

TOXWATCH
DATA ANALYSIS REPORT
(1999-2008)

Prepared by the
Air Programs Branch
Indiana Department of Environmental Management

April 12, 2010

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Report Summary

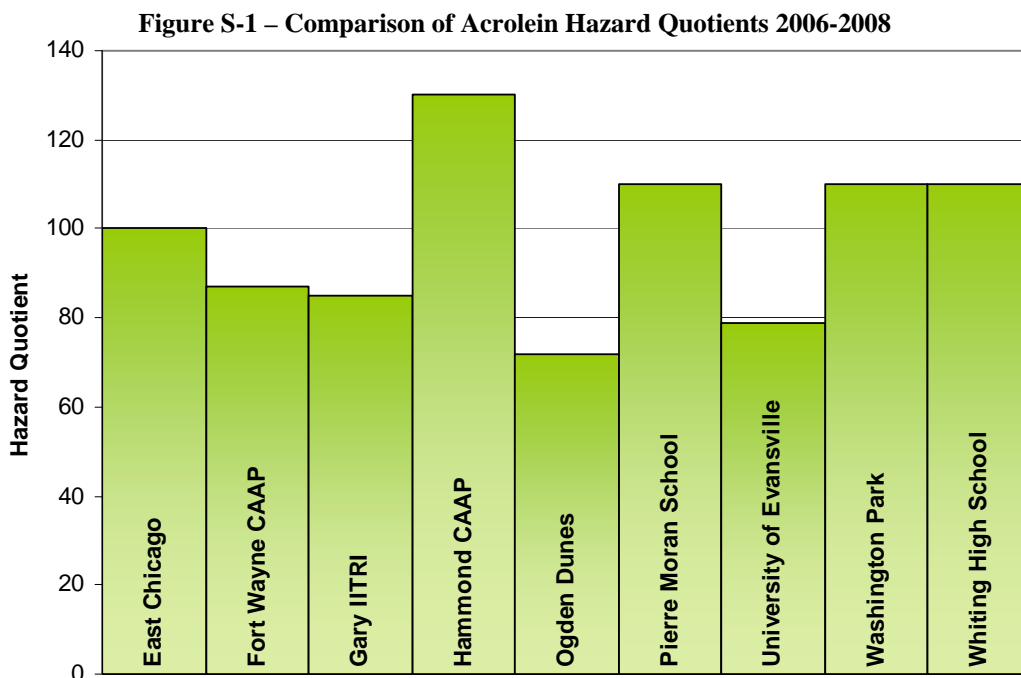
The ToxWatch monitoring network is a series of air toxics monitors located in primarily urban areas of Indiana. At any given time, there are approximately ten (10) active monitors in the network. This report covers all monitors that were active for at least 5 years during the period of 1999 through 2008. See page 1-1 for a complete list of current and past monitoring locations within the ToxWatch network.

This report has two primary goals; the first is to develop risk and hazard estimates to evaluate if any significant problems related to air toxics exist within the state, and secondly to determine if air toxics concentrations are increasing or decreasing across the state. This information will help inform future decisions regarding air toxics in the state. Risk and hazard estimates were calculated using standard U.S. EPA statistical procedures, and trends were examined both by visual inspection of graphed data and by using a Mann-Kendal trend analysis. Section 1.0 of this report outlines these procedures in more detail.

Pollutants of Concern

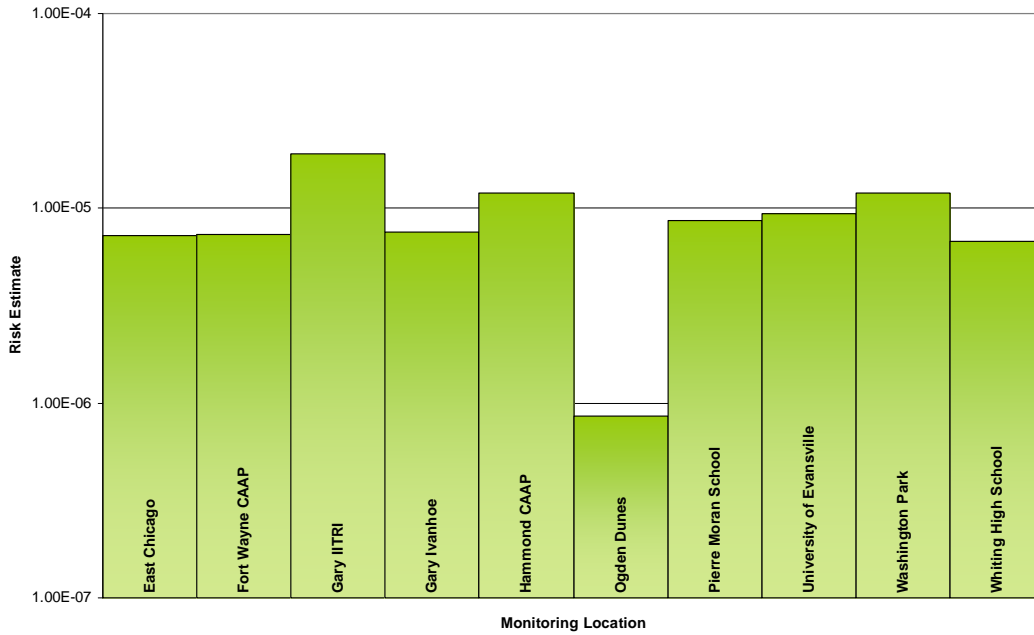
Acrolein is by far the biggest non-carcinogenic concern in the state. Hazard quotients for acrolein ranged from 72 at the Ogden Dunes monitor to 130 at the Hammond CAAP monitor. A hazard quotient less than 1.0 is considered health protective. There are many unresolved concerns regarding acrolein in Indiana and around the nation. While Indiana's acrolein concentrations are high enough to warrant further investigation, when compared to acrolein concentrations observed in other states, it becomes obvious that concerns with acrolein are not unique to Indiana. See section 1.2 of this report for more information about problems encountered with acrolein.

