Toxics Air Study in Connecticut

NESCAUM Team:
John Graham, Iyad Kheirbek, Phil Johnson, Ingrid Ulbrich & Lisa Rector

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Overview

- Motivation for work
- Background:
  - MASC and Section 29
  - HLV Revisions
  - Ambient Measurements (TASC)
- Project Scope and Tasks
- Synthesis

Motivation for Work

To identify toxic pollutants present in Connecticut's air and determine ambient levels, develop understanding of their sources and build emission inventory, subsequently use this information to design risk reduction strategies to mitigate exposure of general population to toxic pollutants.

Background: Section 29 & MASC

- Section 29 Adopted in 1986 regulating ~850 chemicals primarily from stationary sources
- Periodic inspection of point sources
- Maximum Allowable Stack Concentration
  - Based on two short-term HLVs derived from Occupational Health Exposure levels
  - Conservative Gaussian Plume assumptions
  - Facility info: Stack Ht., Emis.Rate, Fenceline dist.
- Regulations under review

Background: HLV Revisions

- Early 90's initiated process to prioritize chemicals
  - 54 of 850 species identified
- 1998 DEP/DPH partnership to develop risk based standards
- Committee established to:
  - Develop process for deriving Hazard Limiting Values
  - Use process to establish proposed 1-hour and annual for priority chemicals
- Technical Support Document from DPH released in February 2002

Background: Ambient Measurements

- Toxics Air Study in Connecticut (TASC)
  - Assess Spatial and Seasonal Variability in Air Toxics in Connecticut near Title V facilities
  - Begun in 1998 covering six “facility” sites and one background location
  - Metals, Volatile Organic Carbon (VOCs), Polycyclic Aromatic Hydrocarbons (PAHs), Carbonyls
  - Five years of data (3/1999-2/2003)

Background: Ambient Measurements

- PAMS Network
  - Carbonyls, VOCs
  - Currently two sites, some years up to four
- Dioxin
- Mercury
- Ozone
- Fine Particles
  - IMPROVE, Speciation Trends Network (STN), FRM

Project Scope and Tasks

Provide assistance to CT DEP by conducting analysis of hazardous air pollutant (HAP) monitoring data that has been collected. These data are key elements in characterizing the ambient concentrations of HAPs in a given area, the fate and transport of HAPs in the atmosphere, and the long-term trends to evaluate the effectiveness of HAP reduction strategies. This information can be used in the development of a strategy to reduce the impacts of air toxics in Connecticut.

Additionally, a HAPs emissions compliance review of Title V sources will be conducted and potential changes in Hazard Limiting Values (HLVs) and state hazardous air pollutant regulatory framework will be assessed.

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Project Scope and Tasks

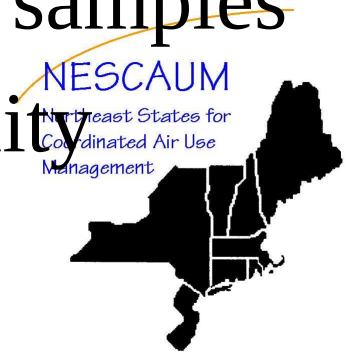
1) Compile Database
2) QA TASC Data
3) Conduct Data Analysis
4) Review ASPEN Modeling
5) Report findings, develop recommendations
6) Evaluate MASC Compliance for Title V facilities and Assess Impact of HLV revisions

Project Scope and Tasks
(1) Compile Database

- Datasets include:
  - TASC data from 3/99 to 2/03- obtained in 3 blocks
  - PAMS Data from 1994-2002
  - Dioxin Data from 10/93 through 4/02
  - Mercury Data from 11/96 to 12/99
  - IMPROVE Data from 9/01 to 12/02
  - FRM Fine Particle Data from 10/98 to 3/03

Project Scope and Tasks
(2) QA TASC Data

- Review SOPs
- Spot Check Field Data Sheets
- Review EPA and contractor laboratory audit information
  - Based on audit, VOC lab data reviewed in detail
  - Multiple visits to contractor
- Blanks, Precision samples, Collocated samples
- Overall Data Assessment- Data Usability



Project Scope and Tasks
(3) Conduct Data Analysis

- Four Pollutant Classes
  a) Carbonyls
  b) PAHs
  c) VOCs
  d) Metals
- Comparison of TASC to PAMS for select Carbonyls and VOCs

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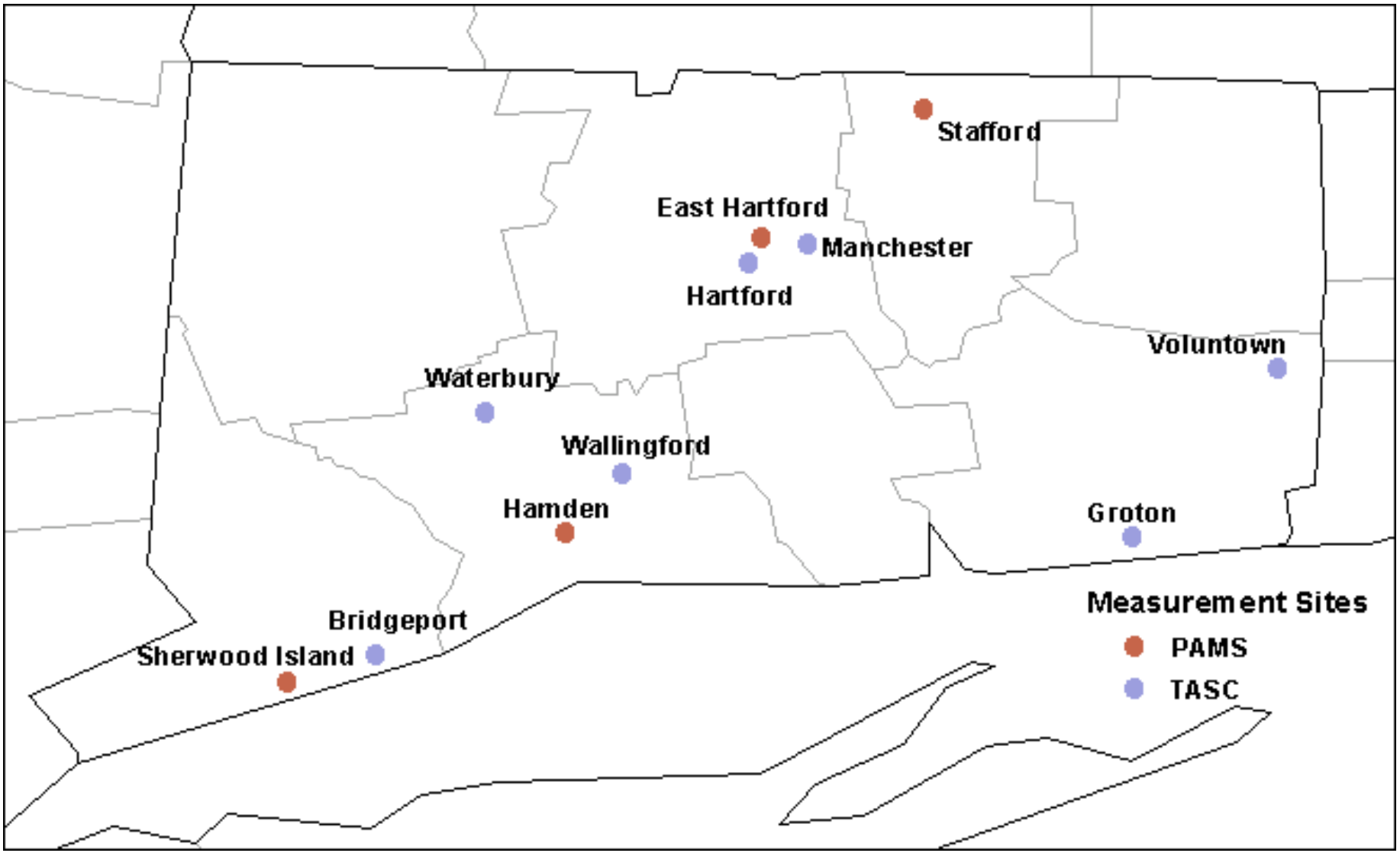
Project Scope and Tasks

(3) Conduct Data Analysis



Project Scope and Tasks
(3a) Conduct Data Analysis: Carbonyls

- TASC data
  - 24-Hour Average
  - Every sixth day
  - Wide range of compounds, analytical issues
- PAMS
  - 3-Hour Average
  - Daily or every third day
  - Formaldehyde and Acetaldehyde

