

Chemical Mixture Method— Case Study

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What we'll cover today...

- Chemical Mixture Method (CMM)
 - Review basic concepts
- When to use CMM—New Draft EMG
- Simple 3-chemical example mixture
 - Using CMM Excel Workbook
 - ALOHA 5.4 for concentration at site boundary input
- **BEFORE** Scenario—exceeds PAC
- Mitigation options implemented
 - Re-run ALOHA—input new concentrations
 - Re-run CMM workbook
- **AFTER** Scenario—Below PAC???



CMM—Review

- Based on
 - **Hazard Index** concept
 - **Health Code Number (HCN) “binning”**
 - Target-organ effects categories



Review—Hazard Index (HI)

What is it?

- **HI = C / PAC ...a ratio...where...**
 - HI = Hazard Index of chemical
 - C = Airborne conc. of chemical at
 - Receptor point of interest
 - **User-supplied concentration (from ALOHA 5.4)**
 - PAC = Protective Action Criterion
 - For a chemical
 - AEGL, ERPG, or TEEL—In this order
 - **User-selected PAC Level: 3,2,1,0 (Usually Level-2)**
- To be **BELOW PAC: $HI \leq 1$**



Review—HCN “Binning”

What’s an HCN?

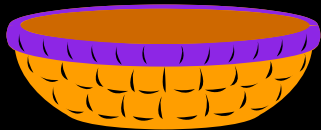
- Describes **toxic effects** of each chemical
- A **code** like medical diagnostic code
- Used to **categorize** or “bin” health effects
- HCN **Examples**
 - HCN **11.00**: Lung effects
 - HCN **3.10**: Liver effects
 - HCN **7.00**: Nervous system effects
- 45 current HCN codes—SCAPA website
<http://www.orau.gov/emi/scapa/healthcodenumbers.htm>



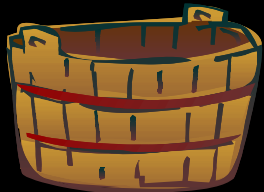
Review—HCN “Binning”

What’s an “HCN bin”?

- Like different kinds of baskets (kinds of effects)
- Ready to be filled



HCN 11.00: Lung organ bin



HCN 3.10: Liver organ bin



HCN 7.00: Nervous system bin



Review—HCN “Binning”

What’s IN an “HCN bin”?

- One kind of “fruit”—like “all apples”
 - **Sum All HIs** (like “all apples”)
 - for **one HCN effect** (HCN “bin”)
 - from **any chemical**



Review—

How does HCN “Binning” work?



Mixture of effects

Sum All HIs
for lung effects
HCN 11.00



Sum All HIs
for liver effects
HCN 3.10



Sum All HIs
for nerve effects
HCN 7.00



Review—HCN “Binning”: Simple math addition!

- **Simply ...**
- **Add ALL HIs in EACH target-organ bin**
- **To be BELOW PAC**
 - Sum of all HIs for Each HCN bin ≤ 1



Chemical Mixture—When to Analyze?

Source: *Draft EMG Vol II, “Hazards Surveys and Hazards Assessments”*, 2.6.2(1), 12-16-2005

- **Chemical Mixture...analyzed...ONLY IF:**
 - Plausible scenario

AND

 - Exceeds lab-scale threshold
 - In general...5 gal-liquids, 40 lb-solids, 10 lb-gases

AND

 - Released from same location at same time



Example Mixture

- Two chemicals
 - Carbon Tetrachloride
 - Chloroform
 - Chlorophenol



CMM-Input Sheet

A	B	C	D	E	F
No.	Chemical Compound	CASRN	Receptor Point (RP)	Conc. Limit (Li) at Receptor Point.	Conc. (Ci) at Receptor Point (mg/m3)
1	Carbon tetrachloride	56-23-5	Site Boundary 0.5 mi	TEEL-2	
2	Chloroform	67-66-3	Site Boundary 0.5 mi	TEEL-2	
3	2-Chlorophenol	95-57-8	Site Boundary 0.5 mi	TEEL-2	

Input /
 Import /
 HIs by mode /
 HIs by target organ /
 Output /
 HCN-TEEL /



Example Mixture—HCN “Bins”