See Figure S-1 for a graphical representation of all acrolein hazard quotients in the ToxWatch network. Because acrolein monitoring did not begin until mid-2006, these hazard quotients are based on approximately 2½ years of sampling data.



Benzene is the primary carcinogenic concern within the state. Benzene is consistently detected at all monitoring locations within the state at rates near or exceeding 90%. Risk estimates for benzene exceed 1-in-1,000,000 at all monitoring locations except Ogden Dunes. The only other carcinogen approaching benzene in its ubiquitousness and risk levels is carbon tetrachloride. However, carbon tetrachloride’s manufacture and use within the United States has been drastically cut and most carbon tetrachloride in the air is generally attributed to its persistence in environment. Because of this, carbon tetrachloride is generally considered a global background pollutant and little can be done further to reduce its concentrations in air. See Figure S-2 for a graphical representation of all benzene risk estimates in the ToxWatch network

Figure S-2 – Comparison of Benzene Risks 1999-2008

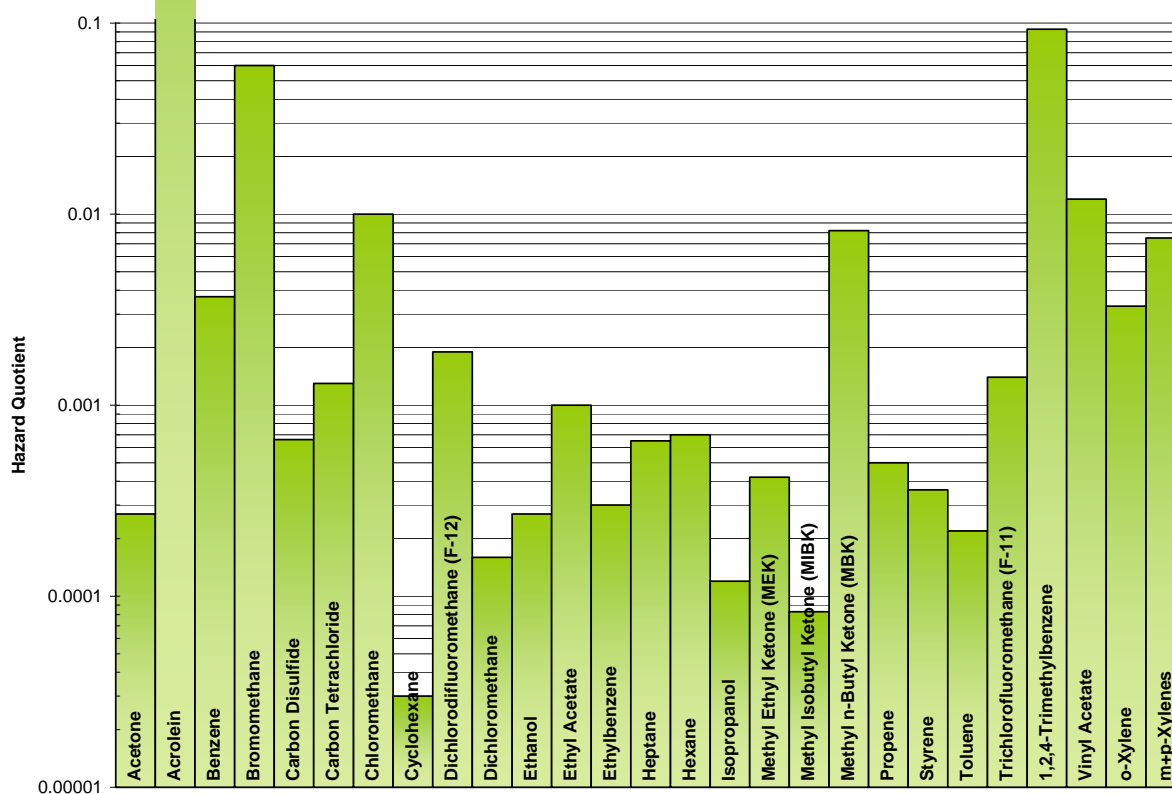


Monitoring Locations

Monitors in the ToxWatch network are generally sited in areas where one might expect there to be elevated concentrations of air toxics. As such, any discussion of risks or hazards within the network should not be considered indicative of the overall quality of air within the state. For example, the Ogden Dunes monitor recorded some of the lowest pollutant concentrations within the ToxWatch network. This should not be interpreted to mean that Ogden Dunes has the “cleanest” air in the state, and all other areas of the state are worse. It only means that Ogden Dunes generally has the lowest pollutant concentrations of any of the ToxWatch monitors.

That being said, Ogden Dunes does consistently show some of the lowest air toxics concentrations of any monitor within the state. As stated above, Ogden Dunes had the lowest acrolein hazard quotient in the network, and was the only monitor to show a benzene risk of less than 1-in-1,000,000. Please refer to Figure S-3 for a graphical representation of pollutant hazard quotients at the Ogden Dunes monitor.