Project Scope and Tasks
(3a) Conduct Data Analysis: Carbonyls

- Acetone, Formaldehyde, Acetaldehyde routinely detected
- Ambient levels well above blank levels
- Replicates and Collocated samples compare well

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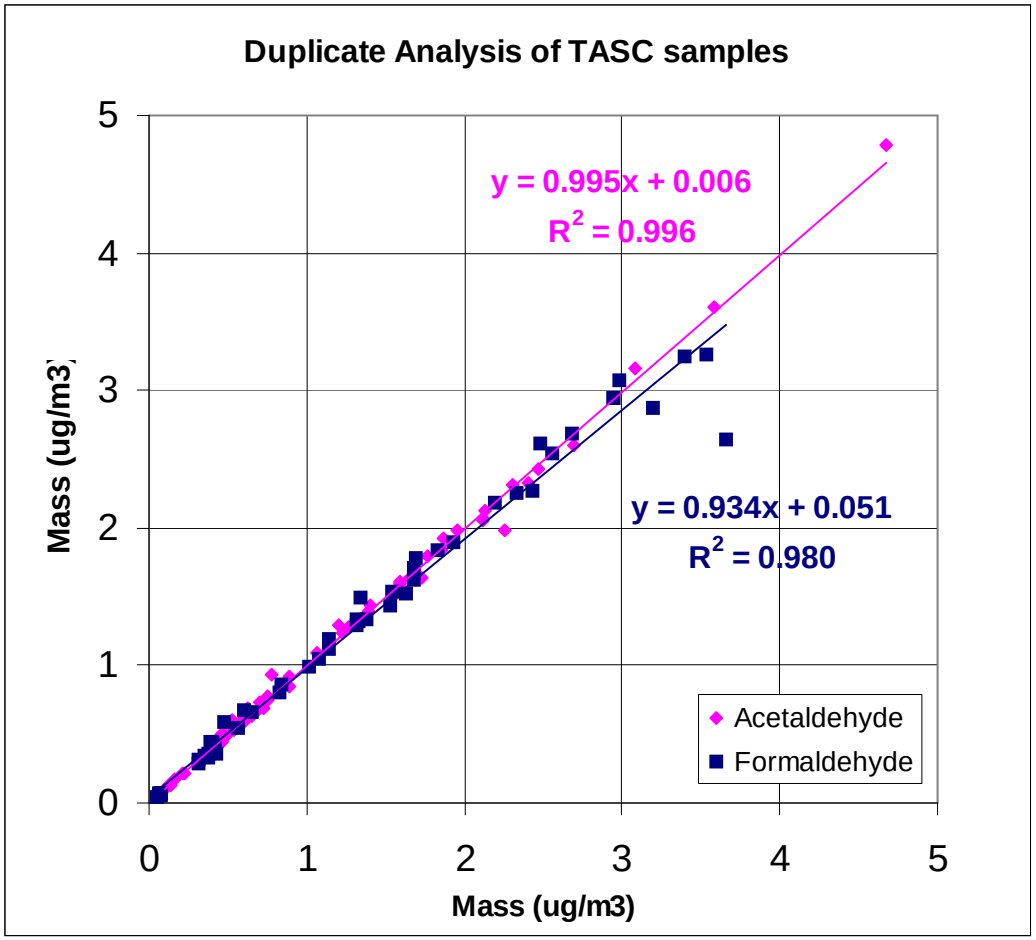
Project Scope and Tasks

(3a) Conduct Data Analysis: Carbonyls



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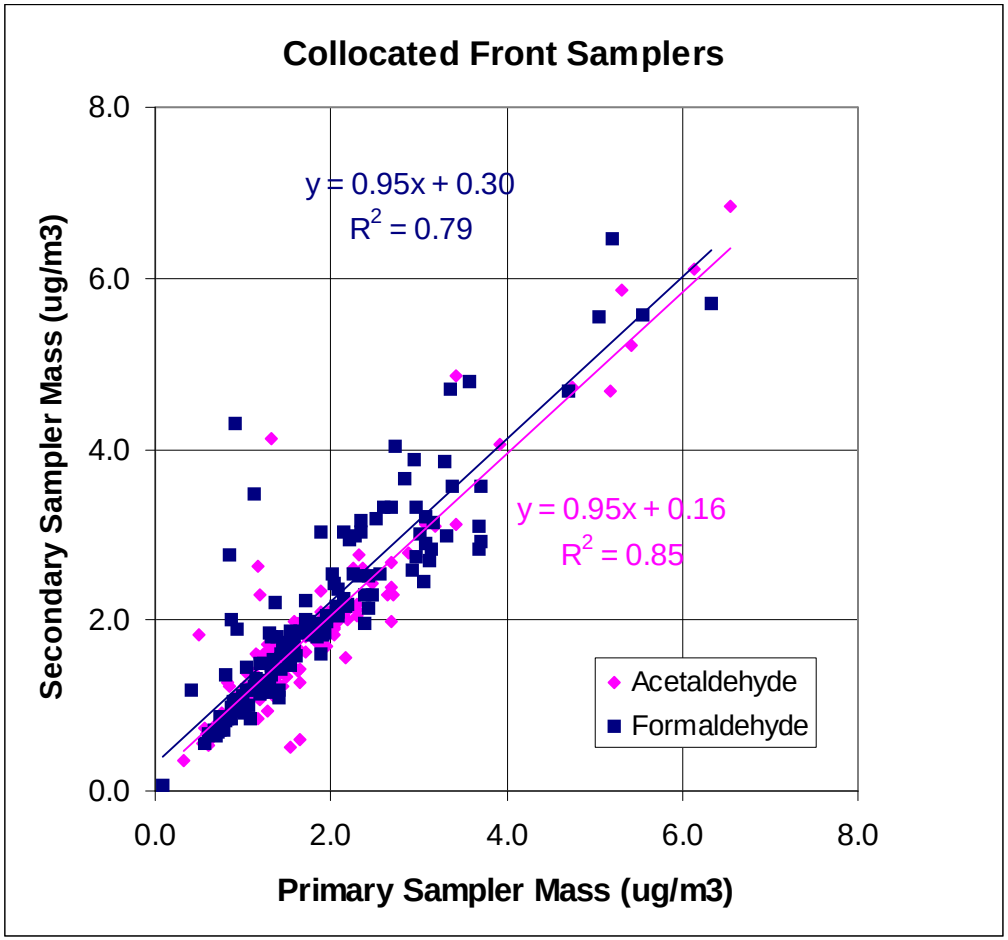
Project Scope and Tasks

