

## GAPS IN TOXIC INDUSTRIAL CHEMICAL (TIC) MODEL SYSTEMS

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**Abstract:** There are concerns regarding the hazards to the public due to the releases of toxic industrial chemicals (TICs) to the atmosphere as a result of accidents or intentional acts. For recent chlorine railcar accidents, where 30 to 60 tons of pressurized liquefied chlorine were released in rural areas, the number of casualties estimated by several widely-used model systems far exceeded the number of casualties observed, raising concerns by decision makers about the accuracy of the model systems. The comprehensive model system consists of a scenario definition, a source emission model, a transport and dispersion model, an exposure model, and a health risk model. A few of the deficiencies or gaps in the model system are summarized in this paper, including 1) incomplete knowledge of the scenario, 2) uncertainties in the state-of-the-art of source emission models, 3) inadequate transport and dispersion models, 4) limitations of knowledge concerning the population and their movement, and 5) biases and uncertainties in health risk models.

**Key words:** *Hazardous gas dispersion; dense gas dispersion; Toxic industrial chemical dispersion; chlorine releases from railcars; dry deposition; chemical removal of chlorine.*

### 1. INTRODUCTION

A primary scenario of concern to the U.S. Department of Homeland Security (DHS) and the U.S. Defense Threat Reduction Agency (DTRA) is a release to the atmosphere of pressurized liquefied gas from an industrial site or a railcar. The recent paper by Hanna et al. (2008a) compares the predictions of six widely-used dense gas models for Toxic Industrial Chemicals (TICs) for three recent chlorine railcar accidents (Festus, Missouri; Macdona, Texas; and Graniteville, South Carolina). For example, about 50 tons of chlorine were released in a few minutes in the Macdona and Graniteville accidents, where the jagged hole had an effective diameter of about 10 to 20 cm. At Graniteville, most was thought to have been released as a two-phase jet in the first minute. There were no on-site observations, so the emissions estimates and the behavior of the cloud are based on limited anecdotes. Figure 1 shows the predicted maximum plume centerline concentrations for the six models as a function of distance for Graniteville. The predicted 10-minute average chlorine concentrations all exceed 2000 ppm at a distance of 1 km and exceed 20 ppm at a distance of 10 km. According to the health standards for chlorine, this would imply that everyone within 1 km would be a fatality and within 10 km would have health effects of some sort. But at the Festus, Macdona, and Graniteville sites, the only fatalities were very close (within 100 m) to the source. This has led some persons to say that “the models are wrong, with large overpredictions”. Because the accidents were in rural areas and the release lasted only a few minutes, there are no on-site observations of chlorine concentrations. The current paper addresses several aspects of this problem and shows how a properly constructed complete model system might be more realistic.

The model runs by Hanna et al. (2008a) used a prescribed source emissions rate for each location, as determined by the on-site observations (e.g., X kg of chlorine was released in Y seconds, with an initial known tank pressure and temperature, and known ambient conditions), and confirmed by some calculations using current models for two-phase jets. The “models” that were run were standard dense gas transport and dispersion models, which do not account for complex terrain effects or for removal by chemical reactions or deposition. Finally the assumed relations between concentrations and health effects are based by expert committee recommendations and the degree of conservatism is not well agreed-upon.

### 2. DEFINITIONS OF SCENARIOS

The accuracy of any model system depends on the accuracy of the inputs. But of course in any real emergency associated with an accident or terrorist activity, there will never be good input information available. For example, at Macdona, the emergency responders did not even realize that there was a chlorine release until they arrived on the scene, and, once at the scene, could not get close enough to the railcar to tell where the hole was or its size. The nearest meteorological site is likely to be an airport over 50 km or 100 km away. Local terrain details such as drainage ditch locations and surrounding hills are not available immediately. In the months after each accident, there has been much analysis and modelling carried out, and there are still uncertainties about many conditions such as the temperature of the contents of the railcar. Thus it is recommended to model a range of possible scenarios in order to capture the range of possible outputs.