Figure S-3 – Comparison of Hazard Quotients at Ogden Dunes Monitor 1999-2008



1.0 INTRODUCTION

ToxWatch is an ambient-air-quality monitoring program conducted by the Office of Air Quality (OAQ) within the Indiana Department of Environmental Management (IDEM). The program has been actively monitoring air toxics concentrations within the state for over a decade. At any given time there are approximately 10 active monitoring locations within the state, each taking 1 in 6 day samples for approximately 60 air toxics. These samples are analyzed by IDEM's in-house laboratory and the results are made available to the public through IDEM's website. Table 1.1 is a list of past and present monitoring locations within the ToxWatch network.

Table 1.1 - ToxWatch Monitoring Locations

Location Name	Address	County	Years Sampled
Culver School	1301 Judson St., Evansville	Vanderburgh	2000
East Chicago	3330 Aldis St., East Chicago	Lake	1999-2008
Elkhart Firestation #5	515 Simpson St., Elkhart	Elkhart	1999-2000, 2003
Fort Wayne CAAP	2022 N. Beacon St., Ft. Wayne	Allen	2003-2007
Gary ITRI	201 Mississippi St., Gary	Lake	1999-2008
Gary Ivanhoe	5700 W. 15th St., Gary	Lake	2000-2003
Hammond CAAP	1300 E. 141st St., Hammond	Lake	1999-2008
Hammond Purdue	6937 Woodmar Ave., Hammond	Lake	2000-2001
Harding Street	1321 S. Harding St., Indianapolis	Marion	1999, 2006-2008
Lafayette – Cinergy	3401 Greenbush St., Lafayette	Tippecanoe	2008
Lincoln Elementary	4221 S. Towle Ave., Hammond	Lake	2000-2001
Mount Vernon School	701 Tile Factory Rd., Mt. Vernon	Posey	2000
Naval Avionics	6125 E. 16 th St., Indianapolis	Marion	1999
New Albany/Clarksville	201 W. Riverside Dr., Clarksville	Clark	2008
North High School	2319 Stringtown Rd., Evansville	Vanderburgh	2000
Northside School	300 Lawrence St., Elkhart	Elkhart	1999-2000
Ogden Dunes	84 Diana Rd., Ogden Dunes	Porter	1999-2008
Pierre Moran School	200 W. Lusher Ave., Elkhart	Elkhart	1999-2007
Pinewood School	3420 E. Bristol St., Elkhart	Elkhart	1999-2000
Pulaski Dunbar	920 E. 19 th Ave., Gary	Lake	2000-2001
School 21	2815 English Ave., Indianapolis	Marion	2001-2008
School 90	3351 W. 18 th St., Indianapolis	Marion	1999
Stoutfield	2002 S. Holt Rd., Indianapolis	Marion	2006-2008
University of Evansville	1800 Walnut St., Evansville	Vanderburgh	1999-2008
Washington Park	3120 E. 30 th St., Indianapolis	Marion	1999-2008
Whiting High School	1751 Oliver St., Whiting	Lake	2005-2008

1.1 METHODOLOGY

The ToxWatch database is a very large database, which includes a decade worth of monitoring data for many of the monitoring locations. Over the course of the monitoring program many things have changed: laboratory analysis methods were updated, analytes were added and dropped, monitoring equipment was moved from one location to another, etc. All these changes result in a diverse dataset which requires special attention to be sure that conclusions drawn from it are both accurate and defensible. This section will discuss the methods used to analyze the data within the database.

1.1.1 Narrowing the Dataset

Not all monitoring locations had sufficient data, or were sampled recently enough, to warrant inclusion in this report. As such, only sampling locations that had at least five consecutive years of monitoring data within the period from 1999-2008 were included in the analysis. These criteria resulted in 10 monitoring locations being included within this report:

- East Chicago,
- Fort Wayne CAAP,
- Gary IITRI,
- Gary Ivanhoe,
- Hammond CAAP,
- Ogden Dunes,
- Pierre Moran School,
- University of Evansville,
- Washington Park, and
- Whiting High School

Harding Street and Stout Field were excluded from the list because they are being analyzed separately for the Southwest Indianapolis Air Toxics Study. School 21 was excluded because the data have already been analyzed as part of its own study.

Beginning in 2002, IDEM's laboratory switched from using U.S. EPA method TO-14 for analysis of the ToxWatch ambient air samples, to U.S. EPA method TO-15. This switch caused some analytes to be dropped from the database and others to be added. Due to the age of the change, it was decided that only compounds that were part of the TO-15 analyte list would be included in this analysis.

1.1.2 Toxicity Hierarchy

There are several sources of published toxicity parameters available on the internet and elsewhere. None of these sources is exhaustive and they do not always agree on the risk or hazard posed by a particular compound. As such, several sources were examined when developing the toxicity parameters for the analysis. The sources in the first tier are generally considered the most reliable sources of toxicity data in the environmental arena:

1. U.S. EPA Office of Air Quality Planning and Standards (OAQPS)

OAQPS compiles a list of available inhalation toxicity data for use in air risk assessments. It is updated on a regular basis and uses many of the other sources on this list, making it a valuable starting point.

2. Integrated Risk Information Service (IRIS)

IRIS is U.S. EPA's online database of toxicity parameters. It is maintained by the National Center for Environmental Assessment (NCEA) and is widely considered to be the definitive source of toxicity parameters within the United States.

3. Agency for Toxic Substances and Disease Registry (ATSDR)

ATSDR is a division of the U.S. Department of Health and Human Services tasked with implementing the health-related sections of laws that protect the public from hazardous wastes and environmental spills of hazardous substances. Part of this task has been fulfilled by developing a series of “Toxicological Profiles” which include acute, intermediate (sub-chronic), and chronic reference doses and reference concentrations (RfCs) for several compounds. ATSDR’s primary focus is on non-carcinogenic effects and has developed few, if any, inhalation unit risks (IURs).