(3b) Conduct Data Analysis: Carbonyls



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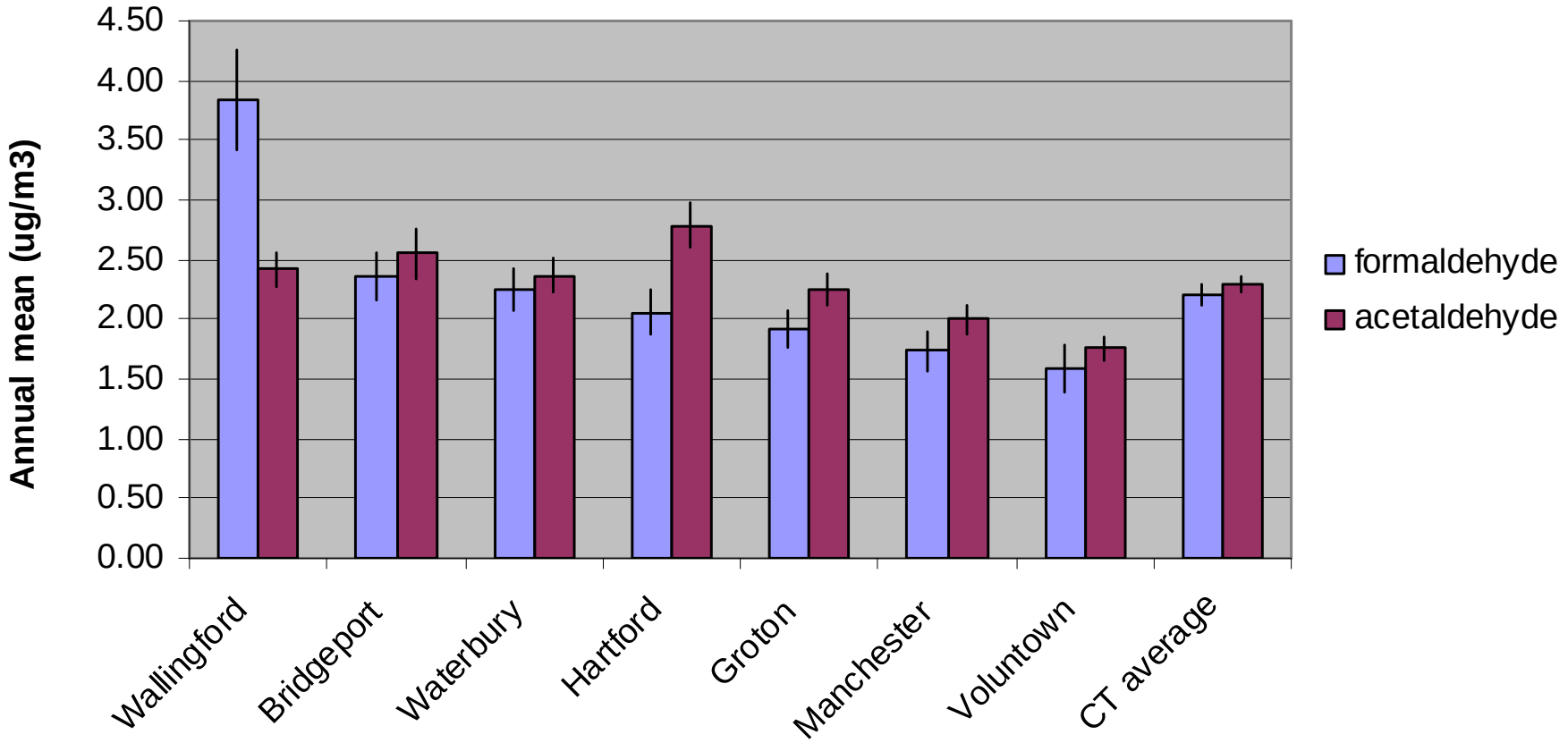
Project Scope and Tasks

(3b) Conduct Data Analysis: Carbonyls

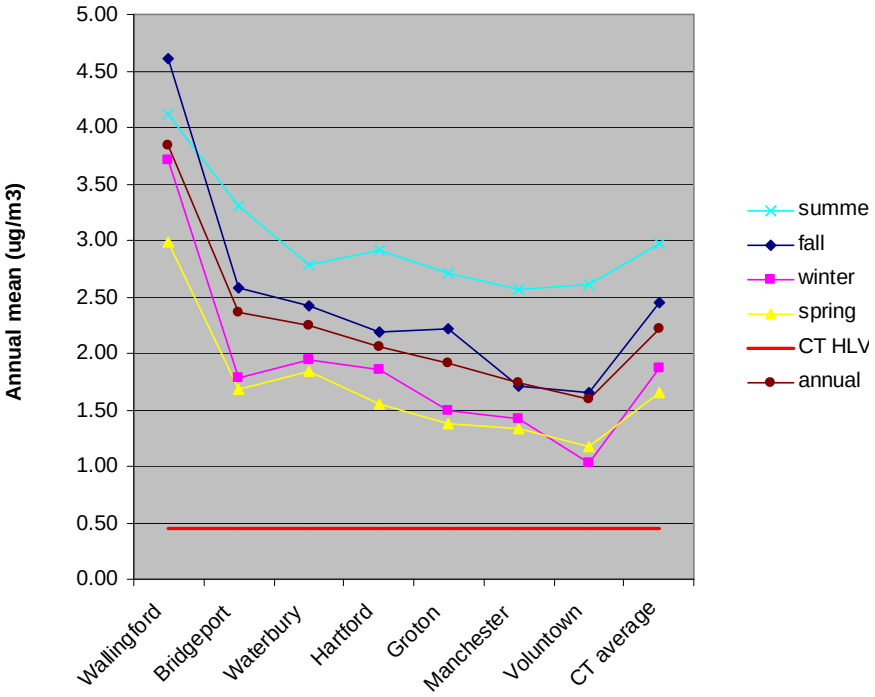
TASC site mean annual concentration of acetaldehyde and formaldehyde

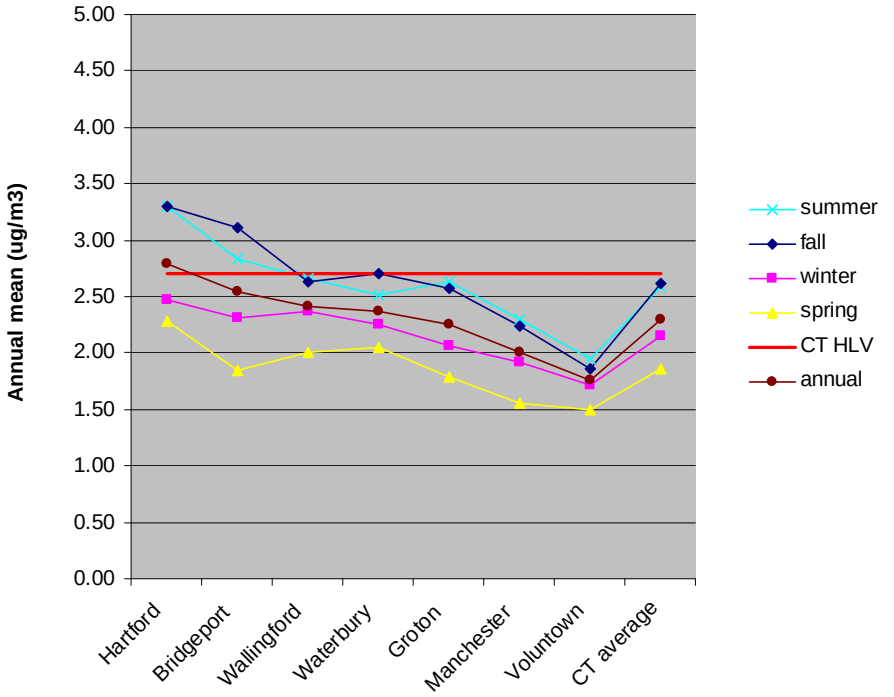


Project Scope and Tasks

(3b) Conduct Data Analysis: Carbonyls

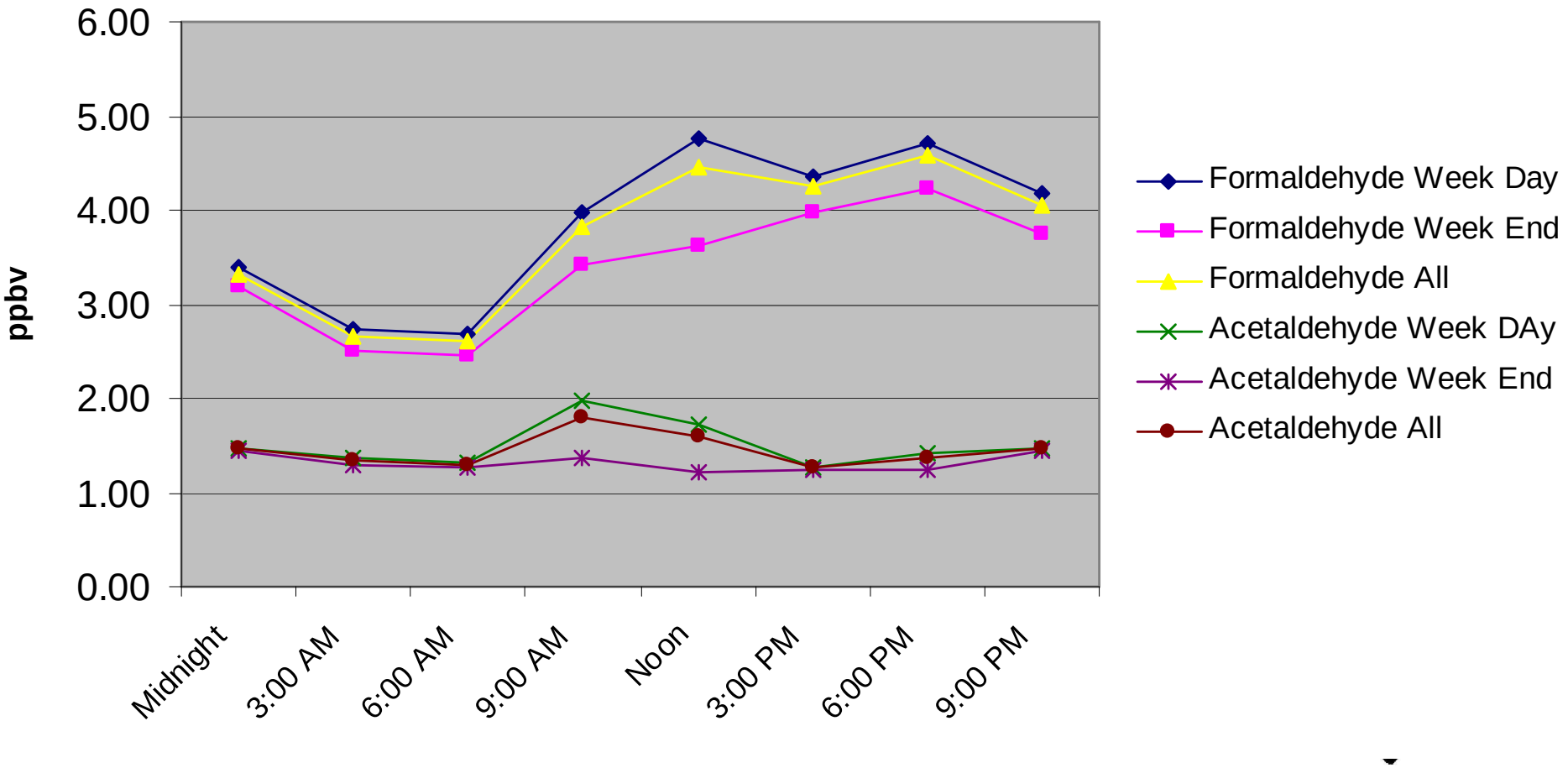
TASC site mean seasonal concentration of formaldehyde and acetaldehyde