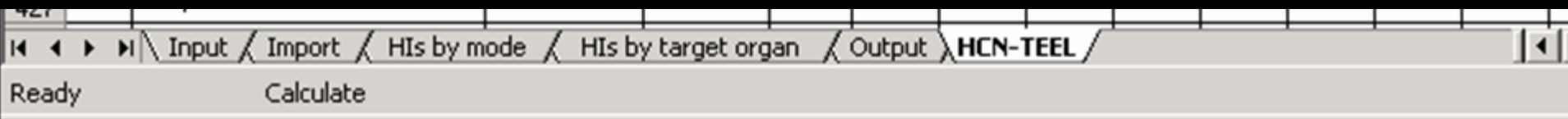
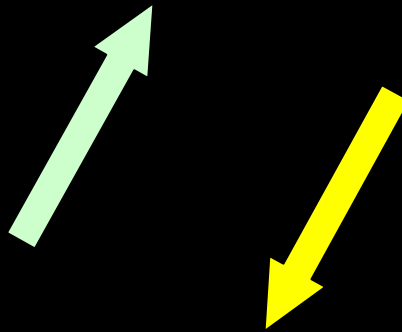
TARGET ORGAN	CHEMICAL IN MIXTURE		
	Carbon Tet (CT)	Chloroform (CF)	2-Chlorophenol (CP)
Liver	3.10	3.10	
Kidney		3.09	
Repro Sys	5.00		5.00
Narcotic	8.00	8.00	
Cancer	2.00	2.00	
Acute, generic			4.00



Changing HCNs in CMM File

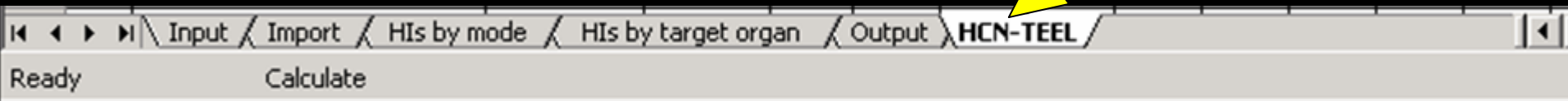
- HCN-TEEL sheet
 - Tools → Protection → Unprotect Sheet → OK

1 2 3	A	B	C	D	Health code Numbers (04) [Revisions]				TEELs Rev 20 (mg/m ³)				Units of original limits	
	No.	Chemical Name	CASRN	SAX number	HCN-1	HCN-2	HCN-3	HCN-4	Category	TEEL-0	TEEL-1	TEEL-2		TEEL-3
	414	411	Carbon tetrachloride	56-23-5	CBY000	3.10	2.00	5.00	8.00	4	60	128		639



DOE Protective Action Criteria (PACs)

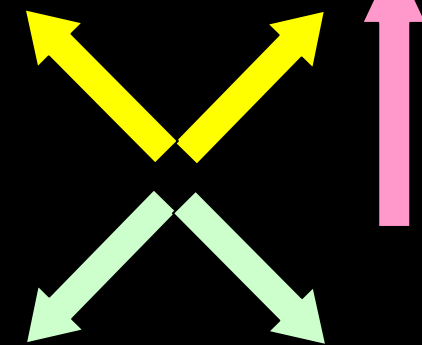
- **AEGLs (60-min) → ERPGs → TEELs**
 - AEGLs → Final or Interim (NOT Proposed)
- **Chlorophenol**
 - TEELs in CMM file
 - No AEGLs or ERPGs
- **Carbon Tet & Chloroform**
 - ERPGs (TEELs Rev 20) in CMM file
 - AEGLs (Interim) currently exist
 - Need to change PACs on HCN-TEEL sheet



Changing Carbon Tet PACs

- On HCN-TEEL sheet

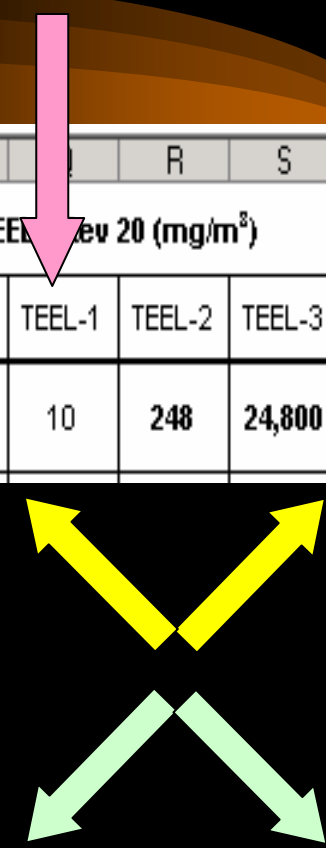
1 2 3	A	B	C	D	E				F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
	No.	Chemical Name	CASRN	SAX number	Health code Numbers (04) [Revisions]				TEELs Rev 20 (mg/m ³)				Units of original limits										
					HCN-1	HCN-2	HCN-3	HCN-4	Category	TEEL-0	TEEL-1	TEEL-2		TEEL-3									
414	411	Carbon tetrachloride	56-23-5	CBY000	3.10	2.00	5.00	8.00	4	60	128	639	4,790	ppm									
414	411	Carbon tetrachloride	56-23-5	CBY000	3.10	2.00	5.00	8.00	4	60	277	1,190	3,270	ppm									