4. California Environmental Protection Agency (Cal/EPA)

Cal/EPA is the state-level agency responsible for the protection of human health and the environment in the State of California. Cal/EPA has done extensive independent toxicity research and has developed many of its own toxicity parameters. Many of these toxicity parameters have been cited by state and federal agencies across the nation.

Each of these sources was checked in turn for available toxicity parameters. If the above sources were unable to provide toxicity information, data from a second tier of sources that were deemed not to be as reliable or as widely accepted as their counterparts above were compiled in an attempt to fill gaps in the dataset. These sources included:

1. The National Institute for Public Health and the Environment (RIVM)

RIVM is the environmental agency of the Netherlands. They have derived many toxicological parameters that are applied in the Netherlands and the rest of Europe. However, as their values do not undergo external peer review and are not widely used within the United States, they were not included among the list of Tier 1 sources.

2. Health Canada

Health Canada is the federal department within the Canadian government responsible for the health of Canadian citizens. They fill the role of environmental regulator in Canada as well as administering social programs such as the national healthcare system. Health Canada maintains a database of toxicity parameters for use in the environmental field. This database was searched but was unable to provide any new toxicity parameters.

3. Health Effects Assessment Summary Tables (HEAST)

HEAST was published by U.S. EPA’s National Center for Environmental Assessment (NCEA) until 1997. The HEAST tables contained non-carcinogenic toxicity parameters that U.S. EPA did not recognize as “high quality, Agency-wide consensus information”. HEAST is still widely cited, but due to the lack of updates, was included in the lower tier of sources.

4. IDEM Office of Land Quality (OLQ)

OLQ maintains a table of default closure levels (DCLs) used in environmental remediation oversight by the IDEM. These DCLs are derived by using toxicity data collected from many of the sources already described in the lists above. However,

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when toxicity parameters are not available from a traditional source, OLQ will derive provisional toxicity values for use on a site-by-site basis.

After compiling all available data from the above sources, an analysis of American Council of Government Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) was conducted to determine whether they could be modified to serve as RfCs. TLVs are air concentrations that are meant to be protective of human health in a workplace environment. ACGIH does not, as is often thought, incorporate economic or technological considerations into their derivation of TLVs. As such, it was decided that, with proper adjustment, they could serve as RfCs.

To determine a proper adjustment factor, a list was compiled of all available RfCs from IRIS. This list was then compared against the 2008 TLV list to generate a table that contained compounds that had both an RfC in IRIS and a TLV. These TLVs were then converted to a continuous exposure concentration using the following equation:

Equation 1.1 - TLV Continuous Exposure Conversion

$TLV_{CE} = TLV \times \frac{5\text{days}}{7\text{days}} \times \frac{10\text{m}^3}{20\text{m}^3}$	
Value	Description
TLV_{CE}	Continuous Exposure Threshold Limit Value
TLV	Threshold Limit Value
5days	Workdays per Week
7days	Total Days per Week
10m^3	Occupation Daily Breathing Rate
20m^3	Total Daily Breathing Rate

This basic approach was modified from one outlined in section I.A.4. of IRIS's discussion of Aluminum Phosphide's oral reference dose. (<http://www.epa.gov/ncea/iris/subst/0005.htm>)

A scatter plot of the IRIS RfCs and the continuous exposure TLVs was generated and a best-fit line was determined. Microsoft Excel offers several trend lines and each was tested to determine which had the best correlation with the available data. Once a best-fit line was determined, a level of conservatism was added to ensure that 95% of the predicted values would be at least as conservative as the IRIS RfC. The final result was the following equation:

Equation 1.2 - RfC Derivation from TLV_{CE}

$RfC = 0.000328 TLV_{CE}^{1.126}$	
Value	Description
RfC	Reference Concentration
TLV_{CE}	Continuous Exposure Threshold Limit Value

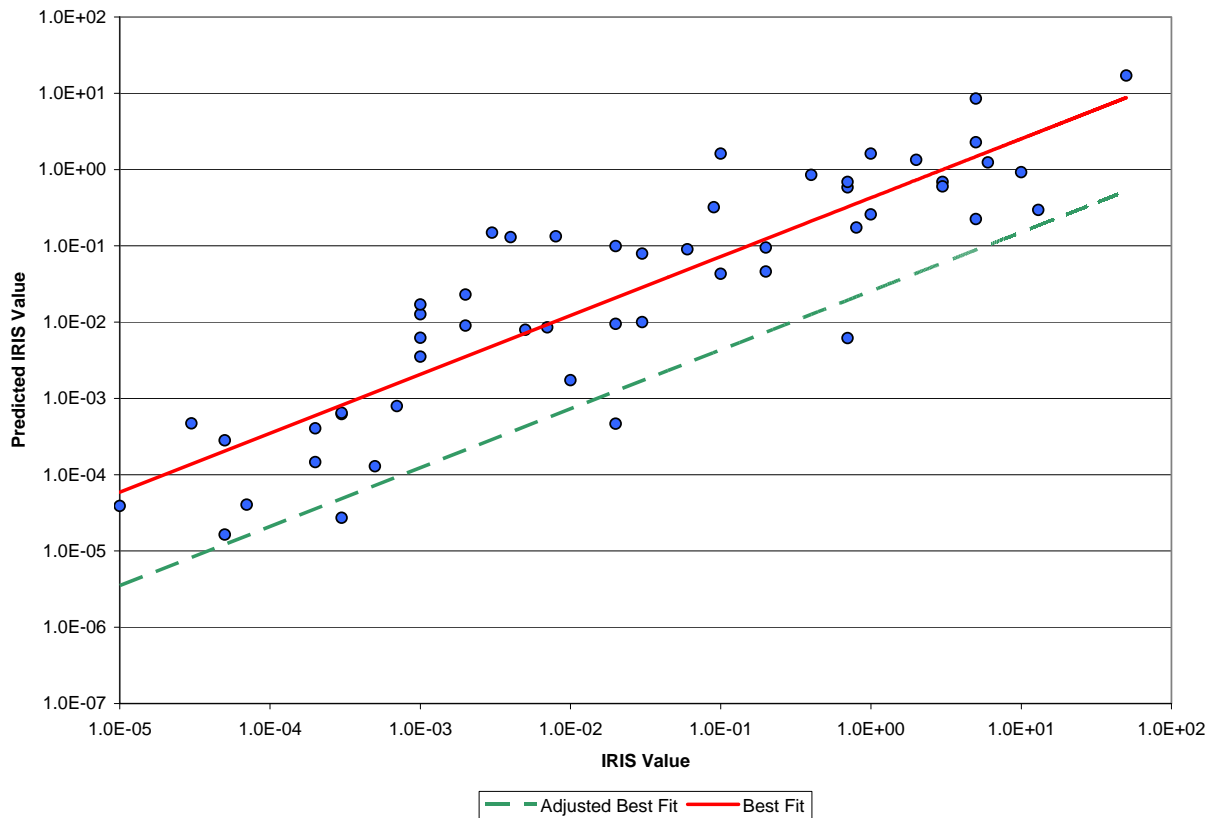
Figure 1.1 - Predicted Iris Values vs. Actual IRIS Values