Project Scope and Tasks
(3b) Conduct Data Analysis: Carbonyls

East Hartford Data 1994-2002. Note 2001/02 collected only 6 AM to 6 PM



Project Scope and Tasks
(3b) Conduct Data Analysis: PAHs

- 19 PAHs on target list
  - 15 with proposed HLVs
- Sample Duration
  - Weeklong samples early years
  - 24-hour sample more recent years
- Ambient levels lower than proposed HLVs
  - Naphthalene, Fluorene, Phenanthrene, Fluoranthene & Pyrene detected in almost all samples, but these are least potent PAHs

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Project Scope and Tasks
(3b) Conduct Data Analysis: PAHs

- Method Detection Limit well below levels of concern
- Trip and Field Blank levels generally <20% ambient levels detected
- Collocated results for most compounds show Relative percent difference O(20-30%)

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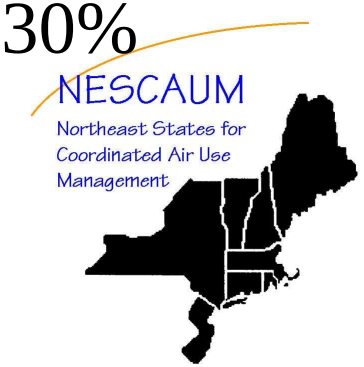
Project Scope and Tasks

(3b) Conduct Data Analysis: PAHs

PAH	*2-year Average Concentration (ug/m^3) pre-July01/post-July01*	*Annual HLV (ug/m3)*	*Ratio of Concentration to HLV (%)*
Fluorene	0.0080/0.0046	15	<<1%
Phenanthrene	0.0148/0.0118	15	<<1%
Fluoranthene	0.0037/0.0040	15	<<1%
Pyrene	0.0021/0.0023	15	<<1%
Benzo(a)anthracene	0.0002/0.0005	0.034	O (1%)
Chrysene	0.0004/0.0008	1.14	<<1%
Benzo(b+j+k)fluoranthene	0.0008/0.0015	0.03	O (5%)
Benzo(a)pyrene	0.0002/0.0004	0.005	O (8%)
Indeno(1,2,3-cd)pyrene	0.0001/0.0005	0.09	O (1%)
Dibenz(a,c+a,h)anthracene	0.0002/0.0003	0.0045	O (7%)

Project Scope and Tasks
(3c) Conduct Data Analysis: VOCs

- 54 VOCs on target list
  - 22 with proposed HLVs
- 24-Hour sample taken once every six days
- Most compounds below detection limit (DL)
  - Only 8 detected in at least half the samples
- DL higher than HLV for 5 compounds
  - Measurements not sensitive enough
- Collocated precision RPD generally within 30%
- Contamination issues for some compounds



Project Scope and Tasks
(3c) Conduct Data Analysis: VOCs

Benzene Data 2002	Field Blanks	Ambient Samples on Field Blank Days	Trip Blanks	Ambient Samples on Trip Blank Days
Percent Detected (%)	73.7	92.9	84.9	91. 7
Mean Concentration (ug/m^3)	3.65	3.74	3.68	4.17
Median Concentration (ug/m^3)	3.43	3.75	3.63	4.20

- Contamination in most Blank Samples
- Blank levels similar to Ambient
- Inconsistent (year to year) integration of peaks in Blank Samples
- Acetone results show similarly high blanks (up to ½ ambient level)

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Project Scope and Tasks

(3c) Conduct Data Analysis: VOCs

Year	Acetone	Methylene Chloride	Benzene	Toluene
6/99-12/00	87.0	85.8	7.4	11.1
1/01-12/01	8.3	4.2	0	2.1
1/02-2/03	72.7	57.6	84.9	21.2

Percent of trip blanks with levels above the detection limit

Project Scope and Tasks

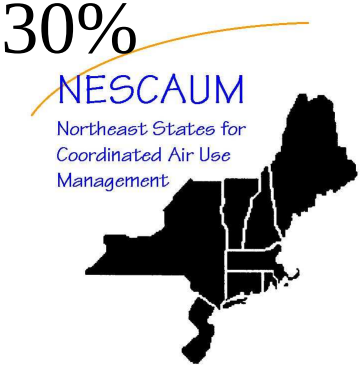
(3c) Conduct Data Analysis: VOCs

Year	Bridgeport TASC	Sherwood Island PAMS	TASC/PAMS
1999	2.79	1.19	2.35
2000	2.33	1.28	1.83
2001	3.01	1.18	2.55
2002	3.03	1.13	2.68
Year	Manchester TASC	East Hartford PAMS	TASC/PAMS
1999	6.01	1.66	3.61
2000	2.11	1.45	1.46
2001	3.15	1.29	2.44
2002	3.19	1.55	2.06
Year	Wallingford TASC	Hamden PAMS	TASC/PAMS
2000	5.37	1.72	3.13
2001	4.33	1.52	2.85
2002	3.35	1.69	1.98

TOLUENE Summertime Averages

Project Scope and Tasks
(3d) Conduct Data Analysis: Metals

- 12 metals on target list
  - 8 with proposed HLVs
- Sample Duration
  - Weeklong samples early years
  - 24-hour sample more recent years
- Seven metals detected in >90% of samples
- DL lower than HLV, although within 50% for As, Cr
- Collocated precision RPD generally within 30%
- Contamination issues for some Cr, Zn