Changing Chloroform PACs

- On HCN-TEEL sheet

1 2 3	A	B	C	D	E F G H Health code Numbers (04) [Revisions]				O	P Q R S TEEL Level 20 (mg/m ³)				T
	No.	Chemical Name	CASRN	SAX number	HCN-1	HCN-2	HCN-3	HCN-4	Category	TEEL-0	TEEL-1	TEEL-2	TEEL-3	Units of original limits
485	482	Chloroform	67-66-3	CHJ500	2.00	3.10	3.09	8.00	4	10	10	248	24,800	ppm



485	482	Chloroform	67-66-3	CHJ500	2.00	3.10	3.09	8.00	4	10	10	312	15,600	ppm
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Chlorophenol PACs

- On HCN-TEEL sheet

A	B	C	D	E	F	G	H	I	J	K	L	M
No.	Chemical Name	CASRN	SAX number	Health code (04)		Category	TEELs Rev 20 (mg/m ³)				Units of original limits	
				HCN-1	HCN-2		TEEL-0	TEEL-1	TEEL-2	TEEL-3		
494	Chlorophenol, o-	95-57-8	CJK250	4.00	5.00	4	2	6	40	300	ppm	



“Plausible” Scenario

- **Stored together in drums in warehouse**
- **Explosion from “plausible” source**
 - Propels drums laterally through walls
- **Drums & building walls breached**
 - Mixture released to outside environment
- **Chemicals not “transformed” by explosion**



Source Term: General Equation

- **$ST = MAR \times ARF \times RF \times DR \times LPF$**

- **ST = Source Term**

- **MAR = Material at Risk**

- **ARF = Airborne Release Fraction**

- **RF = Respirable Fraction**

- **DR = Damage Ratio**

- **LPF = Leak Path Factor**



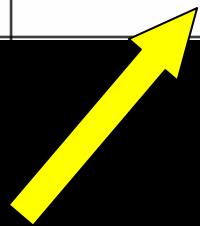
Source Term: BEFORE

- **ST = MAR x ARF x RF x DR x LPF**
 - MAR (Material at Risk)
 - 100 drums of each chemical = 300 drums total
 - 55 gallons / drum
 - ARF, RF, LPF = 1 (vapor)
 - DR = 0.9 → 90% of all drums breached
- **ST = 0.9 MAR = 90 drums of each chemical**
- **ST_{CT} = 4950 gallons**
- **ST_{CF} = 4950 gallons**
- **ST_{CP} = 4950 gallons**



CMM—Input Sheet

A	B	C	D	E	F
No.	Chemical Compound	CASRN	Receptor Point (RP)	Conc. Limit (Li) at Receptor Point.	Conc. (Ci) at Receptor Point (mg/m3)
1	Carbon tetrachloride	56-23-5	Site Boundary 0.5 mi	TEEL-2	
2	Chloroform	67-66-3	Site Boundary 0.5 mi	TEEL-2	
3	2-Chlorophenol	95-57-8	Site Boundary 0.5 mi	TEEL-2	



Input /
 Import /
 HIs by mode /
 HIs by target organ /
 Output /
 HCN-TEEL /



Concentration at Distance—ALOHA 5.4

Carbon Tetrachloride (Before)



ALOHA 5.4

File Edit SiteData SetUp Display Sharing Help

THREAT ZONE:

Model Run: Heavy Gas

Red : 505 yards --- (3270 mg/(cu m)) **AEGL-3**

Orange: 827 yards --- (1190 mg/(cu m)) **AEGL-2**

Yellow: 1754 yards --- (277 mg/(cu m)) **AEGL-1**

THREAT AT POINT:

Concentration Estimates at the point:

Downwind: **880 yards** Off Centerline: 0 yards

Max Concentration:

Outdoor: 1,060 mg/(cu m)

Indoor: 154 mg/(cu m)



Concentration at Distance—ALOHA 5.4

Chloroform (Before)



ALOHA 5.4

File Edit SiteData SetUp Display Sharing Help

THREAT ZONE:

Model Run: Heavy Gas

Red : 322 yards --- (15,600 mg/(cu m))

Orange: 1.1 miles --- (312 mg/(cu m))

Yellow: greater than 6 miles --- (10 mg/(cu m))

AEGL-3

AEGL-2

TEEL-1

THREAT AT POINT:

Concentration Estimates at the point:

Downwind: 880 yards

Off Centerline: 0 yards

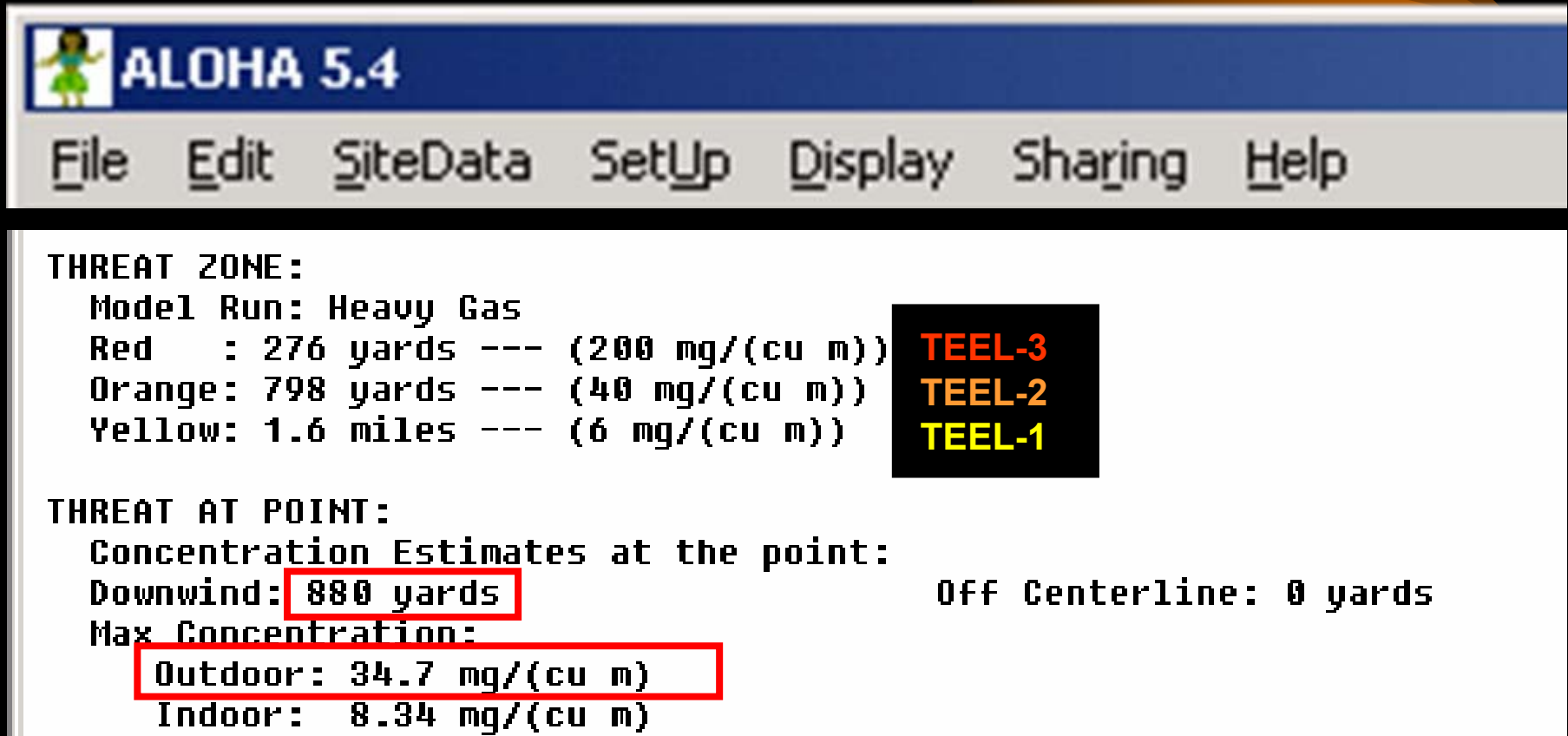
Max Concentration:

Outdoor: 1,530 mg/(cu m)

Indoor: 245 mg/(cu m)



Concentration at Distance—ALOHA 5.4 Chlorophenol (Before)



ALOHA 5.4

File Edit SiteData SetUp Display Sharing Help

THREAT ZONE:
Model Run: Heavy Gas

Red	: 276 yards --- (200 mg/(cu m))	TEEL-3
Orange	: 798 yards --- (40 mg/(cu m))	TEEL-2
Yellow	: 1.6 miles --- (6 mg/(cu m))	TEEL-1

THREAT AT POINT:
Concentration Estimates at the point:
Downwind: 880 yards Off Centerline: 0 yards
Max Concentration:
Outdoor: 34.7 mg/(cu m)
Indoor: 8.34 mg/(cu m)

CMM Input Sheet (Before)— Concentrations at Receptor Point

A	B	C	D	E	F
No.	Chemical Compound	CASRN	Receptor Point (RP)	Conc. Limit (Li) at Receptor Point.	Conc. (Ci) at Receptor Point (mg/m3)
1	Carbon tetrachloride	56-23-5	Site Boundary 0.5 mi	TEEL-2	1060
2	Chloroform	67-66-3	Site Boundary 0.5 mi	TEEL-2	1530
3	2-Chlorophenol	95-57-8	Site Boundary 0.5 mi	TEEL-2	34.7