Figure 1.1 describes the correlation between actual IRIS values and those derived by Equation 1.2. Equation 1.2 was then used, along with information found in the 2008 TLV list, to derive RfCs for the following compounds:

- Benzyl Chloride,
- Dichlorodifluoromethane,
- Ethyl Acetate, and
- Heptane

It should be noted that while IDEM feels that the RfCs derived through this method are adequately conservative for these purposes, they do not carry the same weight as other values found in the hierarchy and should not be treated equally.

1.1.3 Exposure Point Concentrations

An exposure point concentration (EPC) is a conservative estimate of the concentration of a pollutant to which a receptor (i.e., a person) will come in contact. Several considerations must be made before an EPC can be calculated. These considerations include which statistical method will be used to calculate the EPC, how non-detects (i.e. concentrations too low to quantify) will be handled, and what exposure assumptions will be applied.

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Many factors affect the choice of method to use including; size of dataset, statistical distribution, and method of sampling. For datasets which were randomly or systematically sampled and which have enough detected values, a 95% upper confidence limit of the mean (UCL) is the generally preferred method. A 95% UCL represents a value which one can be 95% confident that the true mean of the population is below that value. For the purposes of this analysis, this was the only type of EPC used. For discussion of datasets which were not adequate to calculate a UCL see section 1.1.6 Method Detection Limits (MDLs).

Common practice in the past has been to substitute $\frac{1}{2}$ the detection limit for any non-detect values. Recent guidance from U.S. EPA and others has suggested that this is no longer an acceptable method for dealing with non-detects because it introduces an undue amount of bias into the results. The Kaplan-Meier Product Limit Estimate (Kaplan-Meier, or KM) method has been recommended by U.S. EPA and others, and was chosen for this analysis.

Kaplan-Meier is a non-parametric method that allows the calculation of a less-biased mean and standard error (and by extension, many other statistical values) from a dataset that contains values below the method detection limit (non-detects). Kaplan-Meier has many advantages over other methods for dealing with non-detects. It is a non-parametric method, and as such does not require that the distribution of the data be known. It can be used with datasets that contain many non-detects, and it is more accurate than substitution methods such as using $\frac{1}{2}$ the detection limit.

There are at least two different variations of the Kaplan-Meier method. The main difference in these methods appears to be where censoring occurs in the dataset. The dataset can be censored either at the lowest detection in the dataset or at the lowest detection limit. Censoring at the lowest detection limit will introduce less bias into the results, while censoring at the lowest detection will provide results that are slightly more conservative. To be consistent with U.S. EPA's ProUCL software, this analysis chose to censor at the lowest detection, rather than the lowest detection limit.

Due to the large number of EPCs that needed to be calculated, it was decided that U.S. EPA's ProUCL software would be too cumbersome to use. As such, a Microsoft Excel macro was written that automated the calculation of a Kaplan-Meier student's-t (KM(t)) 95% UCL. The student's-t UCL is a parametric method which requires a normally distributed dataset. However, a sample of data run through ProUCL showed that the differences between ProUCL's recommendation and the KM(t) UCL were minimal. Therefore, it was decided that the timesavings offered by the automated method outweighed the small amount of bias introduced.

Often various exposure assumptions are made when calculating EPCs. These exposure assumptions can include how many years a person is exposed to a pollutant, how many days a year exposure occurs, and even how many hours per day one is exposed. For the purposes of this report, continuous exposure over a lifetime was assumed. This means that risks and hazards calculated for this report assume 24 hours per day of exposure, 365 days per year, for 70 years. These are a conservative set of assumptions and help ensure that decisions made are health protective.

1.1.4 Trend Analysis

Mann-Kendall (MK) trend analysis was the primary method for determining trends in this study. MK trend analysis is a common non-parametric method of determining trends in environmental datasets. It is more commonly used in determining stability in groundwater contamination plumes at environmental remediation sites. However, it was determined to be, with caveats, an acceptable method for this analysis as well.

Gilbert (1987) contains a detailed description of the method and mathematics behind MK analysis and was used to design a series of Microsoft Excel macros that could quickly and accurately calculate large numbers of MK trends. The results of the 95% MK analysis can be found in Appendix A, along with other summary data.