Project Scope and Tasks

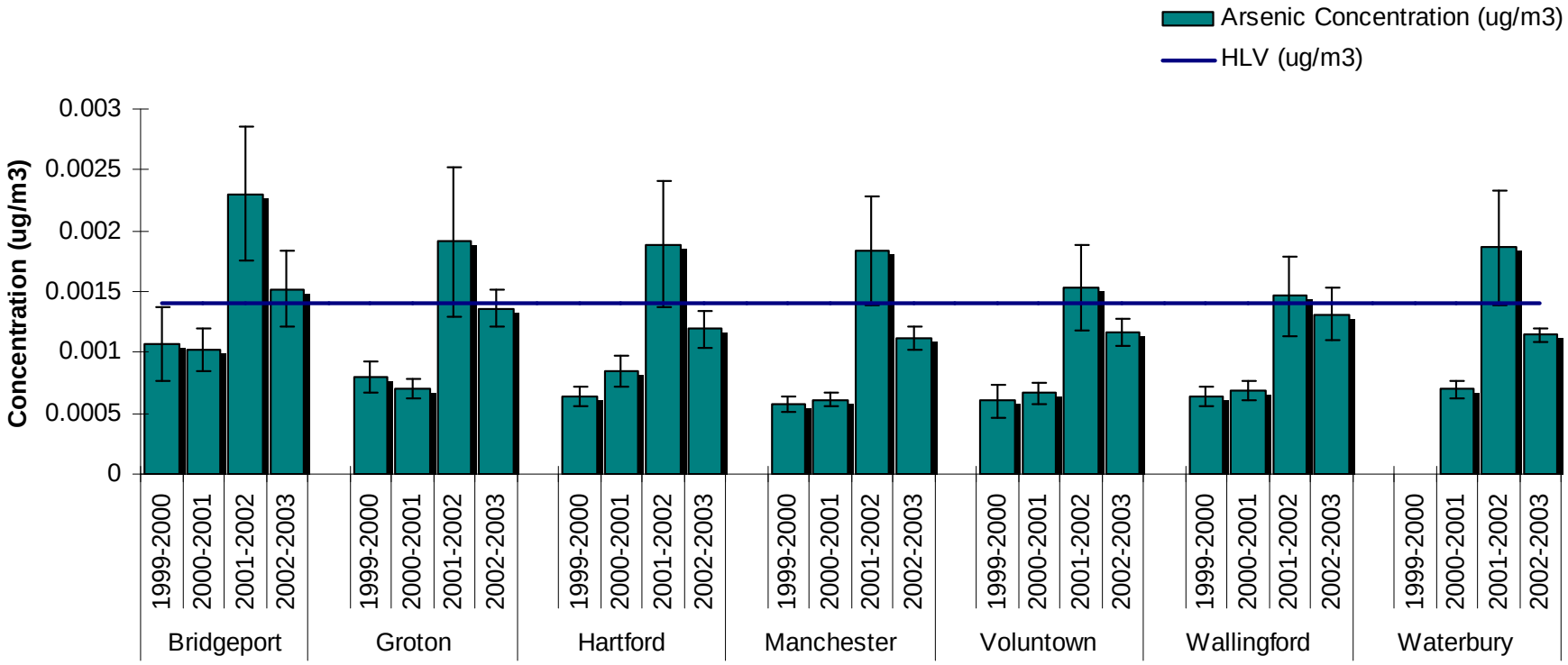
(3d) Conduct Data Analysis: Metals

Comparison of monitored data to the HLV

Metal	*Connecticut 2-yr Average Concentration (ug/m^3) pre-July01/post-July01*	*Annual HLV (ug/m^3)*	*Ratio of Monitored Concentration to HLV*	*Detection Limit (ug/m3)*
Arsenic	**0.0007/0.0016 (>50% BDL)**	**0.0014**	O (HLV)	**0.0005/0.0009**
Beryllium	**93%/99% BDL**	0.0024	O (1/10 HLV)	**0.0001/0.0003**
Cadmium	**0.0006/0.0020 (~75% BDL)**	**0.0032**	O (1/2 HLV)	**0.0005/0.0017**
Manganese	0.0166/0.0268	0.03	**O (HLV)**	0.0001/0.0011
Nickel	0.0062/0.0081	0.05	O (1/10 HLV)	0.0006/0.0013
Lead	0.0131/0.0200	0.5	O (1/25 HLV)	0.0007/0.0009

Project Scope and Tasks

(3d) Conduct Data Analysis: Metals



Annual means of arsenic concentrations at 7 TASC sites

Note: Sample Interval changed in July 2001 to 24-hour from weeklong

Project Scope and Tasks
(4) Review ASPEN Modeling

Assessment System for Population Exposure Nationwide (ASPEN) model

- Gaussian Model
  - Based on frequencies of various meteorological conditions and emissions rates
  - Census Tract Level results
- 1996 predictions for 32 Air Toxics
  - 4 Metals, Grouped PAHs, select VOCs overlap with TASC measurements

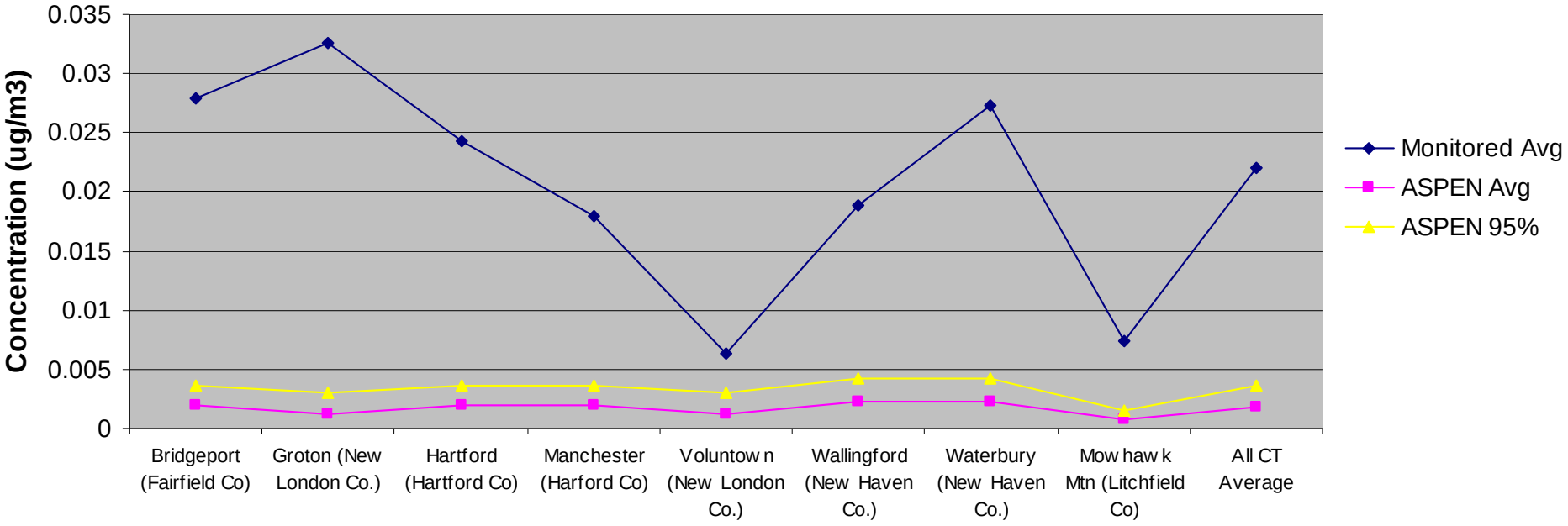
Project Scope and Tasks
(4) Review ASPEN Modeling

