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*SUNNY, WARM,  
MIAMI, FLORIDA !*



# Air Toxics Risk Assessments

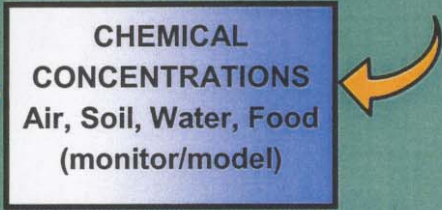
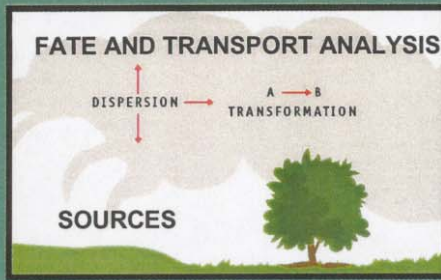
Miami-Dade County Studies

Presented by Carl Pfaffenberger

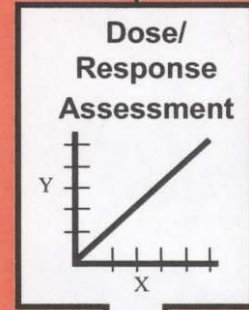
# The Detailed Air Toxics Risk Assessment Process

## Planning and Scoping

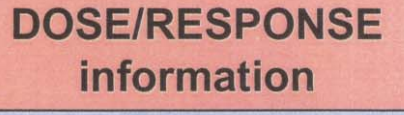
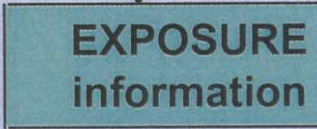
### Exposure Assessment



### Toxicity Assessment



## Risk Characterization



# Work Plan

Using Stainless Steel Canisters, collect 24-hour ambient air samples every 6 days over a year's time from two Miami-Dade County locations situated about 20 miles apart. Have the samples analyzed by gas-chromatographic/mass spectrometric EPA Method TO-15NC; and then perform risk assessments using gc/ms analytical results.

# Hazardous Air Pollutants Detected

11 DiClEthane

111 TriClEthane

1122 TetClEthane

12 DiClBenzene

12 DiClPropane

124 TriMetBenzene

13 DiClBenzene

14 DiClBenzene

Benzene

Carbon Tetrachloride

11 DiClEthene

112 TriClEthane

12 DiBrEthane

12 DiClEthane

124 TriClBenzene

13 Butadiene

135 TriMetBenzene

Acrylonitrile

Bromomethane

Chlorobenzene

# Hazardous Air Pollutants Detected (contd.)

Chloroethane

Chloroform

Chloromethane

*cis*12DiClEthene

*cis*13DiClPropene

DiClDiFlMethane

Ethylbenzene

Freon® 11

Freon® 113

Freon® 114

HexCl13Butadiene

meta+para Xylene

Methylene Chloride

ortho Xylene

Styrene

TetClEthene

Toluene

*trans*12DiClPropene

TriClEthene

Vinyl Chloride

Mean Levels differing by no more than 15%:

11 DiClEthane

x 111 TriClEthane

1122 TetClEthane

12 DiClBenzene

x 12 DiClPropane

124 TriMetBenzene

13 DiClBenzene

14 DiClBenzene

x Benzene

Carbon Tetrachloride

11 DiClEthene

x 112 TriClEthane

12 DiBrEthane

12 DiClEthane

124 TriClBenzene

13 Butadiene

x 135 TriMetBenzene

Acrylonitrile

Bromomethane

Chlorobenzene

Mean Levels differing by no more than 15%:

*Chloroethane*

*Chloromethane*

*cis13DiClPropene*

x *Ethylbenzene*

x *Freon® 113*

*HexCl13Butadiene*

x *Methylene Chloride*

x *Styrene*

x *Toluene*

x *TriClEthene*

x *Chloroform*

*cis12DiClEthene*

*DiClDiFlMethane*

*Freon® 11*

x *Freon® 114*

x *meta+para Xylene*

x *ortho Xylene*

*TetraClEthene*

*trans12DiClPropene*

*Vinyl Chloride*



# Identification of COPCs

A Chemical of Potential Concern (a COPC) is one which is detected at a sampling site above its SQL\* at least 10% of the time.