Only datasets with at least a 25% detection rate were subjected to MK analysis. It should be noted that the higher the detection rate, the higher the confidence in the MK analysis. When examining the MK results, special attention should be paid to the detection rates and sample size when drawing conclusions about trends. To prepare a dataset for MK analysis, all not detected (ND) and below detection limit (BDL) results were replaced with the lowest MDL reported for the pollutant. The lowest MDL was used rather than the yearly MDL because using a varying MDL could produce inaccurate results by introducing variation into the dataset that does not really exist.

As an additional means to examine trends in the datasets, the yearly EPCs for each pollutant at each monitoring location were graphed and visually examined for trends. These graphs are available for each pollutant in section 3.0 of this report.

1.1.5 Correlation Analysis

Pearson's r Correlation Analysis was used to compare each pollutant at a sampling location to every other pollutant at that location. A correlation analysis of pollutants from one site to the other was also conducted, as a simple way to determine if any pollutants were regional, rather than local issues. These analyses did not show any definitive correlation.

1.1.6 Method Detection Limits (MDLs)

It is important to note that just because a compound is ND or is BDL does not mean that the compound was not present in the sample. Sampling and analysis techniques are not perfect, and as such, are unable to detect very small concentrations of compounds in a sample. This is quantified in the MDL. The MDL is a number that represents the lowest concentration of a compound that can be quantitatively measured in a sample with reasonable confidence. Even with the very low MDLs that IDEM is able to achieve (parts per billion), air monitoring commonly results in samples with pollutant concentrations below detection limits. MDLs are meant to take into account factors such as equipment precision, technician variability, etc.

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Each year, IDEM's air monitoring laboratory calculates MDLs for each of the sixty-two compounds that are part of the ToxWatch database. Due to the age of some of the data, MDLs were no longer available for certain years or certain compounds. In cases where MDLs were no longer available, 97.5% of the lowest value detected for that year was chosen as the MDL. Table 1.2 shows the MDLs used in this analysis. Values in dark-shaded boxes were derived using the method described above.

Table 1.2 - Method Detection Limits (MDLs)

Pollutant	CAS	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Acetone	67-64-1				0.441	0.928	0.231	0.694	0.113	0.436	0.254
Acrolein	107-02-8								0.112	0.542	0.178
Benzene	71-43-2	0.249	0.447	0.256	0.28	0.28	0.337	0.0955	0.135	0.0903	0.1
Benzyl Chloride	100-44-7				0.455	0.707	0.635	3.65	0.398	0.188	0.0614
Bromodichloromethane	75-27-4						0.707	0.362	0.159	0.321	0.145
Bromoform	75-25-2						1.07	0.989	0.361	0.558	0.437
Bromomethane	74-83-9		0.349	0.388	0.416	0.416	0.481	0.378	0.0652	0.609	0.172
1,3-Butadiene	106-99-0				0.603	0.668	0.0971	0.116	0.175	0.181	0.0743
Carbon Disulfide	75-15-0				0.455	0.455	0.282	0.16	0.113	0.137	0.143
Carbon Tetrachloride	56-23-5		0.692	0.818			0.747	0.252	0.252	0.106	0.24
Chlorobenzene	108-90-7	0.538	0.414	0.184			0.61	0.212	0.109	0.0998	0.176
Chloroethane	75-00-3	0.952	0.633	0.237	0.695	0.798	0.45	0.451	0.104	0.727	0.158
Chloroform	67-66-3		0.83	0.195			0.504	0.121	0.303	0.121	0.116
Chloromethane	74-87-3	0.221	0.227	0.289	0.241	0.321	0.279	0.129	0.0617	0.0735	0.0583
Cyclohexane	100-82-7	0.201	0.201	0.201	0.235	0.235	0.31	0.139	0.123	0.105	0.0817
Dibromochloromethane	124-48-1						0.97	0.421	0.286	0.481	0.325
1,2-Dibromoethane	106-93-4		0.845	0.768			0.867	0.139	0.258	0.761	0.118
m-Dichlorobenzene	541-73-1	0.352	0.301	0.481	0.82	0.352	0.623	0.289	0.264	0.0921	0.13
p-Dichlorobenzene	106-46-7	0.293	0.24	0.541	0.352	0.41	1.01	0.357	0.26	0.143	0.154
o-Dichlorobenzene	95-50-1		0.361	0.481			0.814	0.434	0.189	0.101	0.24
Dichlorodifluoromethane	75-71-8	0.772	0.297	0.198	0.386	0.531	0.503	0.155	1.48	0.0758	0.083
1,1-Dichloroethane	75-34-3		0.405	1.3			0.415	0.265	0.192	0.141	0.0961
1,2-Dichloroethane	107-06-2		0.283	0.486			0.401	0.269	0.147	0.192	0.062
t-1,2-Dichloroethene	156-60-5						0.397	0.133	0.282	0.167	0.0607
c-1,2-Dichloroethene	156-59-2		0.515	0.396			0.413	0.188	0.144	0.112	0.0941
Dichloromethane	75-09-2	0.338	0.347	0.382	0.372	0.372	0.318	0.147	0.121	0.175	0.0753
1,2-Dichloropropane	78-87-5	0.676	0.647	0.323			0.462	0.251	0.141	0.114	0.1
c-1,3-Dichloropropene	10061-01-3		1.18	0.545			0.415	0.192	0.216	0.256	0.192
t-1,3-Dichloropropene	10061-02-6		0.772	0.408			0.472	0.152	0.29	0.273	0.283
Dichloro-Tetrafluoroethane	76-14-2	0.818	0.559	0.419		1.77	0.355	0.235	2.13	0.235	0.117
1,4-Dioxane	123-91-1				3.09		0.599	0.85	0.352	0.11	0.0924
Ethanol	64-17-5				0.589	1.23	0.246	0.846	0.352	0.948	0.174
Ethyl Acetate	141-78-6				0.176	0.176	0.311	0.35	0.182	0.142	0.126
Ethylbenzene	100-41-4	0.0846	0.304	0.261	0.127	0.127	0.503	0.204	0.103	0.0787	0.171
p-Ethyltoluene	622-96-8	0.192	0.192	0.192	0.24	0.24	0.427	0.194	0.231	0.139	0.139
Heptane	142-82-5	0.12	0.12	0.12	0.16	0.16	0.492	0.207	0.208	0.173	0.101
Hexachlorobutadiene	87-68-3		0.747	1.07	1.46		0.594	1.06	0.38	0.462	0.327
Hexane	110-54-3	0.172	0.172	0.172	0.206	0.206	0.378	0.238	0.156	0.149	0.0764
Isopropanol	67-63-0				0.384	0.384	0.309	0.462	0.438	0.308	0.0533
Methyl Ethyl Ketone	78-93-3				0.489	0.489	0.103	0.231	0.26	0.346	0.353