-ASPEN modeled results tend to underestimate monitored concentrations

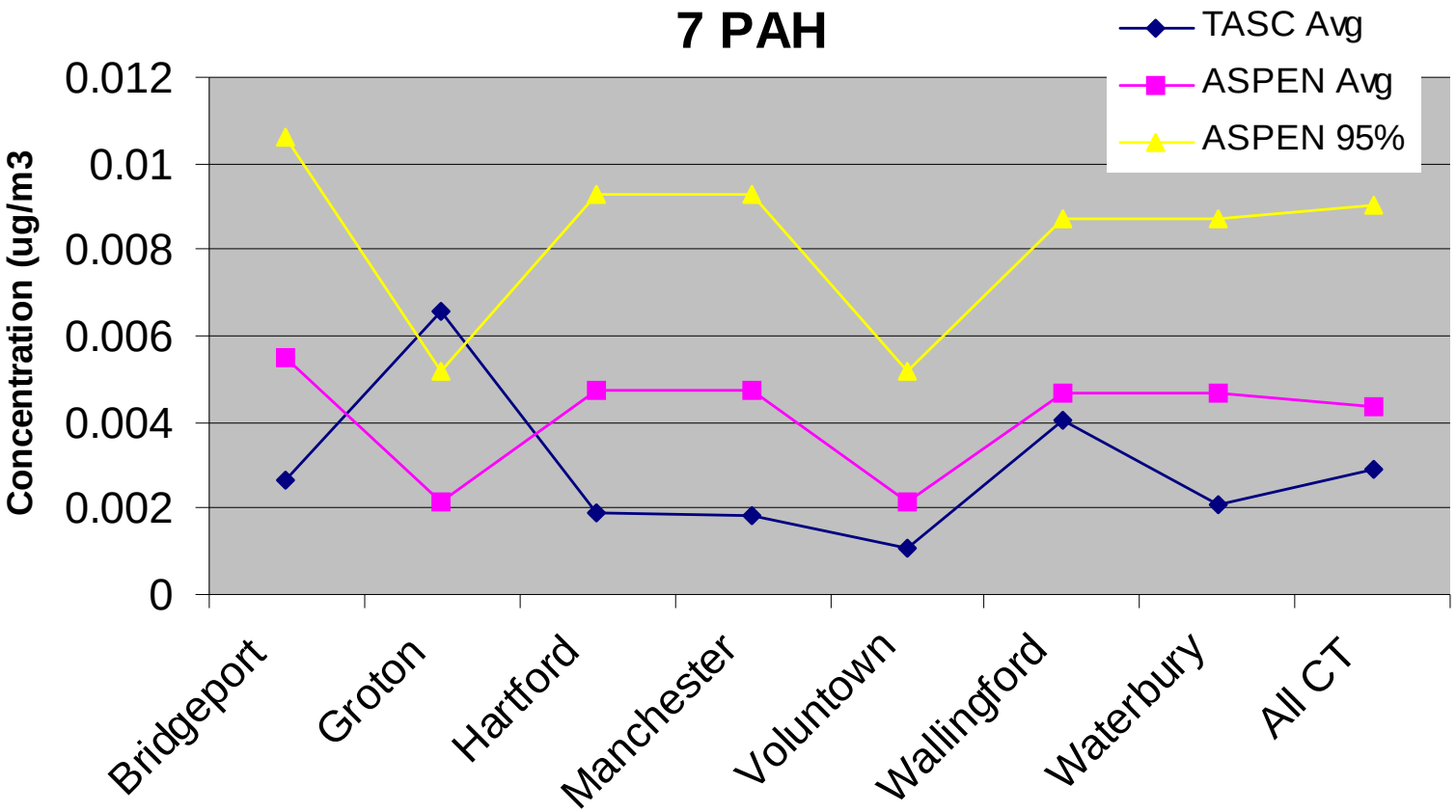
- Incomplete emissions inventories
- Uncertainty related to meteorological conditions (neglect of calm wind and stable atmospheric conditions)
- ASPEN results represent spatial and temporal averages over larger geographical areas. Air toxics networks tend to characterize higher pollution areas.

Project Scope and Tasks
(4) Review ASPEN Modeling

Comparison of CT monitored Mn concentrations to ASPEN modeled levels for seven TASC sites and one IMPROVE site.



Project Scope and Tasks
(4) Review ASPEN Modeling



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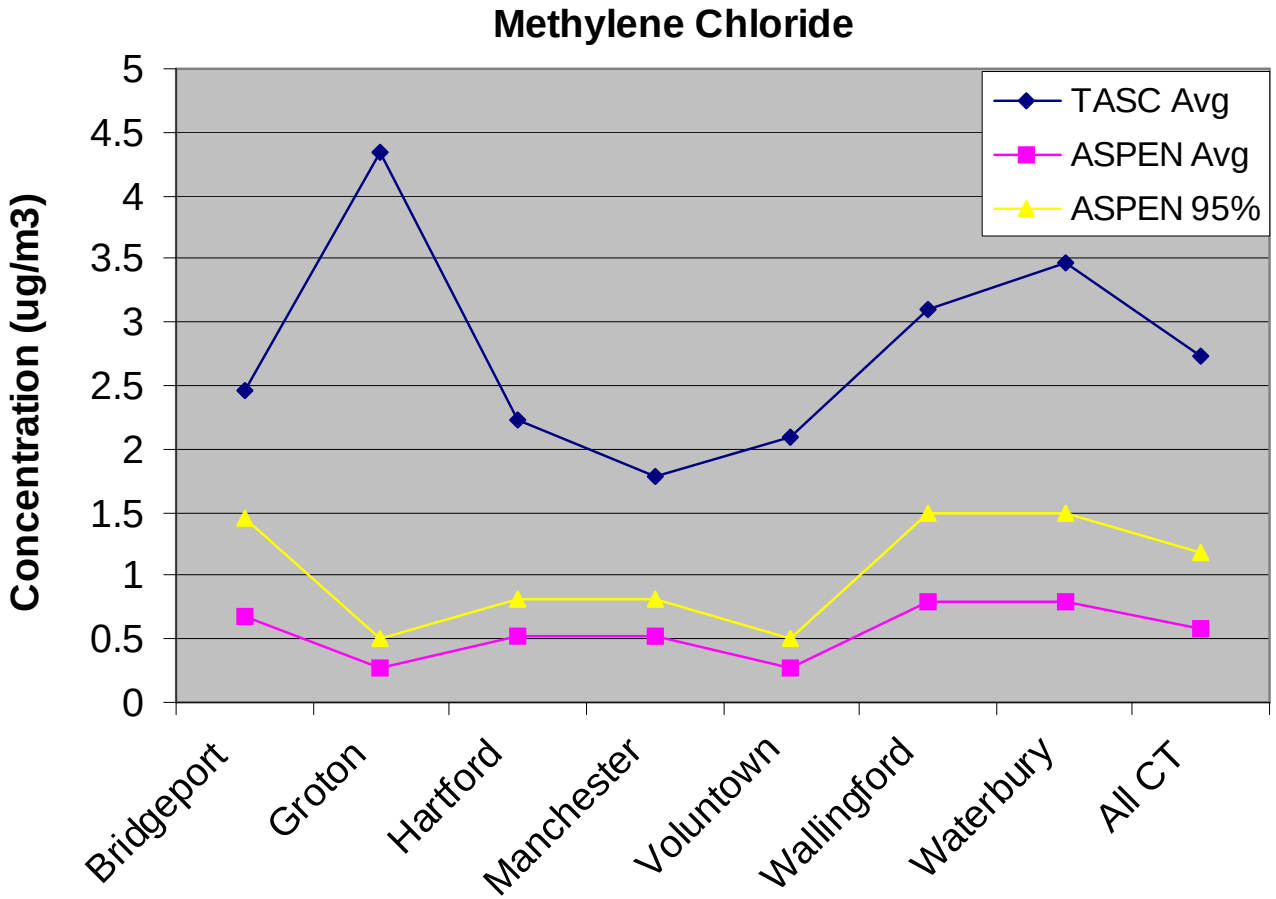
(4) Review ASPEN Modeling



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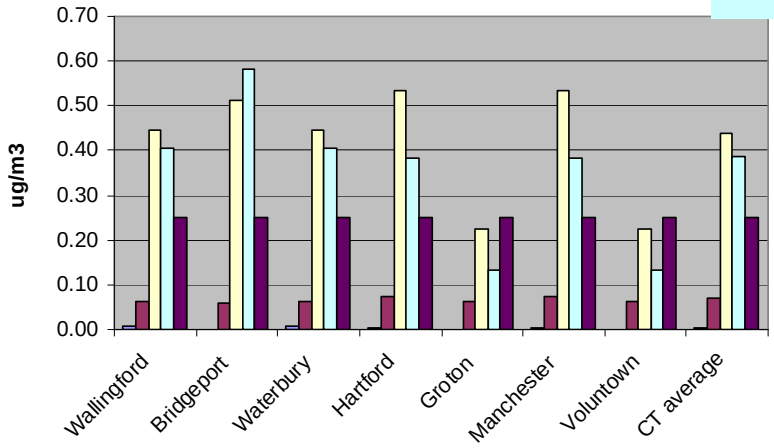
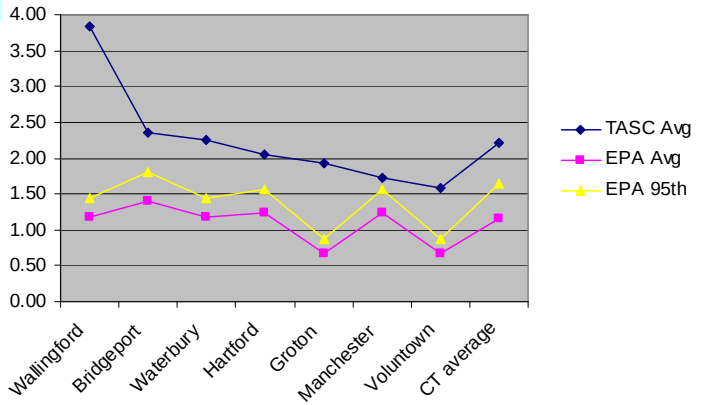
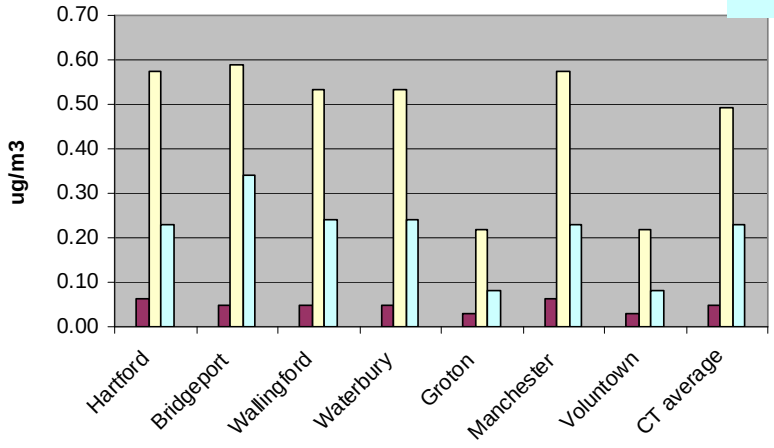
Project Scope and Tasks
(4) Review ASPEN Modeling