Thus the detection frequency at each of the sampling sites (Perdue and WASD) was determined for each of the 40 HAPS found.

\*SQL = Standard Quantitation Limit

# *Chemicals of Potential Concern (COPCs)*

11 DiClEthane

111 TriClEthane

1122 TetClEthane

12 DiClBenzene

12 DiClPropane

➤ *124 TriMetBenzene(W)*

13 DiClBenzene

14 DiClBenzene

➤ *Benzene(W&P)*

Carbon Tetrachloride

11 DiClEthene

112 TriClEthane

12 DiBrEthane

12 DiClEthane

124 TriClBenzene

13 Butadiene

135 TriMetBenzene

Acrylonitrile

Bromomethane

Chlorobenzene

# Chemicals of Potential Concern (COPCs)

*(contd.)*

Chloroethane

➤ *Chloromethane(W&P)*

*cis13DiClPropene*

➤ *Ethylbenzene(W)*

➤ *Freon® 113(P)*

HexCl13Butadiene

➤ *Methylene Chloride(W&P)*

➤ *Styrene(W)*

➤ *Toluene(W&P)*

TriClEthene

Chloroform

*cis12DiClEthene*

➤ *DiClDiFlMethane(W&P)*

➤ *Freon® 11(W&P)*

➤ *Freon® 114(W&P)*

➤ *meta+para Xylene(W)*

➤ *ortho Xylene(W&P)*

TetClEthene

*trans12DiClPropene*

Vinyl Chloride

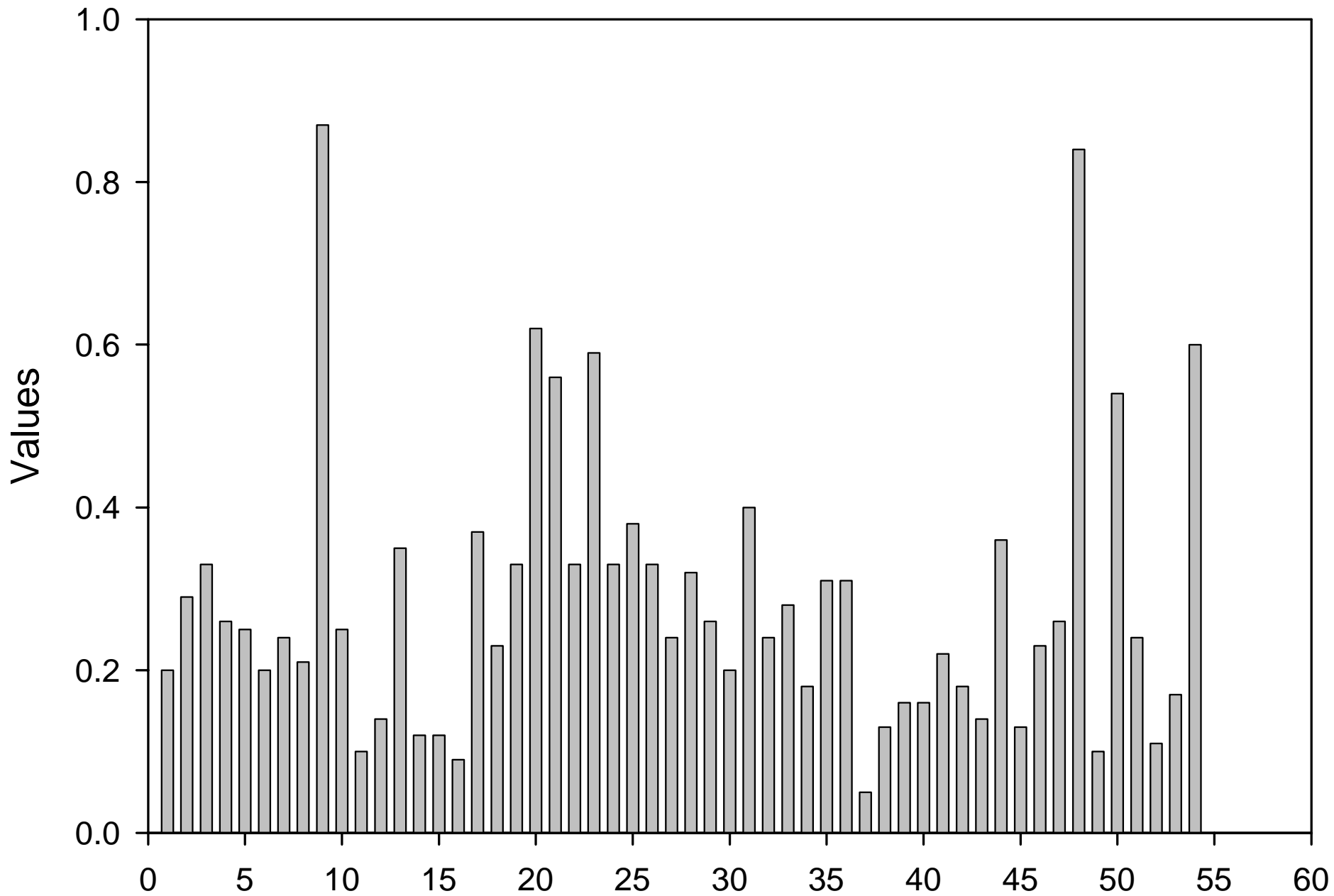
# Summary of Types of COPCs Found

5 Refrigerants producing no known direct human health consequence from chronic exposure – the *Freons*® (11, 12, 113, and 114) and *Chloromethane* refrigerant.

7 Common aromatic automobile fuel vapors – 3 *Xylenes*, *Toluene*, *Ethylbenzene*, *Benzene* and 1,2,4-*Trimethylbenzene*.

