Estimating Emissions of Toxic Industrial Chemicals (TICs) Released as a Result of Accidents or Sabotage

Steven R. Hanna (Hanna Consultants), Gene Lee (Baker Engineering and Risk Consultants, Inc.), David Belonger (Center for Chemical Process Safety for the American Institute of Chemical Engineers), Peter J. Drivas (Drivas Consultants), Rex Britter (University of Cambridge), and Olav Hansen (GexCon A.S., Bergen, Norway)

shanna@hsph.harvard.edu

January 10, 2007

Presented at
CBIS Conference, Austin, TX

P081 Hanna CBIS TIC

Outline

- Matrix of Highest-Priority Toxic Industrial Chemicals (TICs) and Source Scenarios
- Example of Chlorine Railcar Scenario and Emergency Response Guidelines
- Review of Source Emission Formulas and Models in Use and Recommendation of Specific Formulas
- Review of Field Experiments and Identification of Data Gaps where New Experiments are Needed

Matrix of Toxic Industrial Chemicals (TICs) and Source Scenarios

The goal is to determine the most dangerous Toxic Industrial Chemicals (TICs) and source scenarios, with focus on transportation scenarios

This task was mainly carried out by the CCPS/AIChE team, led by Dave Belonger

The main product is a table with rankings of the “top 13” TICs

CAS	Chemical		ERPG 3 ppm	Relative Volume Chlorine = 100	Vapor Pressure mmHg	Toxicity Factor (4)	Hazard Index (7)
			By Rail on CSX Line				
7782-50-5	Chlorine	Bulk	20	100	5168	3.40	340.0
7446-09-5	Sulfur dioxide	Bulk	15	5	2475	2.17	10.9
7664-41-7	Ammonia (anhydrous)	Bulk	750	25	6660	0.12	2.9
			By Truck				
7782-50-5	Chlorine	Cylinders (2)	20	100	5168	3.40	340.0
7664-41-7	Ammonia (anhydrous)	Cylinders (2)	750	800	6660	0.12	93.5
7446-09-5	Sulfur dioxide	Cylinders (2)	15	10	2475	2.17	21.7
7647-01-0	Hydrogen chloride anhydrous	Bulk	150	3	31700	2.78	7.8
75-44-5	Phosgene	Cylinders	1	0.3	1215	15.99	4.8
7726-95-6	Bromine	Bulk	5	8	175	0.46	3.9
107-02-8	Acrolein (6)	Bulk (1)	3	2	210	0.92	1.8
74-90-8	Hydrogen cyanide	Cylinders(2)	25	5	630	0.33	1.5
7790-91-2	Chlorine trifluoride (5), (6)	Cylinders	10	2	346	0.46	0.9
79-22-1	Methyl chloroformate (6)	Bulk	4	2	105	0.35	0.7
8014-95-7	Oleum 65% SO_3 (8) (9)	Bulk	160	35	220	0.02	0.6
7664-39-3	Hydrogen fluoride	Cylinders (2)	50	2	816	0.21	0.5
7719-12-2	Phosphorus trichloride (6)	Bulk	15	2	100	0.09	0.2

(1)Bulk packs up to 5000 gallons

(2) Also in bulk trucks

(3) Bulk trucks normally 5000 gallons for liquids

(4) (Vapor pressure in mmHg) x 10 / (ERPG 3 as ppm) x 760 mmHg

(5) Not on RPM list

(6) Estimated shipping volume equivalent to Hydrogen Fluoride 4.6

Highest-Priority TICs

- Top three (rail and truck) for transportation are chlorine, sulfur dioxide, and ammonia (anhydrous) – all are stored and shipped as pressurized liquified gases and have low boiling points
- Others in this group are chlorine trifluoride, hydrogen chloride (anhydrous), hydrogen fluoride, and phosgene
- Others that are liquids at ambient pressure are acrolein, bromine, hydrogen cyanide, and methyl chloroformate
- Two fuming liquids – oleum (65 % sulfur trioxide) and phosphorus trichloride

Flammables of Concern

- Propane (most prevalent)
- Butadiene (involved in several big accidents)
- Hydrogen
- Ethylene oxide
- Propylene oxide