Input
 Import
 HIs by mode
 HIs by target organ
 Output
 HCN-TEEL



Execute CMM Macros

- **PC→**

“Control” & “=” together OR “F9”

- **Mac→**

“Apple” or “Command” & “=” together



CMM Results (Before)— Lower & Upper Bound

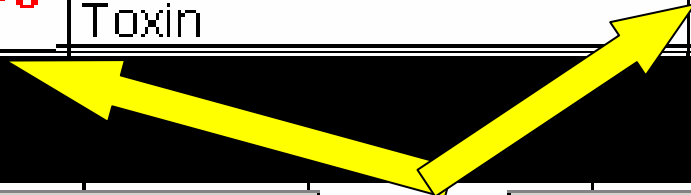
A	B	C	D	E
No.	Chemicals in mixture	Chemical CASRN	Individual Hazard Index (HI)	Sum of all HIs
1	Carbon tetrachloride	56-23-5	0.891	<div style="background-color: blue; color: green; padding: 5px; display: inline-block;">Upper Bound</div> <div style="background-color: blue; color: yellow; padding: 5px; display: inline-block;">Lower Bound</div>
2	Chloroform	67-66-3	4.904	
3	2-Chlorophenol	95-57-8	0.868	
4				


 Input / Import / HIs by mode / HIs by target organ / **Output** / HCN-TEEL



CMM Results (Before) —HCN “Binning”

G	H	I	J
Toxic Mode or Endpoint-specific HIs		Sum of Organ-specific HIs	
Mode or Endpoint	HI sum ≥ 0.25	Organ	HI sum ≥ 0.25
HCN = 1 or 2 Carcinogens	5.79E+0	HCN = 1, 1.01, 2 or 2.01 Bladder Cancer	5.79E+0
		HCN = 1, 1.02, 2 or 2.02 Liver Cancer	5.79E+0
HCN = 3 Chronic Systemic Toxins	5.79E+0		
HCN = 4 Acute Systemic Toxins	8.68E-1		
HCN = 5 Reproductive Toxins	1.76E+0	HCN = 3.09 or 3 Kidney Toxin	4.90E+0
HCN = 8 Narcotics	5.79E+0	HCN = 3.10 or 3 Liver Toxin	5.79E+0



Results Summary (Before)

- Upper Bound—Sum of ALL HIs
 - 6.7—Over conservative
- HCN Binning
 - 5.8—Realistic yet Conservative
- Lower Bound—Individual HIs
 - 4.9, 0.9, 0.9—Non-conservative



Mitigation Options

- Chemical Substitution
- Inventory Reduction
- Engineering Controls
- Administrative Controls
- **OUR CHOICE** → **Inventory Reduction**
 - **Goal: “After” results—be at PAC (HI \approx 1.00)**



CMM Results (Before)— Lower & Upper Bound

A	B	C	D	E
No.	Chemicals in mixture	Chemical CASRN	Individual Hazard Index (HI)	Sum of all HIs
1	Carbon tetrachloride	56-23-5	0.891	<div style="background-color: blue; color: green; padding: 5px; display: inline-block;">Upper Bound</div> <div style="background-color: blue; color: yellow; padding: 5px; display: inline-block;">Lower Bound</div>
2	Chloroform	67-66-3	4.904	
3	2-Chlorophenol	95-57-8	0.868	
4				



Inventory Reduction—

Carbon Tetrachloride Chlorophenol

- **ST → Cut to ONE-QUARTER**
 - 90 dr released (0.25) = 22.5 dr released
 - DR = 0.9
 - 0.9 (**x dr-inv**) = 22.5 dr-rel
 - **x = 22.5/0.9 = 25 dr-inv**
- **Inventory (MAR): 100 dr → 25 dr**



Inventory Reduction—

Chloroform

- **ST → Cut to ONE-TENTH**
 - 90 dr released (0.1) = 9 dr released
 - DR = 0.9
 - 0.9 (**x dr-inv**) = 9 dr-rel
 - **x = 9/0.9 = 10 dr-inv**
- **Inventory (MAR): 100 dr → 10 dr**



Source Term: AFTER

- **ST = MAR x ARF x RF x DR x LPF**
 - MAR
 - 25 drums—Carbon Tetrachloride
 - 10 drums—Chloroform
 - 25 drums—Chlorophenol
 - ARF, RF, LPF = 1 (vapor)
 - DR = 0.9 → 90% of all drums breached
- **ST = 0.9 MAR**
- **ST_{CT} = 1235 gal** [was 4950 gal]
- **ST_{CF} = 495 gal** [was 4950 gal]
- **ST_{CP} = 1235 gal** [was 4950 gal]