2 Possible health hazards – *Styrene* & *Methylene Chloride*.

<u>Benzene Statistics*</u>	<u>WASD</u>	<u>PERDUE</u>
No. of Observations (No. of Detections)	63	54
Min. Value (ppbv)	0.06	0.05
Max. Value (ppbv)	0.97	0.87
<u>Mean (ppbv)</u>	<u>0.4125</u>	<u>0.2861</u>
Median (ppbv)	0.36	0.245
Std. Dev.	0.2097	0.1738
Coefficient of Variation	0.5085	0.6074
Skewness	1.044**	1.615**
Variance	0.044	0.0302
**"Normal" Calculations	**Suggests Non-Normality	



## Non-Parametric Data Sets

Use of computer software provided by the EPA, *e.g.*, *ProUCL*, indicated that all data sets of the COPCs quantified in the Miami-Dade Air Toxics Monitoring Program were non-parametric and skewed in the positive (+) direction. Since this was the case, it was necessary to resort to alternative methods of arriving at an Upper Confidence Level of the population mean. Several options, while non-ideal, can be used to arrive at a reasonable approximation of this value, but the best was found to be Chebyshev (Mean, Std) Values.

# WASD Air Toxics Levels

Risk Assessed HAP	Mean Value – Norm. Stats. (in mg/cu.m)	Chebyshev (Mean Std) Value* (in mg/cu.m)
1,2,4-TrimethylBenzene	0.0010425	0.002175
Benzene	0.0013404	0.002523
Ethylbenzene	0.0008082	0.001645
meta+para Xylene	0.003307	0.005127
Methylene Chloride	0.003353	0.006831
Styrene	0.0005035	0.003896
Toluene	0.005574	0.011131
		*All Higher Values