When defining scenarios, it is difficult to decide what will be the worst case before-hand. This is especially true for dense gas releases, which will characterize most TIC releases. Also, as happened at Macdona and Graniteville, the release may be of short duration and therefore behaves more like an “instantaneous puff” than a “continuous plume”. In this case the usual worst case assumption of “light-wind stable conditions” may not be valid. We tested this sensitivity for a Chicago hypothetical chlorine railcar release scenario (Hanna et al. 2008b and c). For that assumed release of about 200 kgs<sup>-1</sup> for a duration of 300 sec, and for standard models such as SCIPUFF and SLAB calculating the 10 min averaged concentration, it was found that there was little dependence on wind speed of the maximum

concentration as a function of downwind distance, even down to speeds of  $0.25 \text{ ms}^{-1}$ . This is because, for very light winds, the dense gas plume is calculated to “pancake”, spreading out in all directions and not moving downwind significantly. For higher wind speeds, the plume moves downwind as a narrower plume, even though it is moving faster.

### 3. SOURCE TERMS

The source term refers to the part of the model that calculates the magnitude and duration of the TIC release, as well as its physical and chemical properties. For high priority TICs that are stored as pressurized liquefied gases, the estimation of the source term is well-recognized as one of the more difficult problems in fluid dynamics. This is due to many factors, such as the possibility of two-phases forming in the storage tank, at the hole, and/or just outside of the hole. Furthermore, drop sizes must be estimated in order to know how much of the liquid phase will “rain-out”. Even for simple geometric shapes such as perfectly circular hole, this calculation is difficult. Some TIC models can make this calculation (e.g., PHAST, Witlox and Holt, 1999; HPAC, DTRA 2008) but there is still much uncertainty (see Hanna and Britter, 2008d, for a review of the main issues).

For releases from pressurized containers, there will be a high-velocity jet that needs to be modelled. This provides the transition from the source model to the transport and dispersion model. Initially, there is a region where the jet’s pressure is decreasing to ambient values, and this region is usually handled by the source model. But the theories assume no obstructions in the area of the source, other than a flat ground surface, whereas any real site will have obstacles nearby such as buildings, other railcars, trees, etc. Work is underway on parameterizing jets striking obstacles.

### 4. TRANSPORT AND DISPERSION

The transport and dispersion (T&D) model calculates the TIC plume movement and dilution after its initial jet effects become insignificant. The T&D model produces averaged concentrations or dosages at any time after release or any distance from the source, for determining health and vegetation effects. Most of the widely-used dense gas T&D models are relatively simple and treat the plume as if its cross-wind distribution has a certain shape (e.g., SLAB (Ermak, 1990); DEGADIS (Spicer and Havens, 1987), ALOHA (NOAA, 1992), HPAC/SCIPUFF (Sykes et al., 2007); HGSYSTEM (Witlox and McFarlane, 1994), PHAST (Witlox and Holt, 1999), and SAFER (SAFER Systems, 1996)). Some Computational Fluid Dynamics (CFD) models are being applied to the problem (e.g., FLACS, see Hanna et al., 2008b) but require more computer time.

#### Initial cloud spread when very dense and low winds

An analysis by a DHS panel over the past year has suggested that current models are not adequately handling the very dense cloud, called a “mist pool” by Bauer (2008, unpublished), that forms in the immediate area of a very large release such as the Graniteville accident (60,000 kg of chlorine released as a two phase jet in a few minutes). These recent accidents seem to occur in light wind conditions. The physical concept is that there is only slow detrainment of the chlorine from the mist pool into the slight ambient flow over the surface of the pool, causing the effective release rate to be less and therefore downwind concentrations to be less (although spread out over a longer time). The DHS group is planning future research and field experiments to address this issue.

The widely-used dense gas models listed above are all able to parameterize the reduced dilution of the initial dense cloud (mist pool), but the formula tends to break down as wind speed approaches zero. The entrainment formula has the general form,  $w_e = Au^*/(1 + B Ri_b)$ , where  $w_e$  is the vertical entrainment speed of ambient air into the top of the cloud,  $u^*$  is the ambient friction velocity (equal to about 10% of the ambient wind speed), and  $Ri_b$  is the bulk Richardson number of the cloud.  $Ri_b$  is proportional to the cloud excess density divided by  $u^*$  raised to a power and is also a function of the cloud size.  $A$  and  $B$  are “constants” determined by comparisons with laboratory and field experiments. Thus as wind speed decreases and cloud density and size increase,  $w_e$  approaches zero (or actually approaches the molecular (non-turbulent) value). This is where the problem or “gap” in knowledge is occurring for the large TIC releases.