Concentration at Distance—ALOHA 5.4

Carbon Tetrachloride (After)



ALOHA 5.4

File Edit SiteData SetUp Display Sharing Help

THREAT ZONE:

Model Run: Heavy Gas

Red	: 266 yards ---	(3270 mg/(cu m))	AEGL-3
Orange	: 433 yards ---	(1190 mg/(cu m))	AEGL-2
Yellow	: 954 yards ---	(277 mg/(cu m))	AEGL-1

THREAT AT POINT:

Concentration Estimates at the point:

Downwind **880 yards** Off Centerline: 0 yards

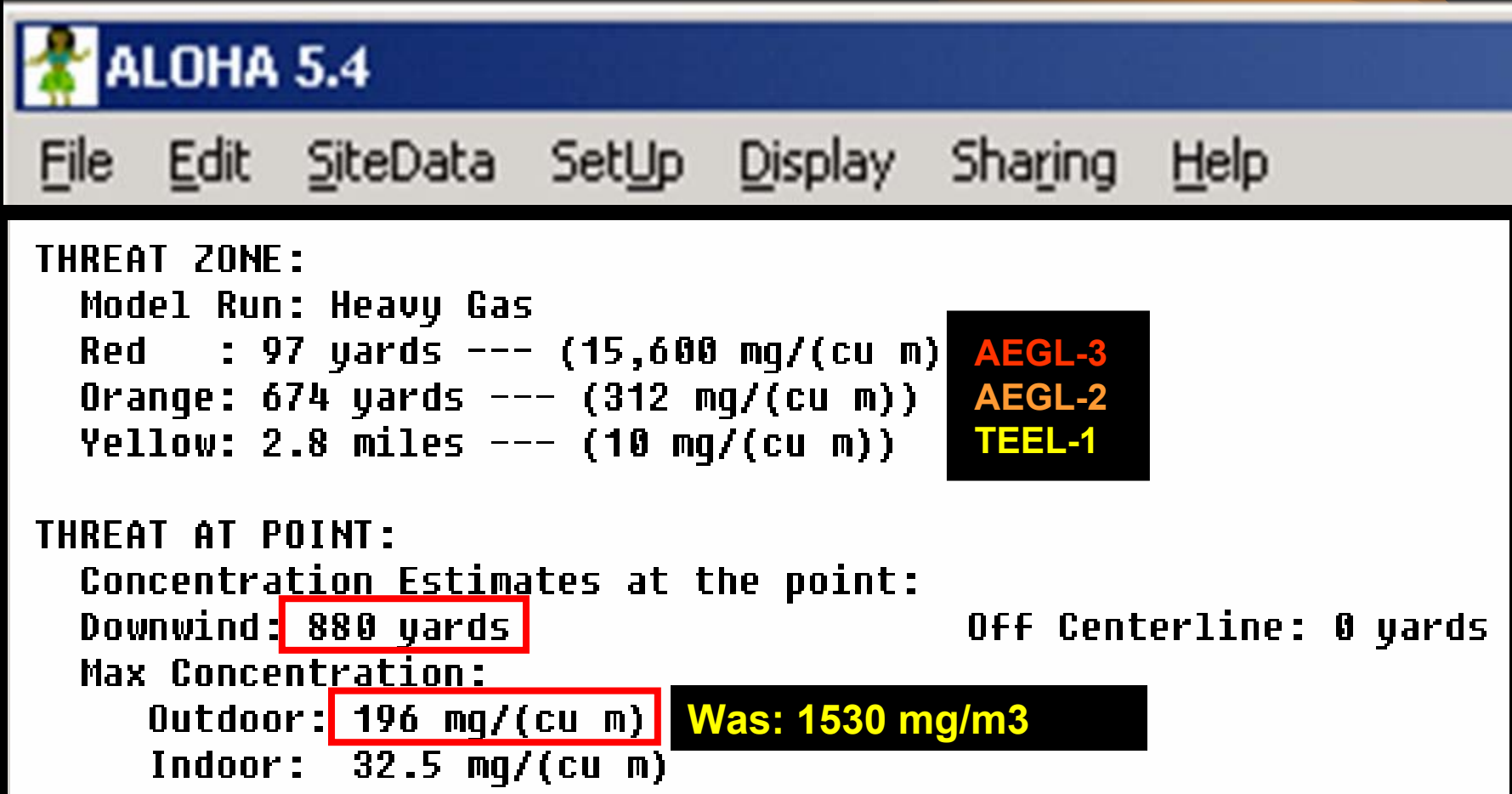
Max Concentration:

Outdoor: 322 mg/(cu m) **Was: 1060 mg/m3**

Indoor: 48.1 mg/(cu m)



Concentration at Distance—ALOHA 5.4 Chloroform (After)