Note shallow yellow chlorine cloud

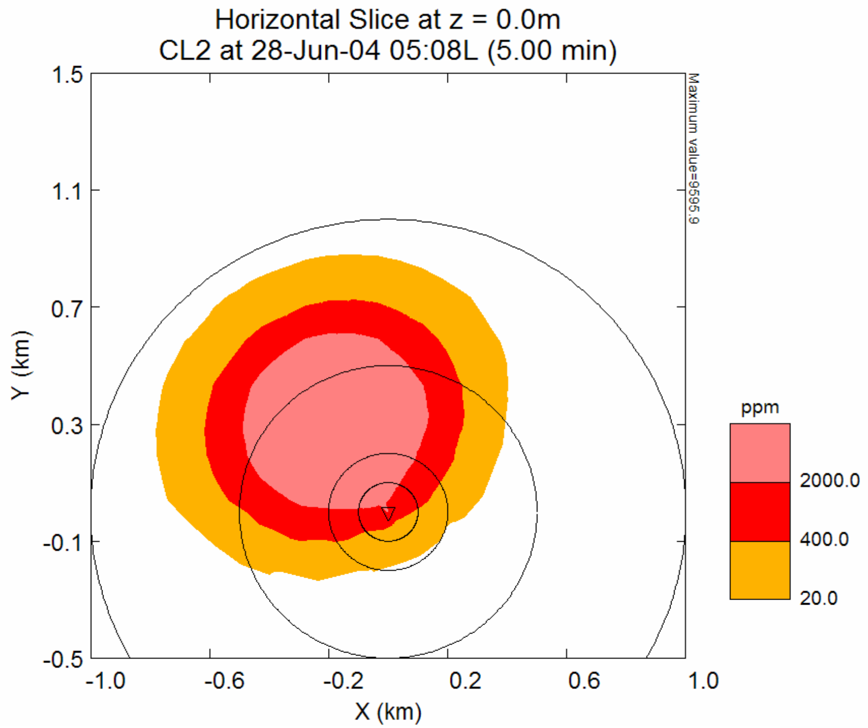
Festus, Mo

Source: US Chemical Safety and Hazard Investigation Board

Macdona, TX

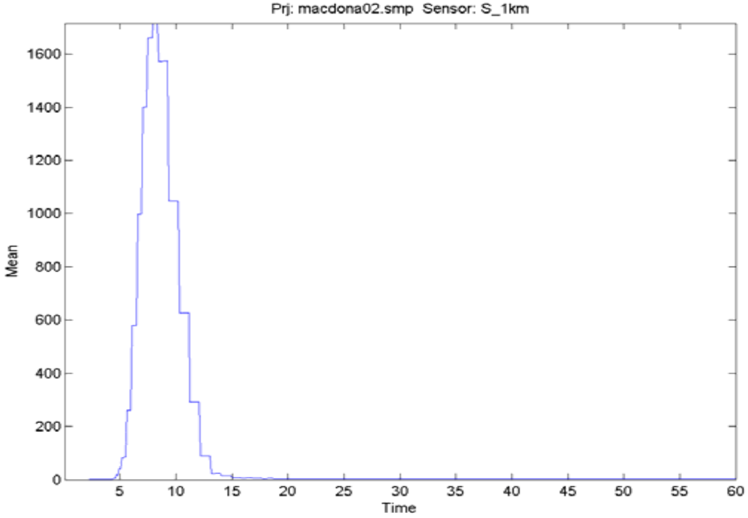
Photos of Graniteville, SC, Train Wreck

Photos Courtesy of Augusta Chronicle



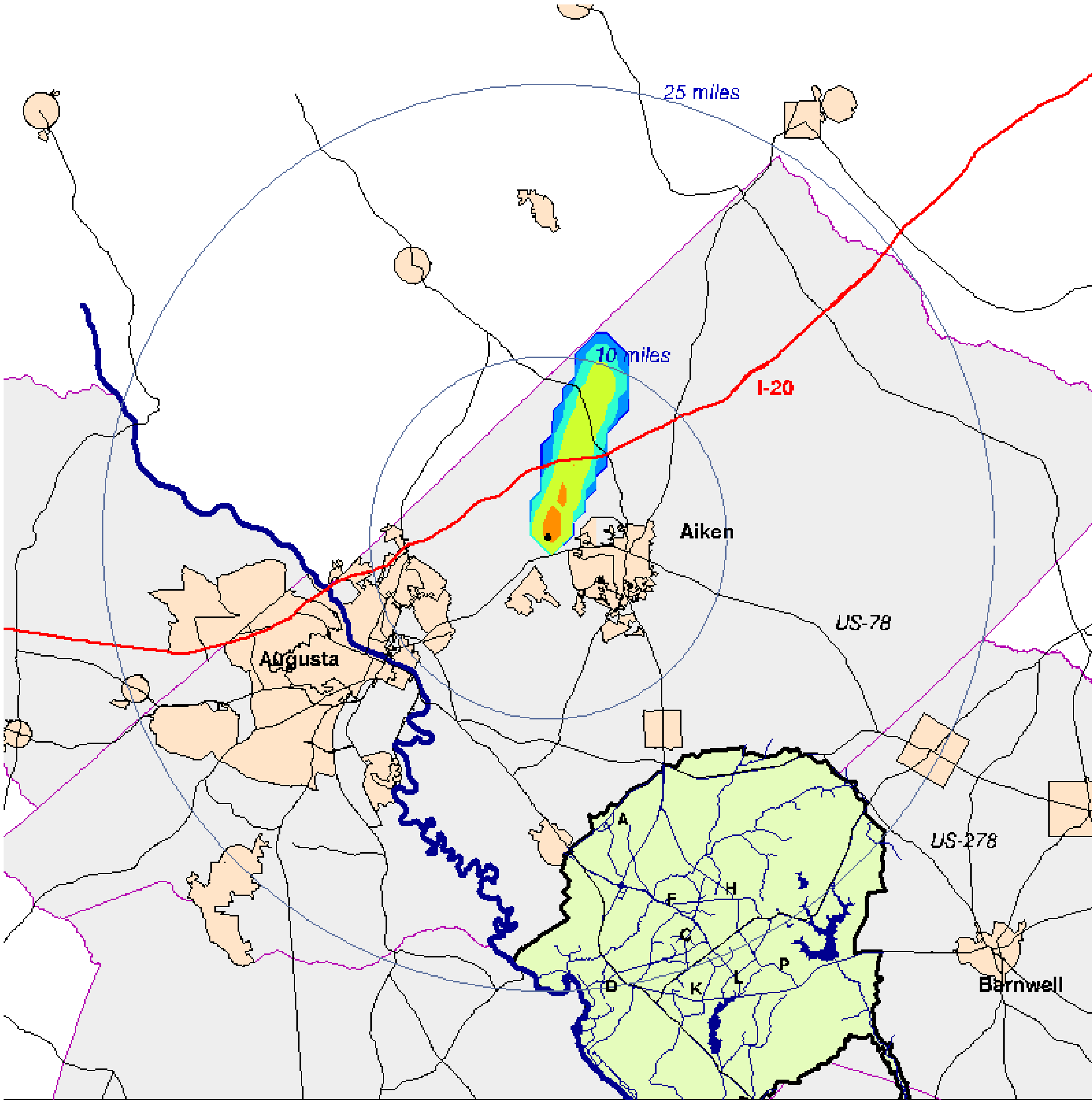
SCIPUFF OUTPUTS FOR MACDONA

CONTOURS AT 5 MINUTES AFTER RELEASE



CONCENTRATION TIME SERIES AT X = 1 KM

Graniteville, SC, initial plume predictions by Savannah River Lab model (no dense gas effects)



WINDS: SRNL
(LPDM)

Release Time:
2005-01-06-0800Z

Forecast Time:
2005-01-06-0900Z

LAT – 33.572 N: LON – -81.797 E

Surface Concentration
Unit Release

Colors Denote Orders of Magnitude

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

Six Models Applied to Three Railcar Accidents

- SCIPUFF, SLAB, HGSYSTEM, ALOHA, TRACE, PHAST
- Models generally agree within a factor of two on plume parameters, assuming all are given the same source
- Max concentrations as a function of downwind distance
- Max distance to 20, 400, 2000 ppm
- Width and depth of plume to 20, 400, 2000 ppm
- For large releases (Macdona and Graniteville), the simulated cloud is 40 times as wide as it is deep, due to dense gas effects

Emergency Response Guidance based on Experiences with Recent Railcar Accidents

- Assume that a significant fraction of the railcar contents is released (in the range from about 10 to 90 tons).
- A dense cloud is formed that consists of a mixture of gas and small aerosol drops. The drops soon evaporate. The gas cloud is visible (see the photo of Festus).
- The dense cloud initially spreads in all directions (even upwind) due to dense gas slumping and will follow terrain slopes.
- The dense cloud is shallow (1 or 2 m deep) and is much broader than passive clouds.
- After a few 100 meters of travel, the cloud starts behaving more like a passive (neutral) plume. The distance is larger for releases from large holes, such as Graniteville.