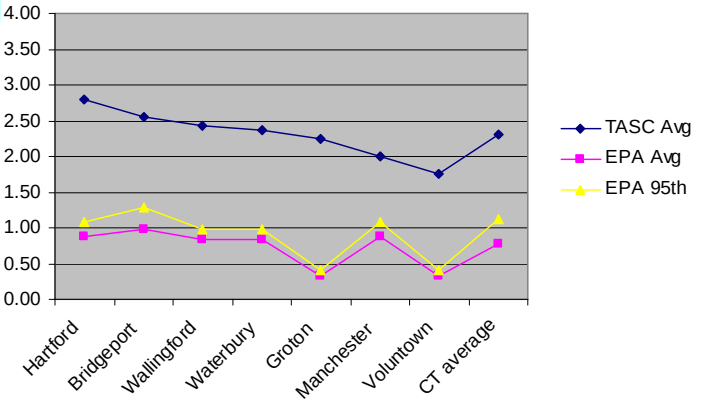
Formaldehyde

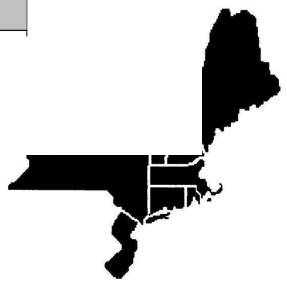




Acetaldehyde







Project Scope and Tasks
(6) Evaluate MASC and Proposed HLVs

- Assess emissions compliance of Title V sources based on the current HLVs and MASC
  - Review Permit files: Title V Permits and Applications; NSR permits and PIQs
    - Develop Database of facility emissions, stack parameters and other data required for MASC calculations
  - Create spreadsheet to calculate compliance
    - Input derived directly from Database Query
    - Calculates compliance with existing HLVs and proposed HLVs

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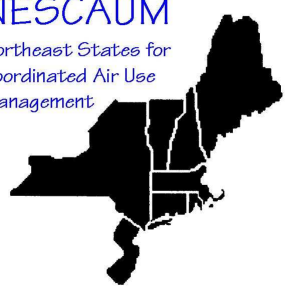
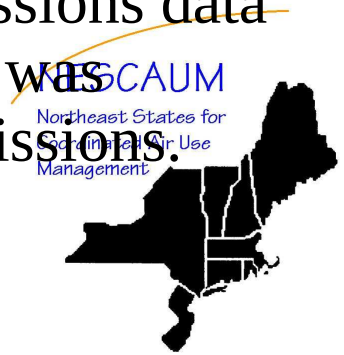
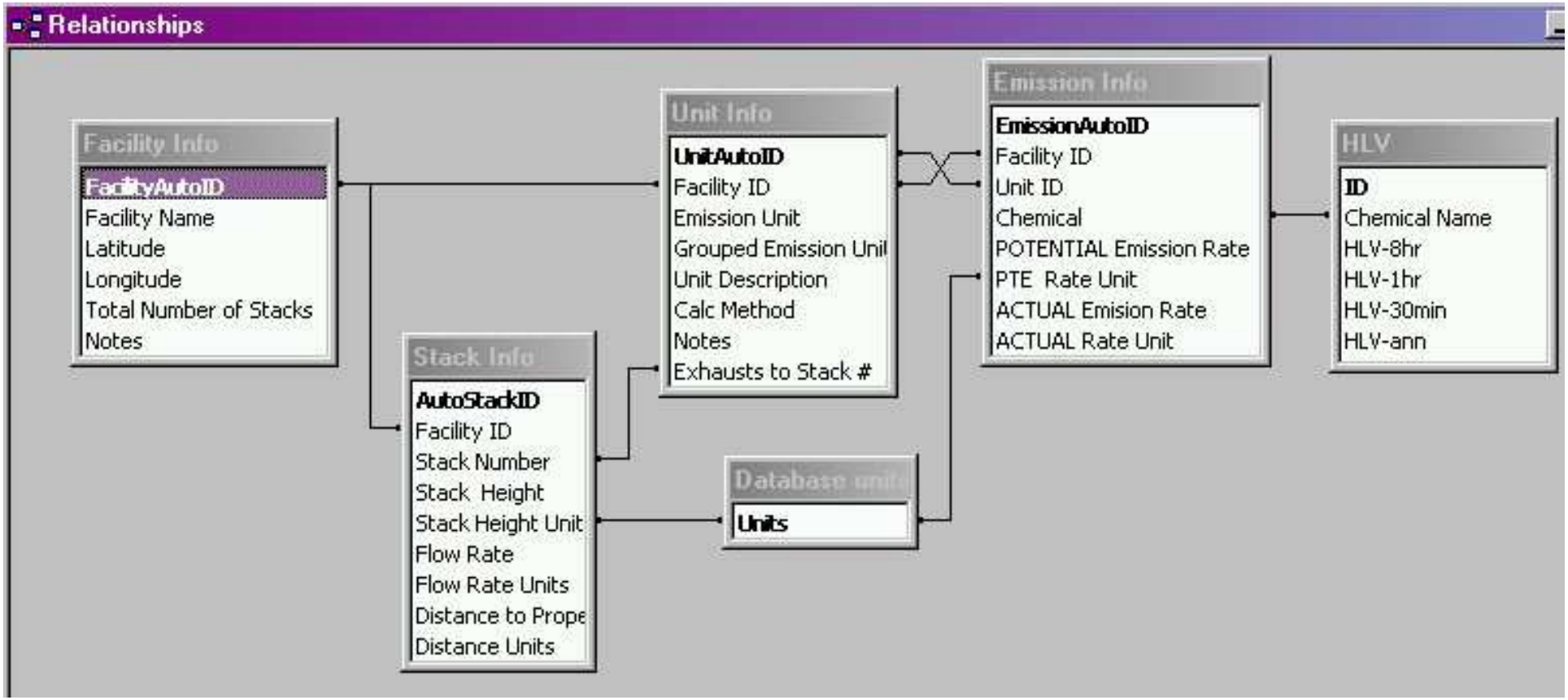


Project Scope and Tasks
(6) Evaluate MASC and Proposed HLVs

- Data from 65 facilities entered into database. This included information for 191 stacks and 203 units. Matching stack and emissions data were available for 362 combinations to evaluate for MASC. Of these 362 stack-compound combinations, 23 stacks were missing flow data and 134 were for compounds that do not have DEP or DPH HLVs. The remaining 205 stack-compound combinations were assessed for compliance with the MASC.
- Actual emissions data were available for 133 combinations, potential emissions data were available for 68 combinations, and both actual and potential emissions data were available for 4 combinations. Compliance was examined based on both actual and potential emissions.