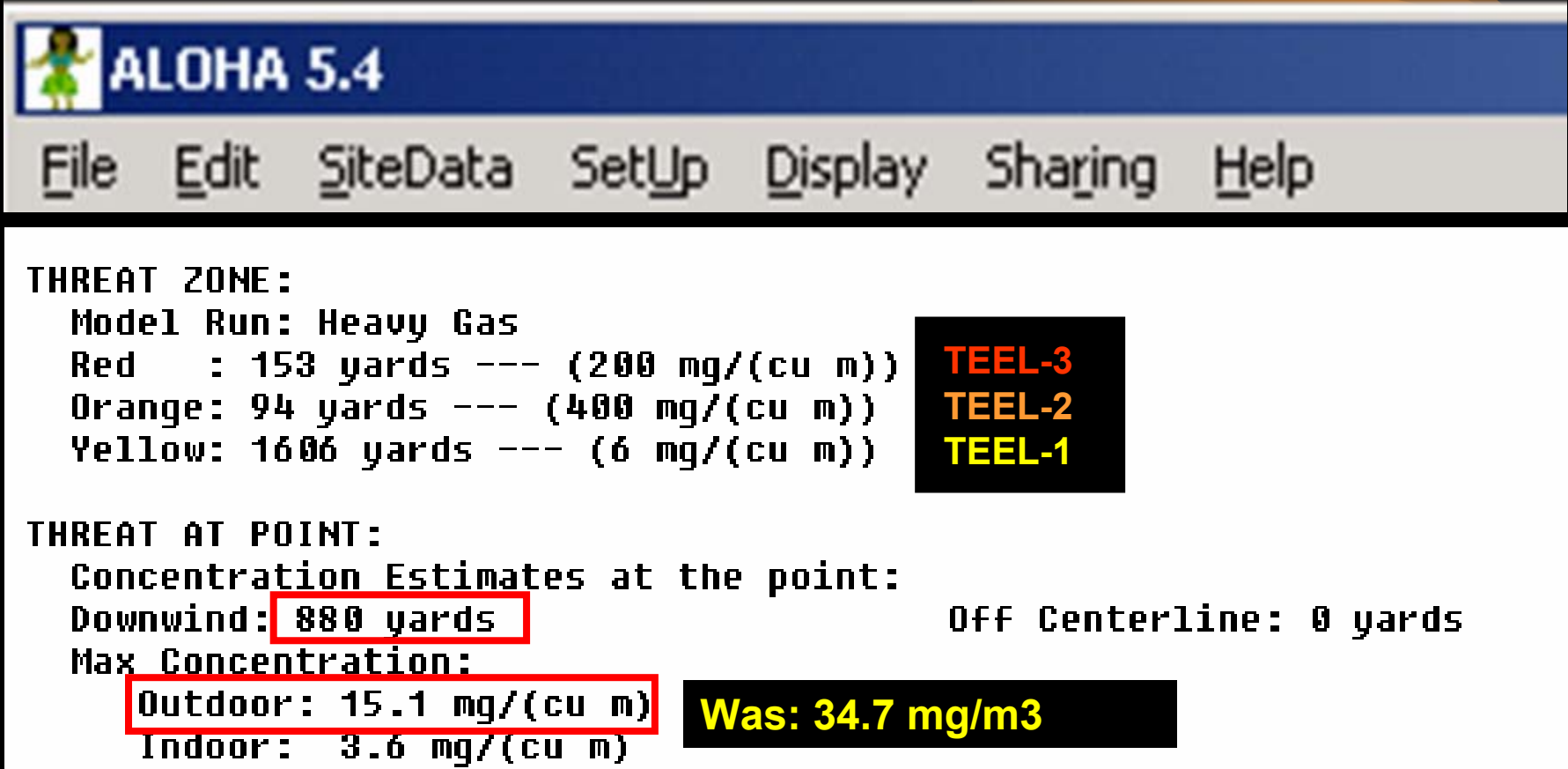
ALOHA 5.4

File Edit SiteData SetUp Display Sharing Help

THREAT ZONE:
Model Run: Heavy Gas
Red : 97 yards --- (15,600 mg/(cu m) **AEGL-3**
Orange: 674 yards --- (312 mg/(cu m) **AEGL-2**
Yellow: 2.8 miles --- (10 mg/(cu m) **TEEL-1**

THREAT AT POINT:
Concentration Estimates at the point:
Downwind: **880 yards** Off Centerline: 0 yards
Max Concentration:
Outdoor: **196 mg/(cu m)** **Was: 1530 mg/m3**
Indoor: 32.5 mg/(cu m)

Concentration at Distance—ALOHA 5.4 Chlorophenol (After)