#### Complex terrain and obstacle effects

The widely-used T&D models generally assume flat terrain and no obstacles. Some models (e.g., HPAC/SCIPUFF) can account for a constant terrain slope. But nearly all real sites will have significant complex terrain and/or obstacles. The terrain is more important for dense gas releases which tend to flow down slopes such as ditches and stream beds in the area. As mentioned above, in an emergency situation, the terrain and obstacles details are likely unavailable. However, for high threat cities or industrial sites, the needed data could be obtained and a detailed CFD model could be run beforehand to determine possible effects. This has been done, for example, by Hanna et al. (2008c and d) for a hypothetical chlorine railcar release in Chicago. The FLACS CFD model was run and the resulting simulations of the 100 ppm contour are shown in Figure 2. It is seen that the buildings slow down the plume, cause enhanced vertical dilution, and can cause hold-up or delay of the plume in wakes behind large buildings. Another figure (not shown here) illustrated the movement of the dense cloud down a river channel in a direction perpendicular to the assumed wind.

## Removal processes

There are several processes that could cause removal of TIC from a plume or cloud released to the atmosphere. There has been limited research on this topic. For example, Kukkonen et al. (1993) describe a model application where they accounted for removal by chemical reactions and dry and wet deposition for a large ammonia release in Lithuania in 1989. The regional air quality modeling community has added a chlorine mechanism to the chemistry model system used in EPA regional models (Tanaka et al., 2003). When the sun is shining, chlorine gas is rapidly removed through photolysis. 50 % of the chlorine gas can be removed in a few minutes. In addition TIC chemistry is being added to DTRA's HPAC/SCIPUFF modeling system (Burns et al., 2007). In order to not slow down the model, the chemistry is parameterized by defining a single removal constant for each TIC. The study has had a recent focus on chlorine chemistry.

Removal processes include gravitational settling of large drops or particles, dry deposition of gases and small particles, wet deposition of gases and particles, and chemical removal. Gravitational settling is estimated by a rather straightforward calculation because the settling speeds of aerosols with diameters larger than 10 micrometer ( $\mu\text{m}$ ) are fairly well-known. For example, the settling speed of a 50  $\mu\text{m}$  diameter drop is on the order of 10  $\text{cm s}^{-1}$ . Dry deposition is generally parameterized by a dry deposition velocity,  $v_d$ , and describes the flux of material (gas and/or small particles) to the surface due to a combination of chemical absorption and impaction. Thus  $v_d$  is nearly zero for inert gases and is largest for very reactive gases. The flux (in units of mass per unit area per unit time) to the surface is assumed to equal  $v_d$  times the gas concentration ( $C_0$ , with units mass per unit volume) in the atmosphere right at the surface. Sehmel (1984) presents large tables of  $v_d$  for various gases along with references. However, few measurements exist for most TICs and their  $v_d$  is therefore estimated by relations to similar gases and approximations. The dry deposition velocity  $v_d$  is often near 1  $\text{cm s}^{-1}$  for most gases and this is "hard-wired" as a default in many models (this value was assumed for ammonia by Kukkonen et al. (1993) in their model runs). Sehmel (1984) suggests  $v_d = 3 \text{ cm s}^{-1}$  for chlorine gas but this appears to be a value assumed for many reactive gases in the table. Wet deposition refers to removal of a chemical from the atmosphere by precipitation or by clouds. This is usually parameterized by a parameter  $\Lambda$ , which has units (seconds) $^{-1}$ , and leads to an exponential variation of concentration,  $C$ , with time,  $C(t) = C(0)\exp(-t)$ , where  $C(0)$  is the initial concentration. Measurements of wet removal have been made for several chemicals and are a function of chemical composition, rainfall rate, drop size, etc. However, as a rough approximation, a default value of  $\Lambda = (\text{one hour})^{-1}$  is used in many models. Thus 63% of the TIC is removed by the precipitation after one hour and is deposited on the ground. Chemical reactions can also remove gases from the atmosphere. Models such as HPAC/SCIPUFF assume linear effective chemical reactions. The removal is parameterized by using  $T_c$  as a time scale for chemical removal, leading to a formula similar to that for wet deposition but with  $\Lambda$  replaced by  $T_c$ . For many pollutants, there is a complex set of interacting chemical equations. As done for the other removal processes, the effective chemical time scale is often assigned a default value, say 1 hour, for reactive air pollutants. Hence, in 1 hour, 63 % of the original chemical is removed. Kukkonen et al. (1993) assumed a chemical removal constant of about two hours for ammonia.