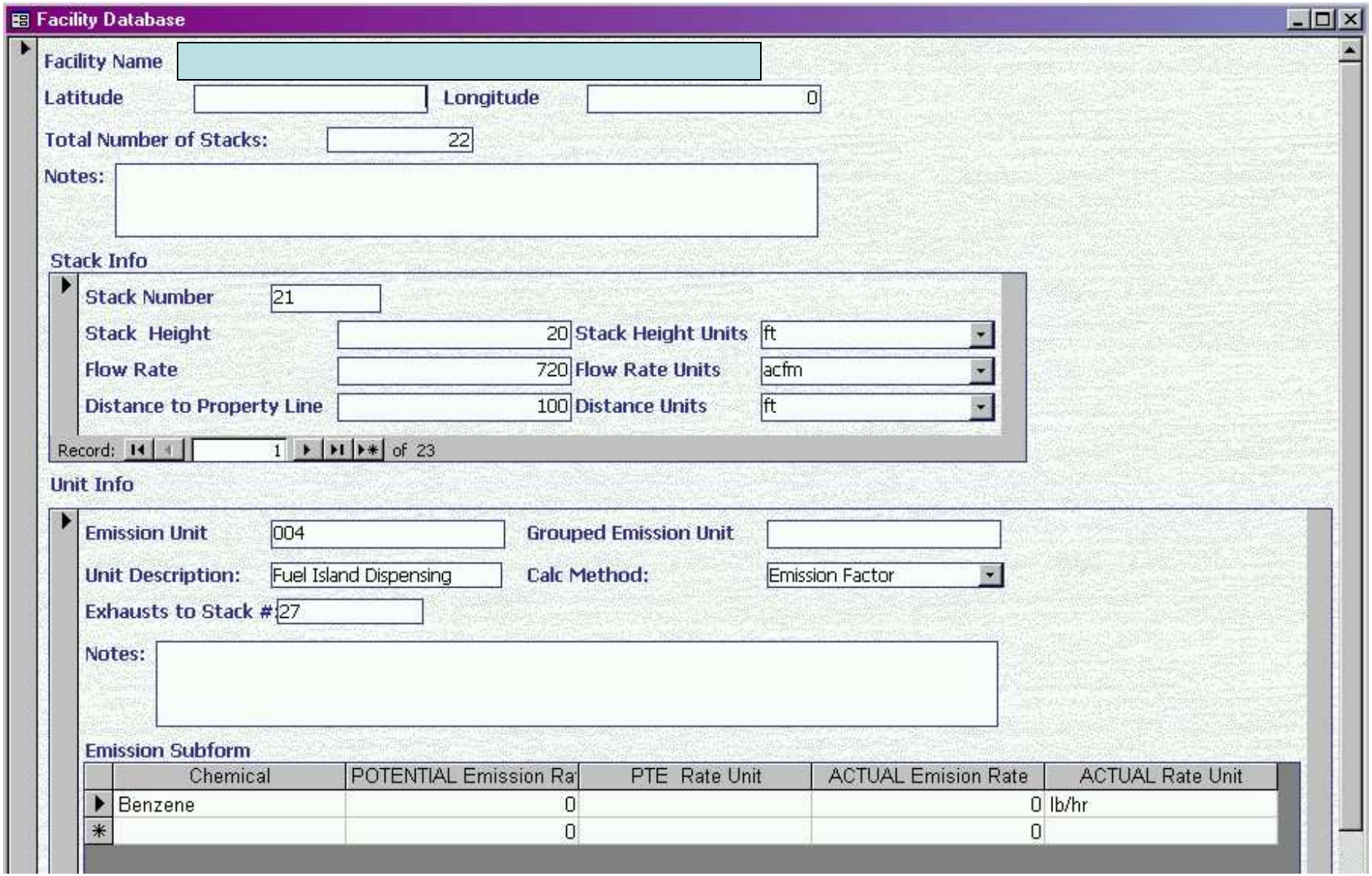


Project Scope and Tasks
(6) Evaluate MASC and Proposed HLVs



Project Scope and Tasks

(6) Evaluate MASC and Proposed HLVs



Project Scope and Tasks
(6) Evaluate MASC and Proposed HLVs

Excel Spreadsheet Example

MASC Calculations

Stack Concentration Calculation sed on Actual or Potential Em

Facility Stack Chemical

MASC comparison

	A	B	I	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ
1	Facility Name	Stack	Chemical		8hr-MASC	1hr-MASC	30min-MA	Ann-MASC		POT SC	ACTUAL SC		POT 8-hr P	POT 1-hr P	POT 30mir	POT Ann	P/F	ACT 8-hr P	ACT 1-hr P	ACT 30mir	ACT Ann P
207		1	Benzene		1612.828	2849.329	8064.138	8.064138			4.897314		no SC	no SC	no SC	no SC		pass	pass	pass	pass
208		1	beryllium								0.027985		no HLV	no HLV	no HLV	no HLV		no HLV	no HLV	no HLV	no HLV
209		1	chromium compounds								0.979463		no HLV	no HLV	no HLV	no HLV		no HLV	no HLV	no HLV	no HLV
210		1	Nickel max		53.76092	10.75218	268.8046	0.537609			0.41977		no SC	no SC	no SC	no SC		pass	pass	pass	pass
211		2	Arsenic		0.609067	12.18134	3.045336	0.017054			0.002099		no SC	no SC	no SC	no SC		pass	pass	pass	pass
212		2	Benzene		1827.202	3228.056	9136.009	9.136009			4.897314		no SC	no SC	no SC	no SC		pass	pass	pass	pass
213		2	beryllium								0.027985		no HLV	no HLV	no HLV	no HLV		no HLV	no HLV	no HLV	no HLV
214		2	chromium compounds								0.979463		no HLV	no HLV	no HLV	no HLV		no HLV	no HLV	no HLV	no HLV
215		2	Nickel max		60.90672	12.18134	304.5336	0.609067			0.41977		no SC	no SC	no SC	no SC		pass	pass	pass	pass
216		3	Arsenic		0.67081	13.41619	3.354048	0.018783			0.002099		no SC	no SC	no SC	no SC		pass	pass	pass	pass
217		3	Benzene		2012.429	3555.291	10062.14	10.06214			4.897314		no SC	no SC	no SC	no SC		pass	pass	pass	pass
218		3	beryllium								0.002798		no HLV	no HLV	no HLV	no HLV		no HLV	no HLV	no HLV	no HLV
219		3	chromium compounds								0.979463		no HLV	no HLV	no HLV	no HLV		no HLV	no HLV	no HLV	no HLV
220		3	Nickel max		67.08096	13.41619	335.4048	0.67081			0.41977		no SC	no SC	no SC	no SC		pass	pass	pass	pass

Project Scope and Tasks

(6) Evaluate MASC and Proposed HLVs

	Actual Emissions								Potential Emissions							
	8-hr HLV		30-min HLV		1-hr HLV		Annual HLV		8-hr HLV		30-min HLV		1-hr HLV		Annual HLV	
Chemical	F	P	F	P	F	P	F	P	F	P	F	P	F	P	F	P
1,3-Butadiene										1		1		1		1
Acetaldehyde										8		8		8		8
Acrolein										7		7		7	**7**	
Acrylonitrile		11		11		11	**2**	9								
Arsenic		12		12		12	**7**	5		2		2		2		2
Benzene		26		26		26	**7**	19		6		6		6	**6**	
Beryllium		7		7		7	**1**	6								
Carbon tetrachloride		1		1		1		1								
Chlorobenzene		1		1		1		1								
Chloroform		1		1		1		1								

Project Scope and Tasks
(6) Evaluate MASC and Proposed HLVs

- Proposed HLVs
  - Actual emissions: All pass the 1-hour standard, but 25 of 82 (31%) stacks fail the annual standard.
  - Potential emissions: All stacks pass the 1-hour standard, while 24 of 71 (34%) stacks have the potential to fail the annual standard.

Project Scope and Tasks

(5) Report Findings, Develop Recommendations

- Strategize to Continue Ambient Measurements
  - Use Project results to prioritize compounds & Siting Monitors
    - Levels wrt Proposed HLVs
    - Class Toxicity
    - Ability to detect/quantify
    - Multiple Use/Program overlap
    - Review and Incorporate latest ASPEN results
    - Use Emission information from facilities

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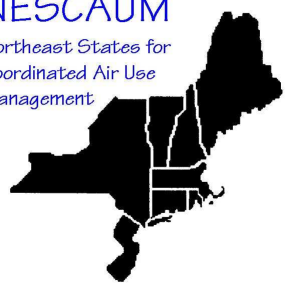

Project Scope and Tasks

(5) Report Findings, Develop Recommendations

- Populate Title V emissions database
  - Include information from any facility subject to MASC
    - Summarize database to develop statewide inventory
    - Assess “goodness” of data, AP-42 factors/fuel use
    - Any stack test data available for comparison?
    - Identify which chemicals from Tables 1,2 & 3 are emitted as potential means to pare listing
  - Use Spreadsheet Calculator to evaluate impact of HLV revisions
    - Emission rate variability: reported per year vs. per hour

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Questions?


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