national dioxin monitoring networks, is recommended for better characterization of spatial differences in concentrations and factors controlling these concentrations.

4)   More detailed and ongoing monitoring of fugitive emissions during different feed types (soils/solids versus liquids/metals) is recommended for all remediation technologies. The differences in feed materials could also have been an issue for Smithville, but there is no way to analyze these differences with the available data.

5)   More monitoring of the feed should be performed for projects of this type to see if ambient air emissions are showing a feed profiles. The analytical methods used for feed analysis must produce results that can be compared to the ambient air data.

6)   The homolog and PCBTOT results from congener specific GC-ECD, congener specific GC-MS, and homolog group analysis by GC-MS should be compared on the same (if possible) or similar samples to determine whether they generate comparable results.

7) It is important to ensure that co-elution issues are recognized and addressed in generating PCB data by GC-ECD because of the difference of up to 2 orders of magnitude in relative response factors for isomers.

8) For projects in which multiple labs are used to generate data that will be compared, a QA/QC program should be implemented. The QA/QC should at a minimum, include the review of methods and cross-comparison of standards and some samples.

9) In this project, the DL was rather high due to the type of air sampler used. The use of Hi-Vol samplers is recommended for air studies. This would allow the lowest detection limit to be achieved.

10) The analysis of multiple types of analytes (e.g. PCB/CB, CP, PCDD/DF, and PAH) should be performed on the same sample where DL and other issues allow it.

11) When separate sampling is taking place for multiple parameters, such as was the case here, it is recommended that all samplers be operated at the same time, on at least some occasions.

12) Consider sampling after periods of 12 hours or less to check for diurnal cycling due to fugitives.

13) It is recommended that sampling and analysis programs be carried out for the mono-deca PCB. If one of the homologs is not regulated it can easily be removed from the results at a later date.

14) The effect of using the average Pvap for homolog vs. the values for each congener should be evaluated.

15) For air samples, Aroclor should not be used for quantification of airborne PCBs unless it can be shown that the profiles are similar.

16) Further work is needed on comparison of homolog patterns for oils versus those observed in air vs. those predicted from vapor pressures.

17) Simultaneous sampling should be carried out for PCB and PCDD/DF to determine the total TEQ of ambient air.

18) The reason(s) for the much higher OCDD presence in ambient air relative to emissions profiles needs to be investigated further.

19) Materials handling (e.g., shredding, etc.), especially for materials with high level (~1%) PCB concentrations, should take place in areas where emissions are controlled, such as by carbon adsorption, in the incinerator, etc.

20)   Additional air sampling of the water treatment plant at the Smithville site should take place in order to evaluate PCB emissions.

21)   During any air sampling project, local (within ~ 1 km) meteorological data should be obtained. This will allow analysis of the analyted data generated for meteorological effects. For maximum benefit an upper air sounding location should be established in the vicinity.

22)   Air modeling could prove helpful in prioritizing sites for analysis in the event of an emergency, as well as in looking for an explanation for trends in the data.

23)   During remediation projects, it is essential to maintain accurate records of on-site activities so that the effect of these activities on local air quality can be evaluated.

24)   Environmental monitoring data should be obtained electronic format and archived indefinitely so that it is accessible at a later date by anyone who might have an interest in reviewing and analyzing the data.

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516

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