A simple analytical solution for estimating the effects of dry deposition is available (see Hanna et al., 1982). The "source depletion model" for dry deposition is one of the earliest and simplest models. The vertical distribution of material is assumed to be Gaussian with standard deviation  $\sigma_z$ . For a plume released at the ground, as is true for most chlorine releases, the ratio of the mass of material in the plume after dry deposition to that initially is:

$$Q(x)/Q(0) = [\exp(\int (dx/\sigma_z)]^{-(\sqrt{2/\pi})v_d/u} \quad (\text{for ground level sources}) \quad (1)$$

Table 10.2 in Hanna et al. (1982) lists the solution for the distance,  $x_{50\%}$ , for 50% depletion of the plume mass (i.e.,  $Q(x)/Q(0)=0.5$ ) for stability classes A, B, C, D, E, and F for a ground-based passive (neutral) plume. The table assumes a wind speed,  $u$ , of 1  $\text{m s}^{-1}$  and a deposition velocity,  $v_d$ , of 1  $\text{cm s}^{-1}$  (i.e.,  $v_d/u = 0.01$ ).

The distances,  $x_{50\%}$ , are given in the table below:

Stability	A and B	C	D	E	F
$\sigma_z$ at $x=1 \text{ km}$	> 100 m	55 m	30 m	18 m	12 m
$x_{50\%}$	> 10 km	1.8 km	0.4 km	0.15 km	0.10 km

The table shows that, for stable (class E or F) conditions, which produce plume  $\sigma_z$  values more typical of a dense gas cloud, 50% of the material is estimated to be removed by a downwind distance of 100 or 150 m. This simple analytical expression was checked with some sensitivity studies made with the SCIPUFF and SLAB dense gas models. SCIPUFF allows input of a dry deposition velocity and some lines were inserted in the SLAB code so that it could treat dry deposition. Concentrations were calculated for the Chicago release scenario, and runs were made for three different surface roughness lengths, four different dry deposition velocities  $v_d$  (0.0., 1.0, 2.5, and 5.0  $\text{cm s}^{-1}$ ), five wind speeds, and three stability classes. An example of the predicted variation with distance of the cloud centerline chlorine concentration is given in Figure 3 for a wind speed of 3.0  $\text{m s}^{-1}$ , a surface roughness of 0.5 m, and stability class F (very stable). The figure shows that, for an expected dry deposition velocity for chlorine of about 2.5 or 5.0  $\text{cm s}^{-1}$ , most of the chlorine mass is removed from the cloud by a downwind distance of 1 km. This agrees approximately with the results from the analytical solution in the table above. Obviously more study is needed, but it

is clear that removal processes can remove significant amounts of the chlorine and cause concentrations at distances beyond a few hundred meters to be several orders of magnitude less than they would be if removal was ignored.

For very large releases, the calculations of dry deposition may break down near the source (say, at  $x < 0.2$  km) because there is so much deposition that the ground and vegetation become saturated, thus changing the effective dry deposition velocity. This would require a change in the assumptions.

## 5. EXPOSURE AND HEALTH RISK

The exposure and health risk model is the link between the concentrations calculated by the T&D model and the health effects estimated for the population. Similarly, vegetation and/or material damage can be calculated. There have been recent reviews of the health risk assumptions for TICs such as chlorine (e.g., National Research Council 2004; Sommerville et al. 2008, USACHPPM 2008). The health risk model is based on limited data (e.g., a few humans and a few research studies with rats, pigs, or other animals) and therefore has a relatively large uncertainty, and sometimes has a degree of conservatism built in. More assessments of this link in the total model system are needed.

The exposure and health risk model depends on knowledge of the population distribution at the time of the release and cloud passage, as well as whether the persons are outdoors or indoors and the type of building that they are in. Sheltering-in-place may be useful when the TIC cloud is of short duration, and concentrations inside the building can be calculated knowing the air exchange rate of the building. There are many uncertainties in the parameters of this system; for example, a wide range of air exchange rates are possible.

## 6. CAVEATS

The review comments and recommendations above are the author's and all aspects of the TIC modelling problem are currently under investigation in order to improve the models and the recommendations for emergency response. Research-grade field experiment data are being analyzed and new field experiments are being planned. However, even though the model system may work well when compared with the research-grade experimental data, in a real event there will always be limited input data available and consequently a great deal of uncertainty in all components of the model system and hence in the final predictions of effects.