ALOHA 5.4

File Edit SiteData SetUp Display Sharing Help

THREAT ZONE:
Model Run: Heavy Gas

Red	: 153 yards --- (200 mg/(cu m))	TEEL-3
Orange	: 94 yards --- (400 mg/(cu m))	TEEL-2
Yellow	: 1606 yards --- (6 mg/(cu m))	TEEL-1

THREAT AT POINT:
Concentration Estimates at the point:
Downwind: **880 yards** Off Centerline: 0 yards
Max Concentration:
Outdoor: 15.1 mg/(cu m) **Was: 34.7 mg/m3**
Indoor: 3.6 mg/(cu m)



CMM Input Sheet (After)— Concentrations at Receptor Point

A	B	C	D	E	F
No.	Chemical Compound	CASRN	Receptor Point (RP)	Conc. Limit (Li) at Receptor Point.	Conc. (Ci) at Receptor Point (mg/m ³)
1	Carbon tetrachloride	56-23-5	Site Boundary 0.5 mi	TEEL-2	322
2	Chloroform	67-66-3	Site Boundary 0.5 mi	TEEL-2	196
3	Chlorophenol, 2-	95-57-8	Site Boundary 0.5 mi	TEEL-2	15.1

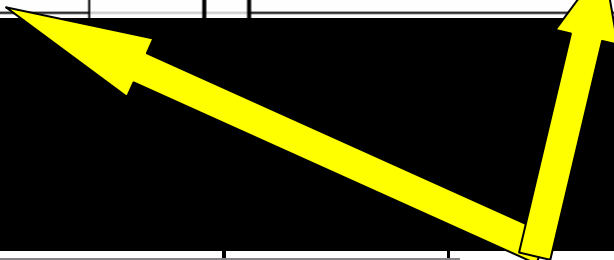


Input /
 Import /
 HIs by mode /
 HIs by target organ /
 Output /
 HCN-TEEL /



CMM Results (After)

A	B	C	D	E	F	G	H	I	J
No.	Chemicals in mixture	Chemical CASRN	Individual Hazard Index (HI)	Sum of all HIs	Toxic Mode or Endpoint-specific HIs		Sum of Organ-specific HIs		
					Mode or Endpoint	HI sum >= 0.25	Organ	HI sum >= 0.25	
1	Carbon tetrachloride	56-23-5	0.271	1.28E+0	HCN = 1 or 2 Carcinogens	8.99E-1	HCN = 1, 1.01, 2 or 2.01 Bladder Cancer	8.99E-1	
2	Chloroform	67-66-3	0.628		HCN = 1, 1.02, 2 or 2.02 Liver Cancer	8.99E-1			
3	Chlorophenol, 2-	95-57-8	0.378		HCN = 3 Chronic Systemic Toxins	8.99E-1			
4					HCN = 4 Acute Systemic Toxins	3.78E-1			
5					HCN = 5 Repro-ductive Toxins	6.48E-1	HCN = 3.09 or 3 Kidney Toxin	6.28E-1	
8					HCN = 8 Narco-tics	8.99E-1	HCN = 3.10 or 3 Liver Toxin	8.99E-1	

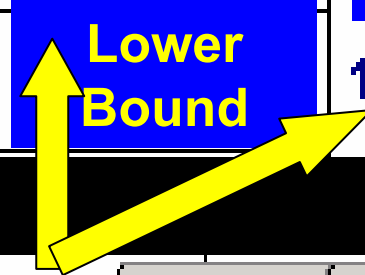


Input	Import	HIs by mode	HIs by target organ	Output	HCN-TEEL
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CMM Results (After)— Lower & Upper Bound

A	B	C	D	E
No.	Chemicals in mixture	Chemical CASRN	Individual Hazard Index (HI)	Sum of all HIs
1	Carbon tetrachloride	56-23-5	0.271	
2	Chloroform	67-66-3	0.628	
3	Chlorophenol, 2-	95-57-8	0.378	Upper Bound
4			Lower Bound	1.28E+0



CMM Results (After) —HCN “Binning”

G	H	I	J
Toxic Mode or Endpoint-specific HIs		Sum of Organ-specific HIs	
Mode or Endpoint	HI sum >= 0.25	Organ	HI sum >= 0.25
HCN = 1 or 2 Carcinogens	8.99E-1	HCN = 1, 1.01, 2 or 2.01 Bladder Cancer	8.99E-1
		HCN = 1, 1.02, 2 or 2.02 Liver Cancer	8.99E-1
HCN = 3 Chronic Systemic Toxins	8.99E-1		
HCN = 4 Acute Systemic Toxins	3.78E-1		
HCN = 5 Repro-ductive Toxins	6.48E-1	HCN = 3.09 or 3 Kidney Toxin	6.28E-1
HCN = 8 Narco-tics	8.99E-1	HCN = 3.10 or 3 Liver Toxin	8.99E-1



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Input /
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