# Perdue Air Toxics Levels

Risk Assessed HAP	Mean Value – Norm. Stats. (in mg/cu.m)	Chebyshev (Mean Std) Value* (in mg/cu.m)*
1,2,4-TrimethylBenzene	0.0009105	0.001331
Benzene	0.0009297	0.001816
Ethylbenzene	0.000545	0.001084
meta+para Xylene	0.002016	0.002833
Methylene Chloride	0.004678	0.008478
Styrene	0.001444	0.015221
Toluene	0.002816	0.006073

\*All Higher Values

# To Calculate Human Non-Cancer Risk from Chronic Inhalation of a HAP:

Use the equation  $EC (\mu\text{g}/\text{cu.m}) / RfC (\mu\text{g}/\text{cu.m})^*$

For benzene at the Perdue Site, using Normal Mean Statistics:

$$0.9297 / 30 = 0.031 \Rightarrow \text{no non-cancer risk}$$

For benzene at the Perdue Site, using Chebyshev Statistics:

$$1.816 / 30 = 0.061 \Rightarrow \text{no non-cancer risk}$$

\*EC = Exposure Concentration & RfC = Reference Concentration

# To Calculate Human Cancer Risk from Chronic Inhalation of a HAP:

Use the equation  $EC (\mu\text{g}/\text{cu.m}) \times IUR (\text{risk}/\mu\text{g}/\text{cu.m})^*$

For benzene at the Perdue Site, using Normal Mean Statistics:

$$0.9297 \times 7.8\text{E-}06 \Rightarrow \underline{\text{cancer risk of } 7\text{E-}6 \text{ or } 7 \text{ in a million}}$$

For benzene at the Perdue Site, using Chebyshev Statistics:

$$1.816 \times 7.8\text{E-}06 \Rightarrow \underline{\text{cancer risk of } 14\text{E-}6 \text{ or } 14 \text{ in a million}}$$

\*EC = Exposure Concentration & IUR = Inhalation Unit Risk

# Air Toxics Risk Assessment Using OAQPS' Recommended Dose Response "Value Table" and WASD Sampling Site Concentrations

Miami-Dade COPC <b>(WASD Site)</b>	WOE for Cancer		Non-Cancer	Source	Cancer	Source
	EPA	IARC	(mg/cu.m)		(1/μg/cu.m)	
Benzene	A	1	0.03	IRIS	7.8E-06	IRIS
<u>Risk from Benzene:</u>			0.045(0.084)**		10E-6(20E-6)**	10(20) in a million
Ethylbenzene	D	--	1	IRIS	--	--
<u>Risk from Ethylbenzene:</u>			0.00081(0.0016)		0	
Methylene chloride	B2	2B	1	ATDSR	4.7E-07	IRIS
<u>Risk from Methylene chloride:</u>			0.0034(0.0068)		2E-6(3E-6)	2(3) in a million
Styrene	--	2B	1	IRIS	--	--
<u>Risk from Styrene:</u>			0.00050(0.0039)		0	

# Air Toxics Risk Assessment Using OAQPS' Recommended Dose Response

## “Value Table” and WASD Sampling Site Concentrations

Miami-Dade COPC ( <u>WASD Site</u> )	WOE for Cancer		Non-Cancer (mg/cu.m)	Source	Cancer (1/μg/cu.m)	Source
	EPA	IARC				
Toluene	D	3	0.4	IRIS	--	--
<u>Risk from Toluene:</u>			0.014(0.028)		0	
1,2,4-Trimethylbenzene (Cumene as surrogate)	D	--	0.4	IRIS	--	--
<u>Risk from 1,2,4-Trimethylbenzene:</u>			0.0026(0.0054)		0	
Xylenes	--	--	0.1	IRIS	--	--
<u>Risk from the Xylenes:</u>			0.033(0.051)		0	
<u>Total Risks:</u>			<u>HI: 0.099(0.18) or 0 Total CA: 12(23) million</u>			