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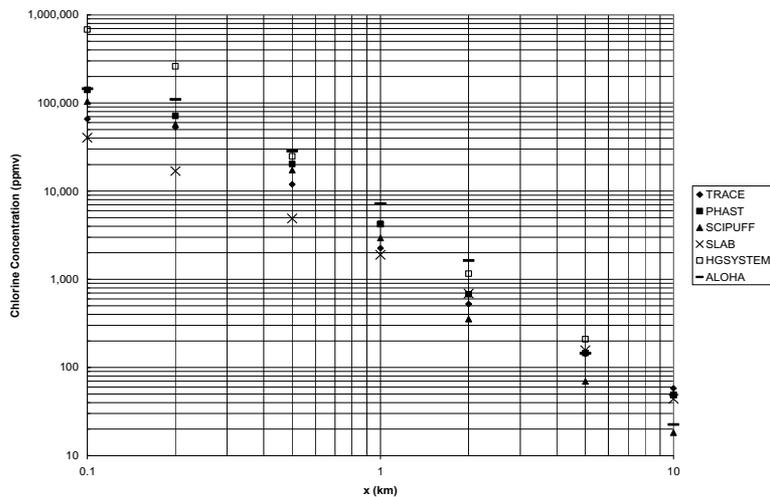


Figure 1. Plot of maximum 10 min average concentration (ppm of chlorine) on plume centerline versus downwind distance,  $x$ , for the six models for Graniteville (from Hanna et al., 2008a).

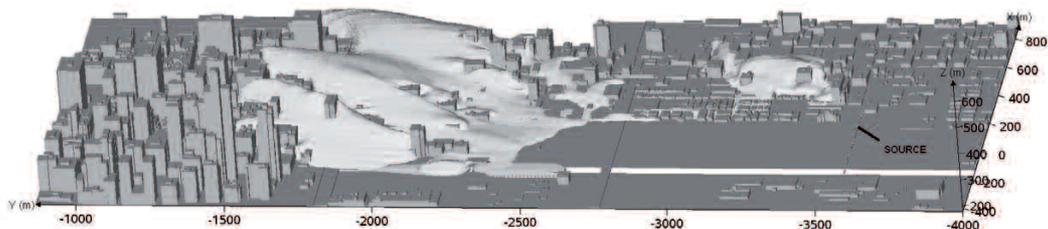


Figure 2. Examples of FLACS CFD model results for Chicago chlorine railcar release scenario with south wind, where 100 ppmv contours are shown, at 1500 s after the 300 s release was initiated. The view is to the east (from Hanna et al., 2008b)

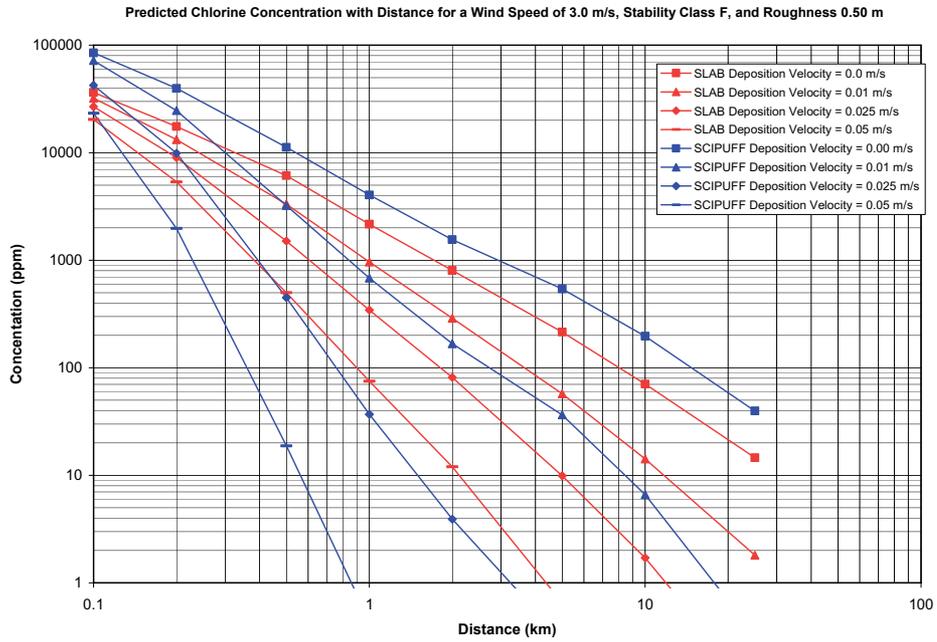


Figure 3. Modeled chlorine concentrations on the cloud centerline downwind of the hypothetical railcar release for the "base case", illustrating the effect of including deposition in SCIPUFF and SLAB simulations.