Emergency Guidance, Continued

- Pockets of toxic gas can remain for a while in low-lying areas and behind buildings Persons who are outside should stay away from low-lying areas
- Usually, after the initial large emission rate lasting an hour or more, there is a smaller emission rate that lasts for several hours, or until the hole is plugged
- Because of the shallow nature of the dense cloud, persons in buildings near the release location should shelter in place in the upper stories of the buildings
- HVAC inlets on the first floor should be shut off
- Persons should realize that the cloud will be very broad in area

Review of Source Emissions Formulas and Models and Recommendations

Started with AIChE/CCPS 1996 Guidelines Book by Hanna, Drivas, and Chang

Added more recent papers and books and experience

Three main categories:

- Evaporation from liquid pool
- Gas jets
- Two phase jets from pressurized liquified gas

Most releases are time-variable and finite duration (i.e., the tank empties)

The two-phase category is the highest priority but is the most poorly-known

Need for a Thermodynamic Package

- The user has to be able to determine if the TIC is a gas or liquid and properties such as temperature and density when it is at ambient pressure
- Several software packages are available from the chemical industries and govt agencies
- A thermodynamics software package from NIST is recommended

Simple basic equations are valid for some types of releases, such as a pressurized ideal gas released through a simple small opening in the tank

If this choked flow condition is met, for an ideal gas exiting through an orifice under isentropic conditions, the gas emission rate will follow the critical flow relationship (Perry *et al.*, 1984), which is independent of downstream pressure:

$$Q = c_o A_h \left(\gamma \rho_p p \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma + 1}{\gamma - 1}} \right)^{1/2} \quad (4\text{-}2)$$

where

- Q = time-dependent gas mass emission rate (kg s-1)
- c_o = discharge coefficient for orifice (dimensionless)
- A_h = puncture area (m2)
- ρ_p = gas density in tank (kg m-3)
- γ = c_p/c_v (ratio of specific heats for gas)

Flashing is important for pressurized liquified gases such as Cl_2. When the liquid is released, a fraction of it becomes a gas and the following formula can be used to calculate the fraction

For a single component and a constant temperature, this heat balance yields a simple expression for the fraction of liquid flashed:

$$\frac{Q_f}{Q_l} = \frac{c_p (T - T_b)}{H_{vap}} \qquad (4\text{-}14)$$

where

Q_f = mass emission rate of liquid that flashes (kg s^{-1})
Q_l = total liquid mass emission rate (kg s^{-1})
c_p = heat capacity of the liquid (averaged between T and T_b) (J kg^{-1} K^{-1})
T = temperature of the liquid in the tank (K)
T_b = normal boiling point of liquid (K), assumed lower than T
H_{vap} = heat of vaporization of the liquid (J kg^{-1})

A big question is whether the unflashed liquid (85 % of the total mass for Cl_2) forms a pool on the ground or remains in the air as small drops

Task 3 – Survey of related field experiments and recommendations of new experiments to fill data gaps

- A comprehensive list of 35 field experiments was tabulated, including overviews of the details of each experiment. To identify critical gaps, the characteristics of each experiment were compared. This material has been taken, with permission, from the Joint Effects Model (JEM) field experiment survey and gap analysis report.

- Beginning with the above list, a subset of field experiments were identified that involved source emissions issues (such as the Desert Tortoise anhydrous ammonia tests).

- Additional recent field experiments that focused on two phase releases were summarized. These include the FLADIS, URAHFREP, FLIE, and RELEASE experiments.

- Data gaps were identified and recommendations made for future field experiments The highest priority data need concerns two phase releases (of pressurized liquid gases such as chlorine, anhydrous ammonia, and sulfur dioxide) from typical railcar and tank truck scenarios.

CCPS/AIChE Sponsored Field Experiments with Releases of Pressurized Liquified Gases

Table 6-3 Characteristics of CCPS/AIChE Releases of Chlorine, Methylamine, and Cyclohexane at Nevada Test Site

	Chlorine	Methylamine	Cyclohexane
Number of tests	22	18	22
Boiling point, K	236	254	338
Temperature, K	245-289	270-296	338-398
Liquid superheat, K	9-53	6-31	0-48
Pressure, psia	21-142	171-560	140-556
Orifice diameter. mm	6.35	6.35	6.35-12.7

Conclusions

- Highest-priority releases are chlorine, sulfur dioxide, and ammonia (anhydrous)
- These lead to dense clouds that are shallow and wide
- Source emissions models are least-developed for this category of release
- Field data gaps exist, especially for large two-phase releases