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Pollutant	CAS	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
Methyl Isobutyl Ketone	108-10-1				2.04	172	0.369	0.569	0.278	0.156	0.0972
Methyl n-Butyl Ketone	591-78-6				2.08	2.24	0.265	0.455	0.354	0.126	0.0972
Methyl Tert-Butyl Ether	1634-04-4				0.246	0.282	0.412	0.295	0.131	0.178	0.113
Propene	115-07-1	0.587	0.101	0.117	0.0335	0.0335	0.376	3.42	2.31	0.0527	0.0514
Styrene	100-42-5	0.249	0.213	0.383	0.291	0.291	0.663	0.202	0.34	0.18	0.105
1,1,2,2-Tetrachloroethane	79-34-5		0.412	0.481			0.698	4.54	0.367	0.21	0.115
Tetrachloroethene	127-18-4	1.39	0.746	0.407	0.992	0.925	0.791	0.301	0.326	0.147	0.228
Tetrahydrofuran	109-99-9				0.23	0.259	0.15	0.59	0.118	0.125	0.193
Toluene	108-88-3	0.11	0.339	0.264	0.147	0.147	0.493	0.137	0.127	0.0895	0.0817
Trichlorotrifluoroethane	76-13-1	0.448	0.46	0.307	0.523	0.523	0.839	0.414	0.307	0.217	0.166
1,2,4-Trichlorobenzene	120-82-1	0.468	0.445	0.535	0.468		3.9	0.704	0.297	0.419	0.367
1,1,1-Trichloroethane	71-55-6	2.24	0.818	0.982	1.01		0.537	0.242	0.218	0.154	0.118
1,1,2-Trichloroethane	79-00-5	0.799	0.436	0.546			0.705	0.413	0.135	0.167	0.183
Trichloroethene	79-01-6	0.838	0.806	0.322	1.2	0.89	0.549	0.304	0.133	0.128	0.195
Trichlorofluoromethane	75-69-4	0.493	0.506	0.843	0.548	0.548	0.682	0.172	0.144	0.139	0.0943
1,3,5-Trimethylbenzene	108-67-8	0.288	0.246	0.393	0.336	0.384	0.647	0.216	0.342	0.175	0.208
1,2,4-Trimethylbenzene	95-63-6	0.336	0.295	0.295	0.384	0.432	0.388	0.207	0.33	0.121	0.196
Vinyl Acetate	108-05-4								0.137	0.325	0.358
Vinyl Chloride	75-01-4		0.511	0.281			0.0607	0.22	0.153	0.0858	0.0975
Vinylidene Chloride	75-35-4		0.357	0.238			0.358	0.619	0.196	0.121	0.112
o-Xylene	95-47-6	0.423	0.261	0.304	0.465	0.465	0.527	0.107	0.155	0.0665	0.103
m+p-Xylenes	106-42-3	0.0846	1.82	1.17	0.127	0.127	3.24	1.21	0.283	0.55	0.599

For calculation of exposure point concentrations (EPCs), any data point in the database that was reported as “ND” or “BDL” was replaced by the appropriate MDL from the year the sample was taken. In order to be consistent with how ProUCL handles calculation of Kaplan-Meier estimates of the mean, IDEM chose to censor the datasets at the lowest detection rather than the detection limit when calculating EPCs. The result of this decision is to bias the EPCs slightly higher than they would have been if the appropriate detection limit was chosen. For more information on how EPCs were calculated, see section 1.1.3, “Exposure Point Concentrations.”

For trend analysis, half of the lowest MDL reported by the laboratory was used to represent all ND and BDL values. This was done in order to prevent changing MDLs from obscuring the true trend of the data. For more information on how the trend analysis was conducted, see Section 1.1.4, “Trend Analysis.”

A correlation analysis was also conducted in order to see what, if any, relationship exists between chemicals at each monitoring location. Non-detects were handled the same way for correlation analysis as they were for trend analysis.

Another important aspect of MDLs to consider when analyzing data is whether the MDLs are low enough to measure safe concentrations of pollutants. In many cases, the MDL for a compound is above the health protective concentration for that compound. When this is the case, it is impossible to determine that a pollutant does not pose a risk to human health. On the other hand, if there were no detections of a pollutant and its MDL is below the health protective concentration, it can be said with relative certainty that the compound does not pose a risk to human health. Figures 1.2 and 1.3 graphically depict

The error bars represent the non-carcinogenic hazard or the carcinogenic risk posed by the minimum and maximum MDLs in the dataset. As Figure 1.2 shows, only acrolein has an MDL above the health protective level of 1.0, preventing a definitive determination of hazard from being made. This is due more to acrolein's low reference concentration than to any problem with the sampling or analysis of the compound.