# Air Toxics Risk Assessment Using OAQPS' Recommended Dose Response

## “Value Table” and Perdue Sampling Site Concentrations

Miami-Dade COPC ( <u>Perdue Site</u> )	WOE for Cancer		Non-Cancer (mg/cu.m)	Source	Cancer (1/μg/cu.m)	Source
	EPA	IARC				
Benzene	A	1	0.03	IRIS	7.8E-06	IRIS
	<u>Risk from Benzene:</u>		0.031(0.061)**		7E-6(14E-6)**	7(14) in a million
Ethylbenzene	D	--	1	IRIS	--	--
	<u>Risk from Ethylbenzene:</u>		0.00055(0.0011)		0	
Methylene chloride	B2	2B	1	ATDSR	4.7E-07	IRIS
	<u>Risk from Methylene chloride:</u>		0.0047(0.0085)		2E-6(4E-6)	2(4) in a million
Styrene	--	2B	1	IRIS	--	--
	<u>Risk from Styrene:</u>		0.0014(0.015)		0	

# Air Toxics Risk Assessment Using OAQPS' Recommended Dose Response

## “Value Table” and Perdue Sampling Site Concentrations

Miami-Dade COPC (Perdue Site)	WOE for Cancer		Non-Cancer (mg/cu.m)	Source	Cancer (1/μg/cu.m)	Source
	EPA	IARC				
Toluene	D	3	0.4	IRIS	--	--
<u>Risk from Toluene:</u>			0.0070(0.015)		0	
1,2,4-Trimethylbenzene (Cumene as surrogate)	D	--	0.4	IRIS	--	--
<u>Risk from 1,2,4-Trimethylbenzene:</u>			0.0023(0.0033)		0	
Xylenes	--	--	0.1	IRIS	--	--
<u>Risk from the Xylenes:</u>			0.020(0.028)		0	
<u>Total Risks:</u>			<u>HI: 0.067(0.13) or 0 Total CA: 9(18) / million</u>			

Ideally experimental exposure should be made to take place over the entire lifetime of the organism for which adverse effects are predicted. Inasmuch as the adult laboratory rat lives about two years, and human exposure can be for as much as 70 years or more, safety factors must be introduced into any final assessment. Additional safety factors used to protect developing embryos, fetuses, newborn infants, the immunity compromised, and the aged can skew the assessment far into the ultra conservative arena. Moreover, since human activity and highly probable mobility allow for periods during which “decontamination” can occur, an assumption that an exposed individual constantly remains at the point of maximum exposure for his lifetime tends to greatly over-estimate the deleterious effects expected from the exposure. Then there is the problem of biochemical variability among humans, high and low sensitivity to chemical insults (exposures) & the like.



Seven COPCs were identified, and as discussed in this report, only benzene and methylene chloride appeared of real concern. Methylene chloride results may be inaccurate due to the (often) confounding variable of laboratory use of it as a solvent from time to time. However, inasmuch as dichloromethane has been classified as a B2 carcinogen by the EPA and as a 2B carcinogen by the IARC, it was included in the risk analyses. Benzene is an A[EPA] or 1[IARC] carcinogen.

For both sampling locations, HIs (Hazard Indices) of 0 were determined, even when Chebyshev statistics were used to calculate the chemical's mean values.

Both sampling stations suggested increased cancer risk from lifetime human exposures. Use of Normal Mean Values in the calculations led to increased risk of cancer (all types) of 9 in a million around the Perdue site and 12 in a million around the WASD site. When Chebyshev Statistics were used in the calculations, an increase to 18 in a million was predicted around the Perdue site and 23 in a million around the WASD site. These possible increases are well within those currently allowed by the EPA as predictions even as high as one in ten thousand are sometimes allowed.

As a final note, ultimate human cancer morbidity to all causes of the disease is 1 in 3 in America, 1 in 4 Americans of which will suffer cancer mortality.

# Recognition of Collaborators

Dr. Ken Mitchell ☺ Dr. Ken Mitchell ☺ Dr. Mitchell

☺ Patrick Wong ☺ Patrick Wong ☺ Patrick Wong ☺

☺ Debbie Griner ☺ Debbie Griner ☺ Debbie Griner ☺

☺ Broward County Environmental Laboratory ☺