The MDLs' relations to cancer risk estimates are a different story however. U.S. EPA has set a cancer risk of 1 in 1,000,000 as a level that can be considered negligible. However, nearly all of the carcinogens in the ToxWatch database have median MDLs that represent a concentration that exceeds this threshold. One compound, 1,2-dibromoethene, has an MDL that even exceeds the 1 in 10,000 threshold which is the high end of the acceptable risk range set forth by U.S. EPA.

It is important to realize that it is highly unlikely that the true concentrations of samples that are reported as ND or BDL are at or near the MDL. In many cases, the true concentration may be many orders of magnitude below the MDL. Therefore, it should not be assumed that just because a compound's MDL is above the health protective level, the compound poses a threat to human health.

1.1.7 Cancer Risk Levels

At several points in this report, cancer risk levels of 1-in-1,000,000, 100-in-1,000,000, and the range in-between are given special note. U.S. EPA has set this as the acceptable cancer risk range as a matter of policy. Risks below 1-in-1,000,000 are considered negligible. When they are encountered in a screening analysis, no further action is generally taken. Risk levels above 100-in-1,000,000 are often considered the point when additional action should be considered. In between 1-in-1,000,000 and 100-in-1,000,000 is the range in which further work may be necessary including better refinement of the risk analysis. In analyses such as the ToxWatch report where very conservative (i.e., health protective) assumptions have been made, this type of refinement will usually result in lower cancer risks being calculated.

1.2 SPECIAL ISSUES CONCERNING THE ANALYSIS OF ACROLEIN

1.2.1 Acrolein as a National Issue

One of the first results of U.S. EPA's ambient air monitoring program at schools was the discovery of potentially alarming levels of acrolein at several schools across the nation. These results have led many people around the nation to take a closer look at acrolein. This scrutiny has revealed potential problems with both the monitoring and analysis of acrolein. These issues have yet to be resolved but seem to indicate that problems may exist with how sampling for acrolein is conducted. IDEM is closely monitoring these issues and may modify procedures in the future based on the results of this national debate.

An analysis of acrolein data in U.S. EPA's Air Quality System (AQS) database reveals that, while Indiana is above average in its concentrations of acrolein (average hazard

quotient of 91), it is still within the range of values seen across the nation (average hazard quotient of 53). It is important to note when looking at these data that Indiana places its monitors in urban environments where it suspects air toxics concentrations may be highest. This is not necessarily the case with other states. For example, the monitoring location that showed the lowest acrolein concentrations in the nation is located at Niwot Ridge Long Term Ecological Research Site in Colorado. This location is approximately 35 km from the nearest major city (Boulder) and is at an elevation of greater than 3,000 m. It should also be noted that despite its remote and relatively pristine location, it still had an acrolein hazard quotient of 1.6.

1.2.2 Issues with Acrolein Analysis in Indiana

Because of acrolein’s extremely high hazard quotients, additional analysis was conducted to determine whether concentrations in Indiana were out of line with those in other states. Initial results indicated that 8 of the 10 highest acrolein exposure concentrations in the nation occurred in Indiana. IDEM’s Air Toxics Monitoring Section was asked to investigate the data further to determine if an explanation for these high readings could be found. Their investigation identified a period from March to April 2007 during which the reported concentrations of acrolein were suspect.

The Air Toxics Monitoring Section suspected that the 2007 data might have been affected by a systematic error that caused all acrolein concentrations to be reported higher than the true concentration. Staff of the Air Toxics Monitoring Section reviewed all analytical methods associated with the measurement of acrolein in 2007 in order to find the source of the error. The staff members found that in the period of March-April 2007, the section had been using a TO-15 standard that contained acrolein in the standard mixture at concentrations lower than reported. The reported concentration of acrolein in the standard mixture was 100ppb; however, it appears that the actual acrolein concentration in this standard was much lower than reported. The continuing calibration abundance of 2.5ppb of acrolein on the GC/MS system used in 2007 for the analysis of TO-15 samples is shown below, as well as the approximate response factor (the abundance calculated for a 1 ppb amount of acrolein).

Table 1.3 – 2007 GC/MS Response Factors for Acrolein

Time Period	Response Abundance of 2.5 ppbv acrolein on GC/MS	Response Factor
Jan-Feb 2007	52,000 – 70,000 abundance	24,400
Mar-Apr 2007	1,200 – 2,250 abundance	750
May-Dec 2007	55,000 – 67,000 abundance	24,400

Table 1.3 shows that during the period of March-April 2007, a standard was being used by IDEM’s laboratory that contained far less acrolein than what was stated on the certificate of analysis for the standard. This caused the lab to over-report the concentration of acrolein in the affected samples by a factor of approximately 32.5.

INTRODUCTION

Currently, due to the uncertainties of how acrolein reacts with other compounds in a mixture, a separate standard is maintained for acrolein, and mixed with the TO-15 standard immediately before analysis to minimize the possibility of acrolein reacting with other compounds in the standard. This procedure is different from the process used in many other laboratories, but IDEM feels that it yields more accurate and cost-effective results for acrolein.

As a result of this investigation, acrolein data for all monitoring locations in March and April 2007 have been invalidated and removed from the ToxWatch analysis. This resulted in most Hazard Quotients calculated for acrolein being reduced by approximately half.